DOTTORATO DI RICERCA IN
CHIMICA
Ciclo XXIX

Settore Concorsuale di afferenza: 03/C2
Settore Scientifico disciplinare: CHIM/04

CHEMICAL-LOOP APPROACH IN BIO-ALCOHOLS REFORMING

Presentata da: Olena Vozniuk

Coordinatore Dottorato
Chiar.mo Prof. Aldo Roda

Relatore
Prof. Fabrizio Cavani

Relatore
Prof. Francesco Di Renzo

Esame finale anno 2017
Chemical-Loop Reforming

Water Splitting

Hydrogen production

Spinel oxides

Mössbauer spectroscopy

Magnetic measurements

TPR/O

in-situ XPS

in-situ DRIFTS
# TABLE OF CONTENTS

1. **INTRODUCTION** ................................................................................................................. 24  
   1.1. Hydrogen applications .......................................................................................... 24  
      1.1.1. Fuel cells ....................................................................................................... 25  
   1.2. Hydrogen production ......................................................................................... 27  
      1.2.1. Common feedstocks ...................................................................................... 27  
      1.2.2. Common processes for H₂ production .......................................................... 27  
      1.2.3. Hydrogen via Reforming Processes ............................................................... 28  
      1.2.4. Hydrogen via Chemical-Loop (CL) processes ............................................ 32  
   1.3. Spinel oxides: AB₂O₄ ........................................................................................... 38  
      Structure of AB₂O₄ oxides ..................................................................................... 39  
   1.4. Aim of the research project .................................................................................. 41  

2. **CHARACTERIZATION TECHNIQUES AND SET-UP OF LABORATORY PLANT** .................. 43  
   2.1. X-ray diffraction (XRD) ...................................................................................... 43  
   2.2. Raman Spectroscopy ............................................................................................ 45  
   2.3. Mössbauer Spectroscopy ..................................................................................... 45  
   2.4. Surface area measurements ................................................................................ 47  
   2.5. SEM/TEM-EDX analysis ...................................................................................... 48  
   2.6. Temperature programmed reduction/oxidation (TPR1/O/R2) ............................. 48  
   2.7. Carbon content measurements (CHNS) .............................................................. 49  
   2.8. Magnetic measurements ..................................................................................... 49  
   2.9. In-situ X-ray Photoelectron Spectroscopy (XPS) experiments ......................... 49  
   2.10. Diffuse-Reflectance Infrared FT spectroscopy (DRIFTS) experiments ............. 51  
   2.11. Reactivity experiments: Chemical-Loop Reforming (CLR) process ............... 55  

3. **MATERIALS PREPARATION** ....................................................................................... 61  

4. **RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe₂O₄)** ........................... 63  
   Bulk characterization of fresh materials ...................................................................... 63  
   4.1. Energy dispersive spectroscopy (EDX) ............................................................... 63  
   4.2. XRD and N₂ adsorption ...................................................................................... 64  
   4.3. Raman Spectroscopy ............................................................................................ 66  
   4.4. Temperature programmed reduction/oxidation (TPR1/O/R2) ............................. 67  
   4.5. Ex-situ XRD study of MFe₂O₄ ferrites ................................................................. 79  
   4.6. Ex-situ Mössbauer study ..................................................................................... 89  
   4.7. Reactivity tests and characterization of the cycled materials ................................ 95
4.8. Characterization of cycled looping materials: 3 steps CLR - 1 complete cycle (20 min red/20 min re-ox/30 min air) ................................................... 115
4.9. 2 steps CLR vs 3 steps CLR: cycling of looping materials (3 cycles·20 min) ....................... 118
4.10. Conclusions on the study of MF\textsubscript{2}O\textsubscript{4} ferrospinels ........................................ 124

5. RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}) .......................................... 126
5.1. Energy dispersive spectroscopy (EDX) .............................................................................. 126
5.2. XRD and N\textsubscript{2} adsorption .................................................................................. 127
5.3. Raman Spectroscopy .................................................................................................. 128
5.4. Temperature programmed reduction (TPR) ................................................................. 131
5.5. Ferrospinels TYPE II: study of Co\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system .................................................. 136
5.6. Surface characterization: in-situ DRIFTS experiments .................................................. 137
5.7. Surface characterization: in-situ XPS study .................................................................. 142
5.8. Reactivity tests: Co\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system ........................................... 150
5.9. Conclusions on the study of Co\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrospinels .......... 160
5.10. Ferrospinels TYPE II: study of Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system ............................................. 161
5.11. Mössbauer spectroscopy ........................................................................................... 162
5.12. Magnetic measurements.............................................................................................. 166
5.13. Temperature programmed reduction (TPR) study ....................................................... 170
5.15. Ex-situ XRD study of the reduced samples ................................................................. 176
5.16. Mössbauer study of the reduced samples ................................................................... 181
5.17. Reactivity tests: Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system .................................................. 185
5.18. Conclusions on the study of Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system ......................... 194

6. CHEMICAL-LOOP REFORMING: REACTIVITY TESTS\rightarrow M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} ............................................. 197
6.1. 1\textsuperscript{st} step: reduction with ethanol at T-450°C ................................................... 198
6.2. Ex-situ XRD study over cycled materials after 4 cyc·20 min+1\textsuperscript{red} .................. 203
6.3. 2\textsuperscript{nd} step: re-oxidation with water at T-450°C .................................................... 206
6.4. Ex-situ XRD study over cycled materials after 5 cyc·20 min ................................... 208
6.5. Raman spectroscopy over cycled materials ................................................................. 212
6.6. Conclusions on the study of M\textsubscript{0.6-x}Fe\textsubscript{2.4}O\textsubscript{y} ferrospinels ............................. 214

7. TYPE I vs. TYPE II FERROSPINELS ................................................................................. 215
7.1. Conclusions: TYPE I vs. TYPE II ferrospinels ........................................................... 219

LITERATURE .................................................................................................................. 220
ACKNOWLEDGMENTS .................................................................................................... 229
ABSTRACT

Nowadays, hydrogen production is mainly based on the reforming of natural gas or naphtha. Less energy intensive and more sustainable processes for hydrogen production are appealing for both industry and consumer applications. Chemical-loop steam reforming is one of the possible ways to produce H\textsubscript{2} starting from either conventional or renewable sources. Differently from classical reforming, separation costs can be avoided by splitting the process into two alternated steps in order to detach H\textsubscript{2} and CO\textsubscript{x} streams. One of the advantages of this technology relates to its feedstock flexibility.

This PhD project deals with an investigation of a new process, named as Chemical-Loop Reforming (CLR) process, aimed to produce “clean H\textsubscript{2}” with an inherent CO\textsubscript{x} separation. The main principle of the CLR process is that an oxygen-storage material is first reduced by an ethanol stream (T-450°C) and then re-oxidized by water (T-450°C) to produce hydrogen and to restore the original oxidation state of the looping-material. The choice of ethanol as a reducing agent has several advantages: its renewable origin together with the possibility to decompose at a relatively lower temperature with a formation of the hydrogen-rich mixture.

Different M-modified spinel-type mixed oxides: TYPE I – MFe\textsubscript{2}O\textsubscript{4} and TYPE II – M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}, viz. modified ferrospinel, as potentially attractive ionic oxygen and electron carrier looping materials, were prepared via co-precipitation method and tested in terms of both redox properties and catalytic activity to generate hydrogen by oxidation with steam, after a reductive step carried out with ethanol. Particularly, the focus on the reactivity behavior of binary/ternary materials explained by their ability to form thermodynamically stable spinel oxides which allow us to re-obtain the initial spinel phase upon cycling and in turn increase a stability of the looping material itself. In addition, the research includes in-situ DRIFTS and in-situ XPS studies that allowed to extract information at a molecular level and to follow surface changes within the reduction/re-oxidation processes during ethanol chemical-loop reforming. Bulk characterizations have been done using XRD, TPR/O, TEM/SEM/EDX, Magnetic measurements and Raman/Mössbauer spectroscopic techniques. Moreover, a modification of the conventional CLR process with an addition of the 3\textsuperscript{rd} regeneration step (carried out with air) was done to increase the stability of the looping material and to overcome the deactivation problems, such as: a coke deposition/accumulation and an incomplete re-oxidation of M\textsuperscript{0} during the 2\textsuperscript{nd} step; the obtained results are compared to a conventional 2 steps CLR process.
Aujourd'hui, la production d'hydrogène est basée essentiellement sur le reformage du gaz naturel ou des essences légères. Des procédés moins énergivores et plus durables pour la production d'hydrogène sont intéressants tant pour des applications industrielles que pour des produits pour grand public. Le reformage à la vapeur par cycle redox est une des voies possibles pour produire de l'H_{2} à partir de sources traditionnelles comme de sources. A différence du reformage classique, les coûts de séparation peuvent être évités en séparant le procédé en en deux étapes alternées pour isoler les débits d'H_{2} et CO_{x}. L'un des avantages de cette technologie est lié à sa flexibilité envers les matières premières utilisées.

Le sujet de thèse est l'étude exploratoire d'un nouveau procédé de reformage par cycle redox (CLR : Chemical-Loop Reforming) avec séparation intrinsèque des CO_{x}, visant la production d’“H_{2} propre. Le principe essentiel du procédé CLR est basé sur le cycle redox d’un matériau de stockage d’oxygène, qui est d’abord réduit par un flux d’éthanol (T-450°C) et ensuite réoxydé par de la vapeur d’eau (T-450°C) pour produire de l’hydrogène et rétablir l’état d’oxydation initial du matériau à cycle redox. Le choix de l’éthanol comme agent réducteur présente plusieurs avantages, de son origine renouvelable à sa propriété de décomposition à une température relativement basse avec la formation d’un mélange riche en hydrogène.

Les oxydes mixtes de structure spinelle (ferrospinelles modifiées) sont des matériaux potentiellement intéressants pour le cyclage redox d’ions oxygènes et porteurs d’électrons. Plusieurs de ces spinelles M-modifiée de TYPE I – MFe_{2}O_{4} et TYPE II – M_{x/2}Fe_{4-x}O_{4}, M-modifiée de TYPE I – MFe_{2}O_{4} et TYPE II – M_{x/2}Fe_{4-x}O_{4} avec M=Cu, Co, Mn, Mg, Ca et Cu/Co, Cu/Mn, Co/Mn) ont été préparées par une méthode de coprécipitation et elles ont été évaluées soit de par leurs propriétés redox et leur activité catalytique dans la production d’hydrogène par oxydation par la vapeur d’eau après une étape de réduction à l’éthanol. En particulier, l’attention a été portée sur la réactivité des matériaux binaire/ternaire à cause de leur propriété de former des spinelles thermodynamiquement stables, ce qui nous a permis de réobtenir la phase spinelle initiale après cyclage redox tout en augmentant la stabilité du matériau de cyclage. De plus, l’activité de recherché a inclut des études in-situ, DRIFTS et XPS, qui ont permis d’obtenir des informations au niveau moléculaire et de suivre les modifications de surface du matériau au cours des étapes de réduction et réoxydation pendant le reformage de l’éthanol par cyclage redox. Les matériaux ont été caractérisés par DRX, TPR/O, MET/MEB/EDX, mesures magnétiques et techniques spectroscopiques Raman/Mössbauer. De plus, une modification du procédé CLR conventionnel avec l’addition d’une troisième étape de régénération à l’air a permis d’augmenter la stabilité du matériau de cyclage redox et de surmonter les problèmes de désactivation, tels que le dépôt/accumulation de coke et la réoxydation incomplète de M^{0} pendant l’étape de réoxydation à la vapeur d’eau. Les résultats obtenus ont été comparées à un procédé CLR conventionnel à deux étapes.
OBJECTIFS DU PROJET DE RECHERCHE

Le travail de recherché présenté ici est étude sur un nouveau procédé de reformage par cyclage redox (Chemical-Loop Reforming: CLR) pour produire de l’“H₂ propre” avec une séparation intrinsèque des COₓ. Le principe de base du procédé CLR est le cyclage d’un matériau de stockage d’oxygène, qui est d’abord réduit par un flux d’éthanol (T-450°C) et ensuite réoxydé par la vapeur d’eau (T-450°C) pour produire de l’hydrogène et rétablir l’état d’oxydation initial du matériau de cyclage (Figure 1).

Le choix de l’éthanol comme agent réducteur présente plusieurs:
- L’éthanol peut être obtenu à partir de biomasse, ce qui peut contribuer à développer la production d’hydrogène à partir de matières premières différentes des combustibles fossiles;
- L’éthanol est un liquide non toxique, facile à transporter et manipuler, assez stable à température ambiante, bien adapté pour des usages dans des produits pour le grand public;
- L’utilisation de bioalcool en reformage par cycle redox a jusqu’à présent attiré peu d’attention dans la littérature;

La tâche initiale du projet a été la définition des conditions et matériaux adaptés pour l’obtention d’un procédé optimise pour la production d’un flux d’hydrogène qui ne demande aucune opération de séparation ou purification supplémentaire. Par conséquent, plusieurs oxydes mixtes de type spinelle M-modifiées (TYPE I – MFe₂O₄ et TYPE II – M₀.₆Fe₂.₄O₄) ont été synthétisés et testés comme matériaux de cyclage d’ions oxygènes et porteurs d’électrons dans la génération d’hydrogène par oxydation à la vapeur d’eau après une étape de réduction à l’éthanol. Plus spécifiquement, l’attention a été portée sur la réactivité des spinelles secondaires et tertiaires, grâce à leur capacité de former des oxydes thermodynamiquement stables qui pouvaient recouvrir leur phase initiale.
après un cyclage redox. La composition de ferrospinelles $MFe_2O_4$ et $M_{0.6}Fe_{2.4}O_y$ a été variée avec des ions de métaux de transition (Co, Mn, Cu ou Cu/Co, Cu/Mn, Co/Mn) et des ions de métaux alcalinoterreux: Ca, Mg. L’objectif de ces modifications des matériaux a été la recherche d’une sélectivité améliorée pour obtenir des produits valorisables au cours de la première étape de réduction et une plus grande pureté de l’hydrogène produit dans la deuxième étape de réoxydation.

La deuxième tâche a été l’étude de la chimie du procédé, à travers des techniques de caractérisation in-situ et ex-situ et l’étude des propriétés des oxydes mixtes, en terme de propriétés redox, morphologiques et physico-chimiques, en incluant des études de propriétés de chimie de l’état solide des matériaux avant et après cyclage redox.

La recherche a été conduite sur les sites de trois institutions, les détails sur l’organisation du travail étant résumés dans la Figure 2.

**Figure 2. Travail accompli pendant les trois années de recherché doctorale**

**DIFFRACTION DES RAYONS X ET ADSORPTION DE N₂**

La structure des ferrospinelles de TYPE I ($MFe_2O_4$) et TYPE II ($M_{0.6}Fe_{2.4}O_y$) préparées par coprécipitation a été identifiée par les diffractogrammes de poudres reportés en Figures 3. Les diffractogrammes indiquent la formation de spinelles comme phases principaux pour tous les échantillons $MFe_2O_4$ et $M_{0.6}Fe_{2.4}O_y$. Un clair élargissement des raies de diffraction a été observé préférentiellement pour les ferrospinelles des deux types contenant du manganèse, comme $MnFe_2O_4$, $Cu_{0.3}Mn_{0.7}Fe_2O_4$, $Co_{0.3}Mn_{0.7}Fe_2O_4$ and $Mn_{0.6}Fe_{2.4}O_y$, $Co_{0.3}Mn_{0.7}Fe_2O_4$, $Cu_{0.3}Mn_{0.7}Fe_2O_4$...
Co_{0.54}Mn_{0.06}Fe_{2.4}O_y. Cet effet a été attribué à une diminution de la taille des particules ou à une baisse de cristallinité. Dans le Tableau 1 sont indiquées les valeurs de surface spécifique (SSA), taille des cristallites (calculée par l’équation de Scherrer ou la méthode de Williamson-hall) et taille des particules des échantillons calcinés à 450°C pour 8 h.

Figure 3. Diffractogrammes de poudres des spinelles MFe_2O_4 (en haut) et M_{0.6}Fe_{2.4}O_y (en bas) calcinées à 450°C en flux d'air pour 8 h
Toutes les ferrites contenant du Mn présentent une surface spécifique plus élevée aussi après traitement thermique. Cet effet peut être attribué d’abord à la présence de plus petites particules ainsi qu’à la présence d’une phase amorphe, en bon accord avec les résultats de diffraction présentés plus haut. Une confirmation ultérieure a été obtenue par la comparaison de la taille des cristallites obtenue par exploitation de la largeur des raies de diffraction avec la taille des particules calculée à partir de la SSA à travers une supposition sur la forme des particules, assumées sphériques et non poreuses pour les besoins du calcul.

**REDUCTION À TEMPÉRATURE PROGRAMMÉE (TPR)**

La réduction des oxydes de fer(III) (Fe$_3$O$_4$→FeO→Fe) dépend fortement de la présence d’autres oxydes métalliques dans la ferrite M-modifiée résultante. Selon les résultats de DRX discutés plus haut, la phase principale obtenue au bout de la procédure de préparation est une phase spinelle de type Fe$_3$O$_4$ avec une formule générale MFe$_2$O$_4$/M$_{0.6}$Fe$_{2.4}$O$_y$. Dans les courbes TPR profiles des ferrites
M-modifiées reportées en Figure 4, on reconnaît deux étapes principales du processus de réduction : la réduction de l’oxyde de fer à fer métalliques et le processus propre de réduction de l’autre oxyde métallique incorporé à son métal. Toutefois, il est difficile de séparer les étapes de réduction puisque certaines étapes se fondent sans transition, en se superposant l’une dans l’autre. Néanmoins, les résultats obtenus et leur élaboration ultérieure, basée sur la nature des métaux additionnels (M$^{2+}$), leurs potentiels de réduction et les quantités d’H$_2$ consommées, nous ont permis de définir des étapes probables du processus de réduction des MFe$\text{O}_4$, étapes qui sont résumées dans la Figure 5.

En considérant le profil TPR profile de CuFe$\text{O}_4$, le premier pic à 240°C peut être attribué à une réduction rapide de l’oxydes de cuivre présent dans l’échantillon (CuO~21%$\text{w}$) à cuivre métallique (Cu$^0$), ce qui conduit à une fraction de consommation d’H$_2$ α~16%. Le deuxième pic à ~ 340°C a été attribué à la première étape de réduction de la spinelle selon le mécanisme I de Figure 5, avec la formation de phases Cu$^0$ et Fe$_3$O$_4$ (α~27%). La réduction ultérieure de Fe$_3$O$_4$ à FeO et FeO à Fe$^0$ se manifeste à plus haute température jusqu’à α~70%. La réduction des échantillons Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ et Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ suit le mécanisme III de Figure 5, dans lequel le premier pic à basse température correspond à la démixtion par étapes et/ou la réduction des cations M incorporés pour former des phases M (Cu$^0$), MO (MnO/CoO) et Fe$_3$O$_4$. 
Figure 4. Courbes TPR de ferrites $\text{MFe}_2\text{O}_4$ (en haut) et $\text{M}_0.6\text{Fe}_2.4\text{O}_y$ (en bas) avec programmation de température de 50 to 800°C suivie d’une isotherme at 800°C pour 40 min.
La réduction ultérieure des ferrites Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ passe par les étapes suivantes: (1) Fe$_3$O$_4$\(\rightarrow\)FeO (+0.77 eV), (2) CoO\(\rightarrow\)Co$^0$ (-0.28 eV), (3) FeO\(\rightarrow\)Fe$^{\text{incom}}$ (-0.44 eV) et atteint une $\alpha$~65%. D’autre côté, la deuxième phase de réduction des ferrites Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ peut être ainsi schématisée: (1) Fe$_3$O$_4$\(\rightarrow\)FeO, (2) FeO\(\rightarrow\)Fe$^{\text{incom}}$, ce qui correspond à $\alpha$~65%. Il en résulte qu’il est difficile de réduire MnO à son correspondant métallique Mn$^0$, à cause de son potentiel de réduction très négatif (-1.18 eV), donc cette étape peut avoir lieu seulement à des températures très élevées. La réduction des échantillons CoFe$_2$O$_4$, Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ et MnFe$_2$O$_4$ suit le mécanisme II de Figure 5. Dans le cas de CoFe$_2$O$_4$, le premier petit pic à 400°C peut être attribué à la réduction initiale de la spinelle avec une étape de formation de phases CoO et Fe$_3$O$_4$ (correspondant à $\alpha$~8%), tandis que dans les ferrites contenant du manganèse (MnFe$_2$O$_4$ et Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$) cette étape commence à plus basse température. Cependant, le degré de réduction final de CoFe$_2$O$_4$ ($\alpha$~86%) a été bien plus élevé que celui des échantillons Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (61%) et MnFe$_2$O$_4$ (45%), ce qui peut être expliqué par la formation de la phase MnO, difficile à réduire tant que telle ou sous forme de solution solide Mn$_x$Fe$_y$O.

Les mécanismes de réduction proposés sur la base des résultats obtenus sur les ferrospinelles de TYPE I (MFe$_2$O$_4$), reportés en Figure 5, peuvent être appliqués aux courbes TPR des échantillons de TYPE II (M$_{0.6}$Fe$_{2.4}$O$_y$). Un épaulement de réduction à basse température, près de ~200°C, qui correspond à ~5% de la réduction totale, observé expérimentalement pour les échantillons contenant Co, Co/Mn et Mn, a été attribué à la réduction de M$_{0.5}$Fe$_{2.2}$O$_4$ à M$_{0.6}$Fe$_{2.4}$O$_4$, engendrée par la présence de lacunes cationiques dans des matériaux suroxydés hautement défectif. On remarque que la présence de fer seulement sous forme de cations Fe$^{3+}$ dans les échantillons initiaux a été confirmée par expériences Mössbauer où les valeurs d’IS ($\delta$) sont dans le domaine typique des espèces Fe$^{3+}$: 0.31-0.35 mm/s, ce qui implique une suroxydation pour ces échantillons surstoechiométriques en fer. La réduction ultérieure des échantillons Co$_{0.6}$Fe$_{2.4}$O$_y$\(^{[A]}\), Co$_{0.54}$Mn$_{0.06}$Fe$_{2.4}$O$_y$\(^{[B]}\), Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$\(^{[C]}\) et Mn$_{0.4}$Fe$_{2.4}$O$_y$\(^{[D]}\) suit les mêmes étapes des ferrospinelles.
TYPE I avec Co, Co/Mn et Mn (mécanisme II en Figure 5). Le premier petit pic à ~400°C a été attribué à la réduction initiale de la spinelle avec formation par étapes de phases CoO et Fe₃O₄ (ou CoO, MnO et Fe₃O₄), ce qui correspond à un degré d’avancement de la réduction α~8%, tandis que dans la ferrite au manganèse Mn₀.₆Fe₂.₄O₅y, cette étape commence à la plus basse température de ~380°C (Mn₀.₆Fe₂.₄O₅ + 0.2 H₂ donne 0.6 MnO + 0.8 Fe₃O₄ + 0.2 H₂O). De toute façon, les échantillons au cobalt atteignent un degré de réduction significativement plus élevé (α~80%(A), 75%(B) and 55%(C)%) par rapport à l’échantillon au manganèse (α~58%(D)%), ce qui a été encore une fois attribué à la formation d’une phase difficilement réductible, sous la forme de MnO ou d’un oxyde mixte MnₓFeₙO à structure wustite. Dans les courbes TPR des ferrites Cu₀.₆Fe₂.₄O₅(E) et Cu₀.₃Mn₀.₃Fe₂.₄O₅(F), le premier pic à ~350°C a été attribué à la première étape de réduction de la spinelle avec formation finale de phases Cu₀(E)/Cu₀⁺MnO(F) et Fe₃O₄, correspondant à α~23%(E)/16%(F)%, suivant les mécanismes I(E)/III(F) de Figure 5. Les étapes ultérieures de réduction Fe₃O₄ → FeO et FeO → Fe se déroulent à plus haute température avec un degré de réduction global de ~52%(E)/46%(F)%. Comme expliqué plus haut pour les ferrospinelles avec Co/Mn et Mn, la réduction MnO → MnO⁻ (1.18 eV) peut avoir lieu seulement à des températures très élevées, ce qui favorise la formation de phases difficilement réductibles MnO/MnₓFeₙO.

EXPÉRIENCES DE RÉACTIVITÉ SUR FERROSPINELLES TYPE I ET TYPE II

Le choix de conditions de réaction et temps de cycle a été basé sur les études précédents de Cocchi (méthanol comme agent réducteur, Tred – 300 et 420°C/Tre-ox – 420°C, matériaux de cyclage : Fe₃O₄, CoFe₂O₄ et NiFe₂O₄) et Trevisanut (éthanol comme agent réducteur, Tscreen red – 400 et 450°C/Tre-ox – 450°C, matériau de cyclage: Fe₂O₃, CoFe₂O₄ et NiFe₂O₄). Il faut remarquer que le but essentiel de l’étape de réduction était de maximiser le niveau de réduction tout en améliorant la reproductibilité des cycles redox en minimisant la désactivation du matériau de cyclage, conséquence d’une accumulation de coke. Ces résultats précédents ont suggéré comme meilleures conditions de réaction une première étape de réduction par l’éthanol à Tred=450°C et une deuxième étape de réoxydation par la vapeur d’eau à Tre-ox=450°C. Le temps de cyclage a été choisi sur les même bases et a été divisé en cycles longs (durée d’un cycle complet: 1 h red/1 h re-ox) et cycles courts (durée d’un cycle complet: 20 min red/20 min re-ox ou 6 min red/6 min re-ox). La durée optimisée pour chaque étape a été fixée à 20 minutes par cycle. Cependant, les moles globales d’H₂ formées pendant la deuxième étape ont été comparée à la même durée globale pour des cycles à rythme différent: par exemple 1h (total→60 min) = 3 cyc·20 min (total→60 min) = 10 cyc·6 min (total→60 min). La composition des
ferrospinelles \( M_{0.6}Fe_{2.4}O_y \) a aussi été variée en changeant les métaux de transition Co, Mn, Cu ou les métaux alcalinoterreux Ca, Mg. L’objectif de ces modifications a été l’obtention d’une plus grande sélectivité vers des produits valorisables dans la première étape de réduction ainsi qu’une plus grande pureté du \( \text{H}_2 \) produit dans la deuxième étape de réoxydation.

Dans la Figure 6 sont résumées les valeurs intégrales de production d’\( \text{H}_2 \) au cours de l’étape de réduction de l’eau au terme d’un cycle redox complet de 20 minutes sur ferrospinelles \( \text{MFe}_2\text{O}_4 \) et \( M_{0.6}\text{Fe}_{2.4}O_y \). Pour comprendre les résultats d’un point de vue différent, des données de réactivité importantes sont résumé dans le Tableau 2. Plusieurs éléments sont à mettre en évidence, en prenant comme étalon le premier matériau de cyclage redox proposé - \( \text{Fe}_3\text{O}_4 \):

- Un aspect positif de l’incorporation de manganèse dans les ferrites \( \text{MFe}_2\text{O}_4/M_{0.6}\text{Fe}_{2.4}O_y \) est la diminution de la quantité de coke produite, qui tend à s’accumuler pendant la première étape de réduction à l’éthanol, comme montré par les valeurs \( \text{C}_w \) (CHNS) en Table 2;

- Par conséquent, l’incorporation de manganèse augmente le rapport \( \text{H}_2/\text{CO}_x \) (à remarquer: plus élevé le rapport \( \text{H}_2/\text{CO}_x \), plus ‘pure’ est \( \text{H}_2 \) engendré pendant la deuxième étape de réoxydation). On peut comparer le rapport \( \text{H}_2/\text{CO}_x=3.5 \) sur \( \text{Fe}_3\text{O}_4 \) avec des valeurs \( \text{H}_2/\text{CO}_x=15 \) pour les TYPE I \( \text{MnFe}_2\text{O}_4 \) et \( \text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4 \) et, pour le TYPE II, \( \text{H}_2/\text{CO}_x=14 \) sur \( M_{0.6}\text{Fe}_{2.4}O_y \) et \( \text{H}_2/\text{CO}_x=7 \) sur \( \text{Co}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}O_y \). D’autres valeurs \( \text{H}_2/\text{CO}_x \) sont données au Tableau 2;

- L’incorporation de métaux de transition, comme Cu/Co/Mn, avec le rapport Fe:Cu ou Fe: (-Co,-Mn) étant 2 ou 2.4, a des effets bénéfiques sur la quantité totale d’\( \text{H}_2 \) produit par
réduction de H\textsubscript{2}O par rapport à la spinelle Fe\textsubscript{3}O\textsubscript{4} non modifiée. Les meilleurs rendements ont été obtenus sur ces ferrospinelles M-modifiées binaires/ternaires: TYPE I - CuFe\textsubscript{2}O\textsubscript{4} (Y-52%), Cu\textsubscript{0.3}Co\textsubscript{0.7}Fe\textsubscript{2}O\textsubscript{4} (Y-46%), Cu\textsubscript{0.3}Mn\textsubscript{0.7}Fe\textsubscript{2}O\textsubscript{4} (Y-37%) et TYPE II – Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} (Y-50%), Co\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}.

Table 2. Paramètres de réactivité de ferrites MFe\textsubscript{2}O\textsubscript{4} et M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} (valeurs obtenues après un cycle redox complet de 20 min)

<table>
<thead>
<tr>
<th>TYPE I: MFe\textsubscript{2}O\textsubscript{4}</th>
<th>C %\textsubscript{w} after 20 min red with ethanol</th>
<th>H\textsubscript{2}/CO\textsubscript{x}</th>
<th>Moles of H\textsubscript{2}/Moles of Ethanol (n\textsubscript{H2}/n\textsubscript{Eth})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe\textsubscript{2}O\textsubscript{4}</td>
<td>11.6</td>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}</td>
<td>16.3</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>CuFe\textsubscript{2}O\textsubscript{4}</td>
<td>6.9</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu\textsubscript{0.3}Mn\textsubscript{0.7}Fe\textsubscript{2}O\textsubscript{4}</td>
<td>6.1</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>Co\textsubscript{0.3}Mn\textsubscript{0.7}Fe\textsubscript{2}O\textsubscript{4}</td>
<td>1.5</td>
<td>15</td>
<td>0.1</td>
</tr>
<tr>
<td>MnFe\textsubscript{2}O\textsubscript{4}</td>
<td>1.7</td>
<td>15</td>
<td>0.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>REFERENCE MATERIAL</th>
<th>C %\textsubscript{w} after 20 min red with ethanol</th>
<th>H\textsubscript{2}/CO\textsubscript{x}</th>
<th>Moles of H\textsubscript{2}/Moles of Ethanol (n\textsubscript{H2}/n\textsubscript{Eth})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>5.3</td>
<td>3.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TYPE II: M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</th>
<th>C %\textsubscript{w} after 20 min red with ethanol</th>
<th>H\textsubscript{2}/CO\textsubscript{x}</th>
<th>Moles of H\textsubscript{2}/Moles of Ethanol (n\textsubscript{H2}/n\textsubscript{Eth})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>9.7</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>Co\textsubscript{0.3}Mn\textsubscript{0.7}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>7.9</td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>9.8</td>
<td>3</td>
<td>1.1</td>
</tr>
<tr>
<td>Cu\textsubscript{0.3}Mn\textsubscript{0.7}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>5.0</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>2.2</td>
<td>14</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>-</td>
<td>3</td>
<td>0.3</td>
</tr>
<tr>
<td>Mg\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>-</td>
<td>7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

- L’incorporation de cations Cu/Co- induit une augmentation du rapport n\textsubscript{H2}/n\textsubscript{Eth}, comme pour les TYPE I: CuFe\textsubscript{2}O\textsubscript{4} (n\textsubscript{H2}/n\textsubscript{Eth}=1.2), Cu\textsubscript{0.3}Co\textsubscript{0.7}Fe\textsubscript{2}O\textsubscript{4} (n\textsubscript{H2}/n\textsubscript{Eth}=1.0) et les TYPE II: Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} (n\textsubscript{H2}/n\textsubscript{Eth}=1.1), Co\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} (n\textsubscript{H2}/n\textsubscript{Eth}=1.0).

- On pourrait suggérer une corrélation entre la facilité de former H\textsubscript{2} à partir de bioéthanol et la différence entre les potentiels caloriques d’H\textsubscript{2} et éthanol (exprimés comme LHV (Lower Heating Value), MJ/kg): 119,96 pour H\textsubscript{2} et 28.86 pour éthanol. En d’autres mots, le rapport n\textsubscript{H2}/n\textsubscript{Eth}, élevé permet une efficacité potentielle élevée pour le procédé CLR à partir d’éthanol. Evidemment, il y a beaucoup d’autres éléments qu’il faut prendre en compte pour évaluer e coût réel d’un procédé CLR et pour estimer un prix final raisonnable pour H\textsubscript{2} produit par cette technologie. L’objectif final reste une évaluation comparative de l’intérêt.
économique du procédé CLR par rapport aux procédés existants, ce qui n’a pas pu être porté à terme dans la présente étude.

À complément des données d’activité reportées plus haut, une ultérieure comparaison entre ferrospinelles TYPE I and TYPE II est présentée en Figure 7 et Tableau 3, axée sur les quantités d’H₂ produites pendant plusieurs cycles consécutifs (notamment 3 cycles complets de 20 min de réduction et 20 min de réoxydation). On ne présente ici que les données pour les échantillons qui ont donné les meilleurs rendements en hydrogène (voir Figure 6). On peut remarquer que:

**Figure 7.** Quantités intégrées de H₂ et CO₃ produites pendant les deuxième étapes de réoxydation à la vapeur d’eau à 450°C sur ferrospinelles MFe₂O₄ et M₀.₆Fe₂.₄O₂ (note: valeurs obtenues sur 3 cycles complets à étapes de 20 min)

**Tableau 3.** Paramètres d’activité calculés pour ferrites MFe₂O₄ et MₐFe₂.₄O₄ ferrites (note: valeurs obtenues sur 3 cycles complets à étapes de 20 min)

<table>
<thead>
<tr>
<th></th>
<th>H₂/CO₃</th>
<th>Moles of H₂/Moles of Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TYPE I: MFe₂O₄</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoFe₂O₄</td>
<td>5</td>
<td>0.7</td>
</tr>
<tr>
<td>Cu₀.₅Co₀.₅Fe₂O₄</td>
<td>3</td>
<td>0.9</td>
</tr>
<tr>
<td>CuFe₂O₄</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>REFERENCE MATERIAL</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₄</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>TYPE II: M₀.₆Fe₂.₄O₂</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₀.₅Fe₂.₄O₂</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>Co₀.₃Mn₀.₃Fe₂.₄O₂</td>
<td>3</td>
<td>0.9</td>
</tr>
</tbody>
</table>
- L’utilisation de ferrospinelles TYPE I: CoFe$_2$O$_4$, CuFe$_2$O$_4$, Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ et TYPE II: Co$_{0.6}$Fe$_{2.4}$O$_y$, Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$, Cu$_{0.6}$Fe$_{2.4}$O$_y$, Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$, Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ comme matériaux de cyclage redox en plusieurs cycles consécutifs conduit à la production d’une quantité d’hydrogène (exprimée en moles en Figure 7) bien supérieure à la valeur obtenue sur le matériau de référence Fe$_3$O$_4$ (voir Figure 7);

- L’augmentation du temps total $t_{os}$ (il s’agit du temps total des étapes de réduction ou réoxydation) de 20 à 60 min entraîne une forte diminution du rapport $H_2/CO$ ratio, avec une diminution conséquente de la pureté du gaz objectif – $H_2$ (*note* : ce problème peut être résolu par un procédé CLR à trois étapes, la troisième étape étant une réoxydation à l’air);

- CuFe$_2$O$_4$ (à l’intérieur du groupe de matériaux ferrospinelles TYPE I) et Co$_{0.6}$Fe$_{2.4}$O$_y$ (à l’intérieur du groupe de matériaux ferrospinelles TYPE) montrent le rapport $n_{H_2}/n_{Eth}$ le plus élevé: 1 (en considérant les valeurs intégrées sur 3 cycles consécutifs), ce qui est bien le double de la valeur obtenue sur Fe$_3$O$_4$ ($n_{H_2}/n_{Eth}=0.5$).

### CONCLUSIONS

On peut compléter la comparaison entre ferrospinelles substituées TYPE I (MFe$_2$O$_4$, où Fe/M=2/1) et TYPE II (M$_{0.6}$Fe$_{2.4}$O$_y$, où Fe/M=4/1) et le matériau de référence – Fe$_3$O$_4$ :

- L’incorporation de métaux (comme Cu, Co, Mn or Cu/Co, Co/Mn, Cu/Mn) modifie profondément les propriétés redox des matériaux ferrospinelles MFe$_2$O$_4$ and M$_{0.6}$Fe$_{2.4}$O$_y$. De plus, la présence de M en plus petite quantité (dans le TYPE II - M$_{0.6}$Fe$_{2.4}$O$_y$, avec Fe/M=4/1) a déjà été suffisante pour observer des effets positifs sur la production de $H_2$ par CLR à deux étapes du bioéthanol par rapport aux résultats obtenus sur Fe$_3$O$_4$ non modifiée. Une ultérieure augmentation de la fraction de M n’apporte aucune amélioration additionnelle aux performances des matériaux (comme pour le TYPE I - MFe$_2$O$_4$ avec Fe/M=2/1 mais, au contraire, montre un effet opposé (comme dans le cas des ferrites CoFe$_2$O$_4$ et Co$_{0.6}$Fe$_{2.4}$O$_y$, où le phénomène est expliqué par la faible tendance du Co$^0$ à être ré-oxydé avec l’eau comme seul agent oxydant). Ce qui implique que l’utilisation des ferrospinelles de TYPE II - M$_{0.6}$Fe$_{2.4}$O$_y$ comme matériaux porteurs d’oxygène et électrons est la plus attractive pour le CLR du bioéthanol à deux étapes, puisque la réoxidation par la vapeur d’eau dans la
deuxième étape conduit à la réoxydation incomplète des composantes métalliques (Co° et Cu°) formées dans l’étape précédente de réduction. On en conclut que plus de Co et Cu sont présents dans le matériau final M-modifié, moins de matériau sera disponible sous sa forme réoxydée pour être réduit dans les cycles successifs.

En conclusion: bien que plusieurs matériaux améliorés de cyclage redox aient été identifiés, la compréhension complète de leurs performances et ultérieures études d’optimisation sont nécessaires pour évaluer correctement l’efficacité, l’ingénierie et l’économie du procédé de reformage de l’éthanol par cyclage redox.
1. INTRODUCTION

Current processes for the industrial production of hydrogen are mainly based on the reforming of natural gas/naphtha or coil gasification. Such processes are highly energy demanding. Hence, less energy-intensive and more sustainable technologies, exploiting renewable feedstocks (such as biomass, bio-alcohols and water) and renewable primary energy sources (e.g. sunlight, wind, wave or hydro-power), appear to be very attractive for both industry and consumer applications. A variety of new technologies offering a non-fossil based route for hydrogen production are in a different stage of development, and each offers unique opportunities, benefits and challenges.\(^1\)\(^{–}\)\(^{10}\)

Chemical-Loop Steam Reforming is one of the possible ways to produce H\(_2\) starting from either conventional or renewable sources. Differently from classical reforming, separation costs can be avoided by splitting the process into two alternated steps in order to detach H\(_2\) and CO\(_x\) streams. One of the advantages of this technology relates to its feedstock flexibility. The chemical-loop process can be performed using a number of different reductants, such as gas resulting from coal\(^{11}\) or biomass\(^{12}\)\(^{–}\)\(^{14}\) gasification, light hydrocarbons reforming,\(^{15}\) methane,\(^{16}\)\(^{–}\)\(^{18}\) CH\(_4/\)CO\(_2\) and CH\(_4/\)H\(_2\) mixture,\(^{18}\)\(^{,}\)\(^{19}\) pyrolysis oil,\(^{20}\)\(^{,}\)\(^{21}\) methanol\(^{22}\) and pure H\(_2\) (as a method for H\(_2\) storage).\(^{23}\)\(^{,}\)\(^{24}\) Furthermore, the nature of the oxide, used as the ionic oxygen and electron carrier, and the reaction conditions are important parameters since they determine the potential for low costs and high efficiency of this process in order to have a commercial impact.

1.1. Hydrogen applications

Hydrogen is one of the key starting materials used in the chemical industry with an annual worldwide production of about 50 million tonnes. Currently, the largest amount (~95%) of the total manufactured hydrogen is consumed mainly by two industrial segments: the chemical sector, accounting for 65% of the market share (ammonia and methanol synthesis ~63%; liquid hydrocarbons and higher alcohols synthesis ~2%) and the refining sector, which accounts for 30% of the market share (hydrotreating and hydrocracking processes for
obtaining high grade petrochemical products). The other present uses, with ~5% of the total consumption, include the food industry (sorbitol and fat processing), the metallurgical industry (direct reduction of iron ore), the semiconductor industry, and etc (Figure 1-1).

In conclusion, there is a fast-growing need for increased hydrogen production, since H$_2$ itself may become an important “energy vector” with key applications as a carbon free fuel and as a fuel for hydrogen driven fuel cells for automotive uses. However, there are still several major problems to be overcome before it can be used in this way, including its manufacture, storage and distribution.

<table>
<thead>
<tr>
<th>INDUSTRIAL SECTOR</th>
<th>KEY APPLICATIONS</th>
<th>H$_2$ demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMICAL ~ 65%</td>
<td>-AMMONIA PRODUCTION (mix. H$_2$ + N$_2$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-METHANOL PRODUCTION (mix. H$_2$ + CO)</td>
<td></td>
</tr>
<tr>
<td>REFINING ~ 30%</td>
<td>-HYDROTREATING (S,N,O-removal; olefins and aromatics saturation)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-HYDROCRACKING (break C-C bond)</td>
<td></td>
</tr>
<tr>
<td>OTHERS ~ 5%</td>
<td>-FOOD INDUSTRY (hardening of edible oil)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-METALLURGICAL INDUSTRY (iron reduction; blanketing gas; forming gas)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-SEMICONDUCTOR INDUSTRY, etc.</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1-1. Main segments of hydrogen consumption

1.1.1. Fuel cells

Fuel cells are devices that generate electricity based on a chemical reaction and are often referred to as continuously operating batteries. They exploit electrolysis reactions in a similar manner to traditional batteries however the reagents are constantly supplied to the cell, which actually and determines its difference compared to the traditional dischargeable batteries. There are several kinds of fuel cells though the main operating principle remains the same: hydrogen atoms at the anode break down to form electrons and H$^+$ ions (1), the
latter ones migrate through the electrolyte to the cathode (2), where each $H^+$ ion combines with the oxygen to form water (5) (also emitting heat), while the electrons run through the electrical circuit (4), producing a current (3) (Figure 1-2).

![Figure 1-2. General scheme of the fuel cell technology](image)

Nevertheless, its applications can vary depending on the type of hydrogen fed to the anode (they can be chemical elements containing hydrogen) and the nature of the electrolytes (Figure 1-3).

![Figure 1-3. Lower segment: main application of the fuel cell technology; Upper segment: fuel and fuel cell types (taken from https://ec.europa.eu):](image)

- AFC: Alkaline (especially in the space sector)
- PEMFC: Polymer Exchange Membrane
- DMFC: Direct Membrane
- PAFC: Phosphoric Acid
1.2. Hydrogen production

1.2.1. Common feedstocks

Hydrogen can be produced from different resources including conventional fossil fuels, as natural gas, naphtha and coal, or either using renewable sources such as wind, solar, geothermal, biomass and etc. A variety of new technologies offering a non-fossil based route for hydrogen production are in a different stage of development, and each offers unique opportunities, benefits and challenges. A list of the various feedstocks and process technologies is presented in Figure 1-4.

---

**Figure 1-4. Summary of the various feedstocks and process alternatives for H₂ production**

---

1.2.2. Common processes for H₂ production
Hydrogen can be produced using a number of different processes (as illustrated in Figure 1-5). Thermochemical processes use heat and chemical reactions to release hydrogen from organic materials such as fossil fuels and biomass. Water (H₂O) can be split into hydrogen (H₂) and oxygen (O₂) using electrolysis or solar energy. Microorganisms such as bacteria and algae can produce hydrogen through biological processes. This session encompasses the most relevant information about the existing processes to manufacture hydrogen.

1.2.3. Hydrogen via Reforming Processes

Reforming processes are based on the endothermic or exothermic conversion of the feedstock materials with H₂O/CO₂/O₂ into synthetic gas mixture (CO+H₂). The most commonly used feedstocks for the reforming processes are methane or either other light hydrocarbons obtained from oil. Several chemical processes have been developed in order to produce hydrogen via reforming route:

1) Steam Reforming (SMR),
2) Auto Thermal reforming (ATR),
3) Partial Oxidation (POX),
4) Dry Reforming of methane (DMR),
5) Combined Reforming of Methane (CMR),
6) Reforming with Membrane,
7) Tri-Reforming of Methane (TMR)\textsuperscript{25}.

The first three are widely used industrial processes, whereas the last four are recent innovative processes developed with the aim to minimize environmental impact and energy consumption together with the improvements of already existing methods.

**Steam Methane Reforming (SMR) and Water Gas Shift (WGS) reaction**

\[ CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H^\circ = +225,4 \text{ kJ/mol} \]

Steam Methane Reforming (SMR) is the most common way to produce hydrogen rich syngas mixture (H\(_2\)+ CO). A conventional steam reformer unit consists of several hundred fixed-bed reactor tubes filled with a catalyst, which can vary in its size and geometry. High temperatures (> 600°C) and low pressures favour the formation of the H\(_2\) and CO products (Le Chatelier's Principle). However, in practice, the natural gas steam reformer is operated under the pressure of about 20-30 atm (for kinetic reasons) with an exit temperature of 800-870°C (but the tube wall temperature can range from 700°C up to a maximum hot spot of 920°C), where methane and steam are converted into synthesis gas. Primary steam reforming catalysts are nickel based catalyst: 10-20% Ni supported on \(\alpha\)-Al\(_2\)O\(_3\), calcium or magnesium aluminate with a life time from 3 to 5 years. Cobalt and noble metals are also active, but more expensive. Attempts to use non-metallic catalysts have not had commercial success because of the low activity. The catalyst properties are dictated by the severe operating conditions, i.e. temperatures of 450-950°C and steam partial pressures of up to 30 bar.

Normally, the subsequent stage of the SMR process includes WGS reactions which further convert carbon monoxide to carbon dioxide, while generating more hydrogen.
In the first stage, refers to a high temperature shift reaction, the gas is mixed with steam and passed over an Fe/Cr or Fe/Cr/Mg mixed oxide catalyst at $T = 300-450^\circ C$ in a fixed bed reactor; which decreases the carbon monoxide concentration down to 2-3%. In the second stage, the low temperature shift reaction, the mixture of gases is passed over a Cu/Zn oxide catalyst at $T = 190-220^\circ C$, where the carbon monoxide concentration is reduced to 0.1-0.2%. Further hydrogen purification can be achieved using:

- Methanation
- Pressure Swing Adsorption (PSA)
- Membrane reactors and etc.

**Steam Naphtha Reforming**

If naphtha is used as the feedstock, an extra reforming stage is needed. The naphtha is heated to form a vapour, mixed with steam and passed through tubes, heated at $T = 450-500^\circ C$ and packed with a catalyst, nickel supported on a mixture of aluminium and magnesium oxides. The main product is methane together with carbon oxides ($CO_x$), which then processed by SMR, as if it was natural gas, followed by the shift reaction.

**Dry Methane Reforming (DMR)**

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H^\circ = +260,5 \text{ kJ/mol}$$

The DMR process is characterized by a very low intrinsic activity, in addition to the simultaneous occurrence of the reverse water gas shift (RWGS) reaction resulting in a syngas ratio less than unity. Dry reforming of methane has been investigated with noble (Rh, Ru, Pd and Pt) and non-noble metal (Ni, Co and Fe) based catalysts. Noble metal catalysts have drawn attention for their superior coking resistance, higher stability and
activity especially for higher temperature applications. However, for large scale industrial applications, development of the active catalyst is still under investigation.

**Autothermal Reforming (ATR)**

Autothermal reforming (ATR) is an important industrial process used to produce syngas with a low H$_2$/CO ratio (from 1.5 to 3) desired for synthesis of methanol and higher molecular weight hydrocarbons (via Fischer-Tropsch process). The main concept based on a combination of non-catalytic partial oxidation and adiabatic catalytic steam reforming, where the reactor temperature is maintained using the heat emitted from the partial oxidation of the hydrocarbon feedstock, typically methane, with a sub-stoichiometric amount of oxygen.

\[
\begin{align*}
CH_4 + \frac{3}{2}O_2 & \rightarrow CO + 2H_2O & \Delta H^\circ &= -520,0 \text{ kJ/mol} \\
CH_4 + H_2O & \rightarrow 3H_2 + CO & \Delta H^\circ &= +225,4 \text{ kJ/mol}
\end{align*}
\]

This process was developed by Haldor Topsoe A/S with the aim to perform the POx (partial oxidation) and the SR (steam reforming) in a single ATR reactor. The very high temperatures in the ATR unit require a high thermal stability catalyst, which is typically the nickel-based catalyst on a stabilized Al or Mg-Al support.

**Partial oxidation (POX)**

\[
CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 & \Delta H^\circ = -36,0 \text{ kJ/mol}
\]

An alternative way to produce hydrogen based on the partial oxidation of a sub-stoichiometric fuel-air mixture which results in a formation of H$_2$-rich syngas. Partial oxidation is an exothermic reaction and, thus, considered to be more economically feasible than the processes of steam or dry reforming. The exothermic nature of reaction has certain drawbacks that it induces hot spots on catalyst arising from a poor heat removal rate.
causing the difficulties in operation control. A difference is made between thermal partial oxidation (TPOX) and catalytic partial oxidation (CPOX).

**Thermal (non-catalytic) Partial Oxidation**

TPOX is a non-catalytic process in which the feed is partially combusted with a sub-stoichiometric amount of air, oxygen, or enriched air to obtain CO+H\textsubscript{2} mixture, where the production of syngas depends on the oxygen/fuel ratio at operating temperature range of 1200-1500°C. Feedstock is used for the TPOX can be almost any carbonaceous material, from natural gas through liquid feeds such as fuel oils and gas oils as well as coal. A non-catalytic partial oxidation process was developed by Texaco and Shell which results in high syngas yields at high temperature and pressures\textsuperscript{26}.

**Catalytic Partial Oxidation**

CPOX is a catalytic process in which the feed with sub-stoichiometric amount of oxygen (or air) is catalytically converted into CO+H\textsubscript{2} mixture. The use of a catalyst lowers the required reaction temperature down to 800-900°C. Commonly used catalysts are noble (Pt, Rh, Ir, Pd) or non-noble (Ni, Co) metal based catalysts. Catalytic partial oxidation can be performed only if a sulfur content of the feed is below 50 ppm, since the higher sulfur content would poison the catalyst (in such case non-catalytic partial oxidation is more suitable for the use).

**1.2.4. Hydrogen via Chemical-Loop (CL) processes**

CL processes are based on the looping approach that usually consists of two temporarily/spatially separated steps: reduction and re-oxidation. During the reduction step, a transfer of the oxygen to the fuel mediated by a metal oxide carrier material (Me\textsubscript{x}O\textsubscript{y}), which is put in a contact with a reducing stream, thus being reduced and at the same time converting the fuel into products, mainly CO, H\textsubscript{2}O and H\textsubscript{2}. Subsequent oxidation step is performed over the previously reduced material (Me/Me\textsubscript{x}O\textsubscript{y-δ}) with air/H\textsubscript{2}O (water splitting) in order to restore its original oxidation state (Me\textsubscript{x}O\textsubscript{y}) and to produce H\textsubscript{2} (when the re-oxidation step is carried out with a steam). The difference is made whenever air or water
Steam are used to regenerate the oxygen carrier material. Re-oxidation step performed with air is varied between *Steam Reforming integrated to Chemical-Looping Combustion process* (SR-CLC), where CLC is used to energy supply needed for the conventional catalytic steam reforming and *Chemical-Looping Reforming process* (CLR) where primary products from the Chemical-Looping system are H\(_2\) and CO. Other processes use the property of some oxygen depleted materials to react with water steam to generate pure H\(_2\), also known as “water splitting”. In this category, it can be found *Chemical-Looping Hydrogen* (CLH) or *One Step Decarbonization* (OSD) processes, and the so-called Chemical-Looping Gasification technologies: *Syngas Chemical-Looping process* (SCL) and *Coal Direct Chemical-Looping process* (CDCL) and etc. Usually the later processes need several oxidation steps, like an air treatment, which sometimes required for the final regeneration of the oxygen carrier material\(^{27}\). One of the fundamental parameters, that determines the overall efficiency of many chemical looping processes, lies in the effectiveness of the oxygen carrier materials. Hence many research groups focus their attention on further improving the activity and the stability of oxygen carrying materials.

**Chemical-Loop Reforming (CLR) for Hydrogen Generation**

CLR for Hydrogen Generation is developed as an alternative way to produce H\(_2\) starting from either conventional or renewable sources. The Chemical-Loop process can be performed using a number of different reductants, such as gas resulting from coal\(^{11}\) or biomass\(^{12-14}\) gasification, light hydrocarbons reforming,\(^{15}\) methane,\(^{16-18}\) CH\(_4\)/CO\(_2\) and CH\(_4\)/H\(_2\) mixture,\(^{18,19}\) pyrolysis oil,\(^{20,21}\) methanol\(^{22}\) and pure H\(_2\) (as a method for H\(_2\) storage).\(^{23,24}\) Differently from a classical reforming, separation costs can be avoided by splitting the process into two/three alternated steps in order to detach H\(_2\)/CO\(_x\) streams and fully re-oxidize the oxygen carrier material (Figure 1-6). Generally, the reducing fuel (C\(_n\)H\(_{2m}\)) is fed to the FR, where it reacts with the oxygen carrier material (M\(_x\)O\(_y\)) according to the following equation:
After the first step, previously reduced oxygen carrier material is transferred to the steam reactor (SR), where it is oxidized by a water steam to restore its original oxidation state:

\[
(MR) - (n+m/2) \text{M}_x\text{O}_y + m \text{H}_2\text{O} \rightarrow (n+m/2) \text{M}_x\text{O}_{y-2} + m \text{H}_2\text{O} + n \text{CO}_2
\]

A general statement, made on the basis of the results obtained independently by several research groups: as the oxygen ratio in the system decreases, there is a higher tendency towards carbon formation, which in its turn leads to the lowering of the purity of the produced hydrogen. According to Cho et al.\textsuperscript{28}, the rate of carbon formation increased rapidly when more than 80 % of the available oxygen in the Ni-based oxygen carrier was consumed. Galvita and Sundmacher reported that a maximum Fe reduction of 60 % largely minimized carbon formation and a high purity hydrogen stream (< 20 ppm CO) could be obtained\textsuperscript{29}.

Usually, the difficulty to re-obtain original oxidation state of the oxygen carrier material by means of only water steam can lead to the necessity of an additional oxidation step, like an air treatment:

\[
(AR) - (n+m/2) \text{M}_x\text{O}_{y-1} + \frac{1}{2} \text{O}_2 \rightarrow (n+m/2) \text{M}_x\text{O}_y
\]

Oxygen carrier material (M\textsubscript{x}O\textsubscript{y}), in its fully oxidized form, is further re-circulated to the fuel reactor (FR) for subsequent cycles.
Important aspects for the overall effectiveness of the process lie in the choice of operation conditions, reactors design and identification of suitable candidates to be used as corresponding oxygen carrier materials. Appropriate oxygen carriers should have sufficiently high conversion rates in redox reactions, high agglomeration/sintering resistance, complete fuel conversion, negligible carbon deposition, and be economical and environmentally friendly.

**Oxygen carrier materials**

As it has been already mentioned, a choice of the suitable oxygen carrier material for any type of Chemical-Loop process is an important parameter which has to be considered, taking into account several properties: reaction kinetics, thermodynamic feasibility of oxygen transfer, redox properties, oxygen content, long term recyclability and durability, attrition resistance, heat capacity, melting points, tendency to form coke, resistance to carbon deposition, low cost, toxicity and etc. However, one of the most important requirements is the thermodynamic aspect of a suitable redox couple – \( \text{M}_x \text{O}_y/\text{M}_x \), which determines the final effectiveness of the process together with a choice of operating conditions. Figure 1-7 shows the Gibbs free energies (\( \Delta G \)) as a function of temperature for...
some frequently studied oxygen carrier materials; moreover, the values for oxygen transport capacity are listed in Table 1-1.

Figure 1-7. Gibbs free energies for the following redox reactions\textsuperscript{31}: I. Reduction of oxygen carrier with a CH\textsubscript{4}-fuel: a - CH\textsubscript{4} total combustion (CH\textsubscript{4} + 4/y M\textsubscript{x}O\textsubscript{y} → CO\textsubscript{2} + 2 H\textsubscript{2}O + 4x/y M), b - CH\textsubscript{4} partial oxidation (CH\textsubscript{4} + 1/y M\textsubscript{x}O\textsubscript{y} → CO + 2H\textsubscript{2} + x/y M); II. Re-oxidation of reduced oxygen carrier with a steam/air: c - H\textsubscript{2}O oxidation (x M + y H\textsubscript{2}O → M\textsubscript{x}O\textsubscript{y} + y H\textsubscript{2}), d - air oxidation (x M + y/2 O\textsubscript{2} → M\textsubscript{x}O\textsubscript{y}), \*see Table 1-1 for the numeric legends

Table 1-1. Common redox couples\textsuperscript{31}

<table>
<thead>
<tr>
<th></th>
<th>Redox couple</th>
<th>Oxygen transport capacity, kg/kg-metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiO/Ni</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>CuO/Cu</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>Fe\textsubscript{3}O\textsubscript{4}/Fe</td>
<td>0.38</td>
</tr>
</tbody>
</table>
According to the listed data, oxygen carrier materials can be conventionally divided into the materials that are capable to partially oxidize methane, like ZnO/Zn, V$_2$O$_5$/V or CeO$_2$/Ce$_2$O$_3$. Whereas some redox couples, as NiO/Ni, Co$_3$O$_4$/Co and CuO/Cu, favor total methane oxidation; in addition, their further re-oxidation is also favorable over a wide temperature range, as supported by the negative $\Delta G$ values in Figure. Thus, oxygen carrier materials based on the Ni, Co and Cu elements are often regarded as good candidates for Chemical-Loop applications.

A comprehensive review on different oxygen carrier materials for the hydrogen production via Chemical-Loop processes was recently published by Protasova et al$^{30}$. The review encompasses information on the different perovskites and Ni/Fe/Cu/Co-based oxygen carrier materials. Perovskites showed good results for the partial oxidation of methane; whereas with Fe-based materials promising results also have been obtained (moreover they are considered to replace Ni-based oxygen carriers because of their price and toxicity). Several research groups have been exploring modifications of simple iron oxide (Fe$_3$O$_4$ and Fe$_2$O$_3$) in order to prevent deactivation,$^{32}$ to lower the operating temperature$^{33}$ and to increase the structural stability and reducibility,$^{34,35}$ the reaction rate for oxidation and total efficiency of the process.$^{36,37}$ Several studies were dedicated to different metal additives to iron oxide.$^{38,39}$ In addition, ternary metal systems have also been considered in the search for a better synergetic effect.$^{40,41}$ Several research groups have been investigated the effect...
of various M-additives on the stability and redox behavior of iron oxide for chemical hydrogen storage using Pd, Pt, Rh, Ru, Al, Ce, Ti, Zr and Al, Cr, Zr, Ga, V, Mo. And it was found out that Pd, Pt, Rh and Ru additives have an effect on promoting the reduction and lowering the re-oxidation temperature of iron oxide. At the same time, Al, Ce, Ti, Zr, Cr, Ga and V additives prevent deactivation and sintering of iron oxide during repeated redox cycles. Some recent studies on developing of the novel and efficient oxygen carrier materials for Chemical-Loop applications highlight the special interest in spinel oxides which, first of all, can be explained by their ability to form thermodynamically stable spinel oxides which allow to re-obtain the initial spinel phase upon cycling and in turn increase the stability of the looping material itself.

1.3. Spinel oxides: \( \text{AB}_2\text{O}_4 \)

Spinel oxides with a generic formula of \( \text{AB}_2\text{O}_4 \) are chemically and thermally stable materials suitable for various applications including catalysis (Figure 1-8). Many of them are used as magnetic pigments, nanodevices, photoelectric devices, sensors and microwave devices. Besides, spinel ferrites (\( \text{AFe}_2\text{O}_4 \)) are attractive because of the importance in ferrofluids, magnetic drug delivery and hyperthermia for cancer treatment. At the same time, they have well-established catalytic properties for many reactions, such as: oxidative dehydrogenation of hydrocarbons, decomposition of alcohols, selective oxidation reactions, CO and CO\(_2\) removal, VOCs and propane total oxidation, methanol steam reforming, hydrogen peroxide decomposition, \( \text{NO}_x \) selective reduction and WGS reaction. The catalytic effectiveness of these systems explained by the ability of metallic ions to migrate between the sub-lattices without altering the structure, which makes the catalyst efficient for many organic transformation reactions. Versatile catalytic properties are dependent on the chemical composition and nature of substituted ions, charges and their distribution among the \( \text{O}_h \) and \( \text{T}_d \) sites, and this is determined by the synthesis methods.
Structure of $\text{AB}_2\text{O}_4$ oxides

The crystallographic structure of spinel oxide group is formed by a nearly closed-packed face centered cubic (fcc) of anions (Figure 1-9) with two unequivalent sites for cations, which differ in oxygen coordination. A tetrahedral site, $\text{AO}_4$, is comprised of the cation at the center of a cube and four oxygen atoms in the nonadjacent corners. The octahedral site, $\text{BO}_6$, consists of a cation surrounded by six oxygen atoms, two along each dimensional axis, to form an octahedron. The preference of the individual ions for the two types of lattice sites ($\text{O}_{\text{h}}\text{vs}\text{T}_d$) is determined by:

- the ionic radii of the specific ions;
- the size of the interstices;
- the temperature;
- the orbital preference for specific coordination.

On the basis of a cation valency occupation in the molecule of the spinel oxide they can be subdivided into three basic types:

1. $\text{M}_1^{2+}\text{M}_2^{3+}\text{O}_4$, (2-3 spinel): Fe$_3$O$_4$, NiFe$_2$O$_4$, CuFe$_2$O$_4$
2. $\text{M}_1^{3+}\text{M}_2^{2+}\text{O}_4$, (4-2 spinel): GeFe$_2$O$_4$, TiFe$_2$O$_4$
3. $\text{M}_1\text{M}_2^{1+}\text{O}_4$ (6-1 spinel): MoLi$_2$O$_4$, WAg$_2$O$_4$

However, the most common type is 2-3 spinel which comprises of $\text{M}^{2}(\text{II})$ and $\text{M}^{3}(\text{III})$ metal cations in the molecular unit.

According to the distribution of A and B cations between $T_d$ and $O_h$ sites, there are two types of spinel oxides: normal and inverse spinels. In the **normal spinel**, the A cations (divalent) occupy all the tetrahedral sites, and the B cations (trivalent) fill the octahedral sites. Since tetrahedral holes are smaller than octahedral holes, the A ions should be smaller than the B ions. In fact, this condition is not fulfilled in many spinels, and thus there is another type of spinels, which is more common in nature, so called the inverse spinel, just to indicate that they were the opposite of what had already been described. In **inverse spinel**, the B cations occupy the tetrahedral sites, and the octahedral sites contains a mixture of B and A cations. Important parameter which is used to describe the degree of spinel inversion denotes as an inversion parameter ($\delta$), and is equal to 0 in a case of the **normal spinel** and 1 for the **inverse spinel**.
1.4. Aim of the research project

The research work presented here investigates a new process, named as Chemical-Loop Reforming (CLR) process, to produce “clean H$_2$” with an inherent CO$_x$ separation. The main principle of the CLR process is that an oxygen-storage material is first reduced by ethanol stream (T-450°C), and then re-oxidized by water (T-450°C) to produce hydrogen and to restore the original oxidation state of the looping-material (Figure 1-10).

The choice of ethanol as a reducing agent has its several advantages:

- The use of bio-alcohols in cycle reforming has not yet been much studied in literature;
- Ethanol can be obtained from biomasses, that might contribute to unlink the production of hydrogen from fossil fuels;
- Ethanol is a non-toxic liquid, easy to transport and handle, relatively stable at room temperature.

The initial task of the project is to define conditions and materials that may lead to an optimized process, allowing producing a hydrogen stream that does not require any additional purification or separation treatment. Hence, different M-modified spinel-type mixed oxides (TYPE I – $MFe_2O_4$ and TYPE II – $M_{0.6}Fe_{2.4}O_y$) are synthesized and tested as potentially attractive ionic oxygen and electron carrier looping materials to generate hydrogen by oxidation with steam, after a reductive step carried out with ethanol.
Particularly, the focus on the reactivity behavior of secondary/ternary materials explained by their ability to form thermodynamically stable spinel oxides which allow us to re-obtain the initial spinel phase upon cycling and in turn increase the stability of looping material itself. The composition of $\text{MFe}_2\text{O}_4$ and $\text{M}_0.6\text{Fe}_{2.4}\text{O}_y$ ferrospinels is varied in between transition metals: Co, Mn, Cu or Cu/Co, Cu/Mn, Co/Mn and alkaline earth metals: Ca, Mg. The aim of the following modifications is to pursue a higher selectivity to some valuable chemicals produced on the 1$^{\text{st}}$ reduction step along with a high purity $\text{H}_2$ produced during the 2$^{\text{nd}}$ re-oxidation step.

The secondary task is to explore the chemistry of the process, by means of both in-situ and ex-situ techniques, and the characteristics of the mixed oxides, in terms of redox properties, morphology and chemical-physical features which also encompasses the solid-state chemistry investigations of the fresh and cycled looping materials.

This research was apportioned between three institutions, all details about the accomplished work are summarized in Figure 1-11.
2. CHARACTERIZATION TECHNIQUES AND SET-UP OF LABORATORY PLANT

This chapter includes the information on several characterization techniques used to study bulk and surface properties of the fresh/used looping materials (ferrospinels of TYPE I – MFe$_2$O$_4$ and TYPE II – M$_{0.6}$Fe$_{2.4}$O$_y$, where M: Cu, Co, Mn, Mg, Ca and Cu/Co, Cu/Mn, Co/Mn). All the solids were tested in a laboratory-scale plant designed to carry out the Ethanol Chemical-Loop Reforming experiments. In addition, the chapter contains a description of the analysis method used for identification and quantification of the reactants/products including the calculation protocols.

2.1. X-ray diffraction (XRD)

X-ray diffraction is a primary technique used to determine nature of the crystalline phases and to measure a size, shape and internal stress of small crystalline regions. Information on the sample is given by the position, intensity, sharpness and width of the diffraction lines. The diffraction angle 2θ and the spacing between two planes (h,k,l) $d$ are related by the Bragg’s law:

\[ 2d \sin \theta = n \lambda \]

Where:

- $\lambda$ – the wavelength of incident X-ray
- $n$ – the diffraction order
In the present study, the powder X-ray diffraction (XRD) patterns were measured on Bruker D8 Advance diffractometer (using Cu Kα radiation with λ = 1.5406 Å) with a Bragg-Brentano geometry and equipped with a Bruker Lynx Eye detector. The data were recorded varied from 5 to 80° 2θ diffraction angle with an acquisition time of 1 s per each step (0.01 degree).

The Debye-Scherrer equation was used for the calculation of a crystallite size, which is related to the FWHM (Full Width at Half Maximum) through the formula:

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]

Where:
- \( \tau \) – the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size
- \( K \) – the dimensionless shape factor, with a value close to unity (\( K \) is typically eq. to 0.9)
- \( \lambda \) – the X-ray wavelength
- \( \beta \) – the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening
- \( \theta \) – the Bragg angle
TOPAS-4.2 program was used to refine the unit cell parameters of the crystalline phases and to calculate the relative phase content in the fresh/used samples. The calculations are based on the Rietveld refinement method, which permits the reproduction of the whole diffractogram, through the optimization of both structural (peak position and intensity) and non-structural (peaks shape) data.

### 2.2. Raman Spectroscopy

Raman spectroscopy is used to observe the differences in the vibrational modes of the samples with respect to the composition which causes local distortions that are not seen by x-ray diffraction. Raman spectra were recorded using a Bruker spectrometer with a 633 nm He/Ne laser source (filter: \( P_{\text{laser}} \div 10 \); slit 100 μm) equipped with a microscope (50X lens). Each spectrum was taken with 300 sec exposure time and 1 accumulation.

![Figure 2-2. Schematic identifying light scattering after laser exposure on a sample surface](image)

### 2.3. Mössbauer Spectroscopy

The Mössbauer effect consists of the "recoilless" emission of γ-ray photons from certain radioactive nuclei, and the selective re-absorption of those photons by other nearby nuclei. The process is sensitive to small differences between the structure of the emitting and the absorbing nuclei. Mössbauer spectroscopy uses this phenomenon to explore the nuclear and atomic structure of materials.
Through Mössbauer spectroscopy it is possible to obtain important information on the oxidation state and the structure of Fe species in a solid. The main nuclear interactions used for the interpretation of the resonance spectra are three:

- **Isomer Shift (IS)**, which is the shift in nuclear energy levels induced by the static charge of nearby atomic electrons
- **Quadrupole Splitting (QS)** which is the shift in nuclear energy levels induced by a strong electric field gradient due to nearly electrons and
- **Magnetic (or Hyperfine) Splitting (HS)** corresponding to the energy level splitting in a nucleus due to the magnetic fields induced by the nearby atomic electrons.

The Mössbauer spectrometer was a homemade apparatus using a $^{57}$Co/Rh γ-ray source and a conventional constant acceleration Mössbauer spectrometer. The solids were pressed into thin discs and the analysis took about one day to be completed (in some cases it can require even longer time).

Isomer shifts were given with respect to α-Fe. All spectra were taken at room temperature and ambient atmosphere; samples were diluted in sucrose at about 50%$_w$ concentration. Integrated areas under individual deconvoluted peaks were used to obtain the relative populations of different iron species, assuming an equal recoil-free fraction for all the species.

The calculations were made using pure Lorentzian functions. The parameters characterizing a Mössbauer spectrum were determined by least-squares fitting and the goodness of the fit statistics by minimizing the $\chi^2$ quadratic function:

$$\chi^2 = \sum_i \frac{(y_{i,\text{th}} - y_{i,\text{exp}})^2}{y_{i,\text{exp}}} \cdot \frac{1}{N-K}$$

Where:

- **N** - the number of measured points
- **K** - the number of the parameters to be determined
- $y_{i,\text{exp}}$ and $y_{i,\text{th}}$ – measured and calculated spectral values in velocity for each point $i$
Another $^{57}$Fe Mössbauer spectra (taken in Montpellier and discussed in the Paragraph 5.11) were measured using a conventional constant acceleration spectrometer, and a commercial $^{57}$Co:Rh γ-ray source. Both the sample and the absorber were kept at room temperature. The velocity calibration was performed using a α-iron absorber, and the isomer shift (δ) values are given relative to α-Fe metal. The collected spectra were least-square fitted by appropriate combinations of Lorentzian profiles, either with several discrete quadrupole doublets corresponding to different iron environments, or by assuming a distribution of the magnetic hyperfine fields (BHF), corresponding to the continuous distribution of non-equivalent magnetic interactions in the sample.

### 2.4. Surface area measurements

The specific surface area was measured applying the single point BET method. The instrument used for this analysis was a Carlo Erba Sorpty 1750 Fisons Instrument.

The method calculates the surface area of the sample from the volume of the gas corresponding to the monolayer adsorption. So, the variable that has to be measured from the analysis is the gas volume for the monolayer adsorption. The single-point approximation is based only on one measurement of the pressure of adsorption and the corresponding gas volume adsorbed; the formula used is here reported:

$$\frac{P}{V(P_2 - P)} = \frac{1}{V_m \cdot c \cdot \frac{P}{P_2}}$$

where $P$ is the pressure, $P_s$ is the surface tension of the adsorbed gas (nitrogen in this case), $V$ is the adsorbed gas volume, $V_m$ is the monolayer gas volume and $c$ is a constant related to the gas-surface interaction. A second approximation made by the instrument software is that the constant $c$ is very high compared to the other variables and so the final equation is

$$\frac{P}{V(P_s - P)} = \frac{1}{V_m \cdot \frac{P}{P_s}}$$
The percent error that derives from these approximations is about 7% on values over 3 m\(^2\); below this limit, the surface area calculated cannot be considered reliable.

For the analysis, around an amount of 0.5 g of the sample was placed inside the sample holder and then heated at 150°C under vacuum (≤4 Pa) to release water, air, CO\(_2\) or other molecules adsorbed. Subsequently, the sample was placed in liquid nitrogen, and the adsorption of the gaseous N\(_2\) was carried out.

The particle size (d) was calculated on the basis of the following correlation:

\[ d = \frac{6}{SSA \cdot \rho} \]

Where:

SSA – value of the specific surface area, m\(^2\)/g

\( \rho \) – density of the sample, g/m\(^3\)

2.5. SEM/TEM-EDX analysis

TEM/EDX characterisation, samples were suspended in ethanol and homogenized using ultrasonication (for 5 min). The suspension was deposited on a holey-carbon film Cu-grid for TEM analysis, then dried at 100°C. The analyses were carried out by a microscope TEM/STEM FEI TECNAI F20 at 200 keV.

SEM/EDX analyses were performed by using a SEM Zeiss EP EVO 50 with a tungsten electron source, secondary and backscattered electrons detectors. The EDX system is an Oxford Instruments INCA ENERGY 350 including a Si(Li) detector equipped with an ultrathin window (Z>4 (Be)). The images were collected in high vacuum mode @ EHT = 20 keV and the spectra were registered for 60s collection time.

2.6. Temperature programmed reduction/oxidation (TPR1/O/R2)

The objectives of this technique are essentially the following:

1. To find the most efficient redox conditions
2. To characterize complex systems of M-modified ferro spinels: MFe$_2$O$_4$ and M$_{0.6}$Fe$_{2.4}$O$_y$ (where M=Cu, Co, Mn, Mg, Ca and Cu/Mn, Co/Mn, Cu/Co) in order to determine the role of each component on the reduction evolution of the whole material.

The instrument used for TPR/O analysis was the 1100 Micromeritics AutoChem II. 2920 V 4.05 Chemisorption Analyzer. The samples were first pre-treated at 450°C for 45 min in He flow (30 min/min). Reduction 1/Reduction 2 (TPR-1/TPR-2) was carried out with 5 % H$_2$ in the Ar flow (30 ml/min). The oxidation stream (TPO) was 5% O$_2$ in the He flow (30 ml/min). Temperature program started at 50°C and then the temperature increased up to 800°C (with ramp 10°C/min) and maintained there for 40 min. This last step was repeated for all the experiments (TPR-1/TPO/TPR-2).

2.7. Carbon content measurements (CHNS)

The carbon contents of the materials after the each one of the two steps was determined using a CHNS/Oxygen automatic elemental analyzer Thermo Scientific MASS 200R. The samples were homogenized and loaded in small aluminum capsules and analyzed. For each samples two analyses were carried out in order to check for the homogeneity of the solid. Results were given as weight % of C, and the precision of the measurement was 0.3%.

2.8. Magnetic measurements

Static magnetization and low-temperature hysteretic properties (at 300 K) of the AFeNi, AFeMn, and AFeCo samples were measured using a Quantum Design MPMS SQUID magnetometer, equipped with a superconducting magnet producing fields up to 50 kOe.

2.9. In-situ X-ray Photoelectron Spectroscopy (XPS) experiments

X-ray Photoelectron Spectroscopy allows the direct characterization of a surface and it is widely used in catalyst characterization. The technique provides data, via expulsion and analysis of the related energies, of electrons from the solid and gives pieces of information.
on the composition and chemical status of the elements on the solid surface before/after reaction test. XPS is exciting ‘core’ electrons by means of a soft X-ray beam (i.e. Mg/Al Kα). The emitted electrons bring to us the information coming from a depth of 1-10 nm, so providing a good surface picture without its damage (Figure 2-3). The use of XPS in catalyst investigation is increasing and nowadays the availability of synchrotron light instrumentation (super ESCA) is favouring the XPS investigations because they are of great help in surmounting also the sensitivity problem.

Figure 2-3. X-ray photoelectron spectroscopy physics (https://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy)

X-ray Photoemission Spectroscopy (XPS) data were acquired using non-monochromatized AlKα (1486.6 eV) x-ray source, and an Omicron EA125 electron analyser (Figure 2-4). The measurements were carried out in a custom built ultra-high-vacuum system operating at the base pressure of 5x10^-10 mbar equipped with facilities for sample heating and controlled gas dosing. The spectra were acquired at room temperature (RT) on drop casted films of powder samples suspended in water. Different sample treatments have been carried out: annealing in UHV at 450°C, reduction with ethanol at 450°C (5x10^-6 mbar) and re-oxidation at 450°C in water ambient (2x10^-4 mbar). For each of four M-modified ferrospinels (referring to Co_{0.6-x}Mn_xFe_{2.4}O_y) Fe 2p, O1s and Co 2p and/or Mn 2p photoemission spectra were recorded sequentially after introduction in the UHV systems (“as received”), after annealing...
in UHV for 30 min at 450°C, after exposure to ethanol at 450°C and after H₂O exposure at 450°C.

2.10. Diffuse-Reflectance Infrared FT spectroscopy (DRIFTS) experiments

As shown in Figure 2-5, when an infrared beam reaches a sample, the incoming light may be partly reflected regularly (specular reflection) by the sample surface, partly scattered diffusely, and partly penetrates into the sample. The latter part may be absorbed within the particles or be diffracted at grain boundaries, giving rise to diffusely scattered light in all directions. This component of the radiation exits the sample at any angle but, since the light that leaves the surface has traveled through the particles, it contains data on the absorption properties of the material.
Figure 2-5. Representation of DRIFTS principle

In diffuse reflectance spectroscopy, there is no linear relation between the reflected light intensity (band intensity) and concentration, in contrast to traditional transmission spectroscopy in which the band intensity is directly proportional to concentration. Therefore, quantitative analyzes by DRIFTS are rather complicated. The empirical Kubelka-Munk equation relates the intensity of the reflected radiation to the concentration that can be used for quantitative evaluation. The Kubelka-Munk equation is defined as:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s}$$

Where:
- $R$ - reflectance
- $k$ - absorption coefficient
- $s$ - scattering coefficient
- $c$ - concentration of the absorbing species
- $A$ - absorbance

In Kubelka-Munk equation it is assumed that $s$ is the independent of wavelength and the sample is weakly absorbing. The former condition is achieved by proper sample preparation and the latter by dilution of strong absorbing samples with non-absorbing substrate powder (such as KBr or KCl). Therefore, to obtain reproducible results, particle size, sample packing and dilution should be carefully controlled, especially for quantitative analysis\textsuperscript{93}.
Diffuse-Reflectance Infrared FT spectroscopy, coupled with a quadrupole mass spectrometer (DRIFTS-MS) was used to characterise the surface features of materials, the scheme of the instrument is depicted in Figure 2-6. During a standard procedure, the sample was pre-treated at 450°C in a He flow (5mL/min) for 1 h in order to remove molecules possibly adsorbed on the material, mainly carbon dioxide and water. Then the sample was cooled down to 30°C, and the IR background was collected. Afterward ethanol was fed at 0.6 µL/min until saturation was reached (as seen by IR and MS; around 20 min) and whereupon the He flow was maintained until the weakly adsorbed ethanol was evacuated from the cell with loaded catalyst. During evacuation, the DRIFT and mass spectra were taken to follow stabilization of the system. When the mass and DRIFT spectra were stable, the temperature was increased up to 150°C for 2 min and then the system was cooled down to 30°C to record the spectra. This last step was repeated for the other temperatures (150, 200, 250, 300, 350 and 400°C).94

The adsorption of alcohols over metal oxides can lead to different kind of adsorbed species depending on the surface properties of the material under study. Table 2-1 shows the most representative intermediates and collects the characteristic infrared bands for the adsorption of ethanol according to the literature94–99.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>Characteristic frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen bonded ethanol</td>
<td>3000-3700 OH ν</td>
</tr>
<tr>
<td></td>
<td>1380 CH₃ δ</td>
</tr>
<tr>
<td></td>
<td>1500-1200 OH δ (broad)</td>
</tr>
<tr>
<td>Chemisorbed undissociated ethanol</td>
<td>3500-3700 OH ν</td>
</tr>
<tr>
<td></td>
<td>1380 CH₃ δ</td>
</tr>
<tr>
<td></td>
<td>1270 OH δ (sharp)</td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Adsorbed ethoxide</td>
<td><img src="image" alt="Ethoxide Structure" /></td>
</tr>
<tr>
<td>η$^1$-Acetaldehyde</td>
<td><img src="image" alt="Acetaldehyde Structure" /></td>
</tr>
<tr>
<td>η$^2$-Aldehyde</td>
<td><img src="image" alt="Aldehyde Structure" /></td>
</tr>
<tr>
<td>Acyl</td>
<td><img src="image" alt="Acyl Structure" /></td>
</tr>
<tr>
<td>Acetate</td>
<td><img src="image" alt="Acetate Structure" /></td>
</tr>
<tr>
<td>Carbonate</td>
<td><img src="image" alt="Carbonate Structure" /></td>
</tr>
<tr>
<td>Acetone</td>
<td><img src="image" alt="Acetone Structure" /></td>
</tr>
</tbody>
</table>
2.11. Reactivity experiments: Chemical-Loop Reforming (CLR) process

The choice of reaction conditions and cycling time was adopted according to the study of Cocchi (reducing agent: methanol, \(T_{\text{red}}\) – 300 and 420°C/\(T_{\text{re-ox}}\) – 420°C, looping materials: \(\text{Fe}_3\text{O}_4\), \(\text{CoFe}_2\text{O}_4\) and \(\text{NiFe}_2\text{O}_4\))\textsuperscript{100} and Trevisanut (reducing agent: ethanol, \(T_{\text{red}}\) – 400 and 450°C/\(T_{\text{re-ox}}\) – 450°C, looping materials: \(\text{Fe}_3\text{O}_4\), \(\text{CoFe}_2\text{O}_4\) and \(\text{NiFe}_2\text{O}_4\))\textsuperscript{101}. Hence, previously obtained results suggested that the best reaction conditions have to be as follows: 1\textsuperscript{st} step – ethanol reduction at \(T_{\text{red}}\)-450°C and 2\textsuperscript{nd} step – water re-oxidation at \(T_{\text{re-ox}}\)-450°C. Reactivity experiments were carried out by loading app. 400 mg of M-modified ferrite, shaped in particles with diameter ranging from 0.25 to 0.6 mm; the reduction/re-oxidation step was carried out by feeding continuously a stream of ethanol (15.6 mol %)/water (29.3 mol %) vapors in \(\text{N}_2\). Modifications to the conventional process were made in order to achieve its better effectiveness.
Laboratory-scale reactor

The reactivity tests were carried out in a laboratory-scale plant, depicted in Figure 2-7. Schematically, the plant can be subdivided into three zones: 1. Feeding Zone (“FZ”), 2. Reaction Zone (“RZ”), 3. Analysis Zone (“AZ”).

In the 1st“FZ” a flow of carrier gases, mainly N\textsubscript{2}, was controlled by two mass flow-meters (at \(v=30\) mL/min); the outgoing gas was sent through a pre-heated pipe (T-150°C) where it was further mixed with a vaporized ethanol/water stream. Liquid reagents, like ethanol/water, were fed by means of a syringe pump set at a desired rate (ethanol - 0.8 mL/h; water - 0.55 mL/h).

The 2nd“RZ” is the zone where Chemical-Loop Reforming (CLR) reactions took place. The reactivity experiments were carried out in the fixed-bed quartz flow reactor (with an internal diameter of 12 mm and a length of 30 cm; the catalytic bed height was less than 5 mm) inserted into a furnace; while the temperature of the catalytic was measured by means of an axial thermocouple placed inside.

The third part is the “AZ”, where the exit flow is sent to a micro-GC connected to a computer. Two different configurations were adopted for this zone, depending on the used reagent: during the reduction step carried out with ethanol, the stream, containing the products and the unconverted reagent, was sent directly through a heated line to the micro-GC; whereas during the re-oxidation step, carried out with water, the out flowing gases first passed through a water trap and only after that were sent to the micro-GC (such installation was made in order to avoid a damage of the GC-columns). The instrument used was an Agilent 3000A micro-GC installed on-line. The instrument was equipped with 3 columns: (a) a Plot Q column, carrier He, for the separation of CH\textsubscript{4}, CO\textsubscript{2}, H\textsubscript{2}O, ethane, ethylene and propane; (b) a OV1 column, carrier He, for the separation of ethanol, acetaldehyde, H\textsubscript{2}O, acetone, diethylether, ethylacetate, acetic acid, crotonaldehyde, pentanone-2, toluene; (c) a Molecular Sieve 5A column, carrier Ar, for the separation of H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, and CO. A Plot U backflash column was installed in order to avoid CO\textsubscript{2} and H\textsubscript{2}O poisoning of the third column.
The instrument allowed carry out an analysis every 5 min during the 1st step and every 2 min during the 2nd step. This resulted in a large amount of data to be treated; therefore, the use of an Excel “macro” was necessary\textsuperscript{101}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure27.png}
\caption{Schematic representation of the laboratory-scale plant}
\end{figure}

\textbf{Data processing and parameters calculation}

\textit{1st step – reduction}

For the reduction step, we decided to feed a flowing gas containing 15.6 \% of ethanol in 30 ml/min of nitrogen \textsuperscript{100}, at T-450°C. The resulting contact time (\(\tau\)), app. 0.27 s, was calculated using the following equation:

\[
\tau = \frac{V_{\text{cat}}(\text{ml})}{V'_{\text{tot}} \text{ (ml/s)}}
\]
Results obtained from the micro-GC analysis were expressed as \( %_v \) in the outlet stream. In order to calculate yields and conversion the following formulas were used:

\[
Y_{P,A} = \frac{n_{P,\text{out}}}{n_{A,\text{in}}} = \frac{\%_v^{P,\text{out}} \cdot V_{\text{out}}^\text{tot}}{\%_v^{A,\text{in}} \cdot V_{\text{in}}^\text{tot}} = \frac{\%_v^{P,\text{out}}}{\%_v^{A,\text{in}}} \cdot F_{\text{vol}}
\]

\[
X_A = \frac{\dot{n}_{A,\text{in}} - \dot{n}_{A,\text{out}}}{\dot{n}_{A,\text{in}}} = 1 - \frac{\%_v^{A,\text{out}}}{\%_v^{A,\text{in}}} \cdot F_{\text{vol}}
\]

* Considering a generic reaction \( A \rightarrow P \)

\( F_{\text{vol}} \) is volumetric factor, which is obtained experimentally using \( N_2 \) as internal standard, and represents the change of the volumetric flow due to the variation of the number of moles.

\[
F_{\text{vol}} = \frac{\%_v^{N_2,\text{in}}}{\%_v^{N_2,\text{out}}}
\]

After a calibration, it was possible to determine the “instantaneous” molar yield (relative to the sampling instant) of the following compounds: \( \text{CO, CO}_2, \text{CH}_4, \text{acetaldehyde, ethylene, ethane, ethylacetate, diethylether, acetic acid, propylene, propane, pentanone, toluene, acetone, H}_2 \) and \( \text{H}_2\text{O} \).

As the solid released oxygen to form products, until complete reduction was achieved, and due to the fact that coke or carbonaceous residues might accumulate on the solid during reaction, it was not possible to make an atomic balance neither of \( \text{O} \) atoms nor of \( \text{C} \) atoms. Therefore, an instantaneous balance on \( \text{H} \) atoms (the only species which was not contained in an accumulation term in material balances for the flow reactor) was carried out, which allowed to calculate: (a) the instantaneous balance on \( \text{C} \) and hence the amount of \( \text{C} \) accumulating on catalyst (expressed with the term “coke”), (b) the instantaneous balance of \( \text{O} \) and hence the amount of \( \text{O} \) released from the catalyst, and (c) the reduction degree of the solid.
2\textsuperscript{nd} step – re-oxidation

For the oxidation step, since water was trapped before the GC inlet and therefore was not analyzed, it was necessary to determine the concentration of the different products, considering also water, by means of these equations:

\[
\text{Conc}_{\text{vol},i}^\text{vol} = \%_{\text{GC}}^\text{vol} \times \frac{\%_{\text{in}}^\text{vol,N_2}}{\%_{\text{GC}}^\text{vol,N_2}} \quad \text{(where } i = \text{H}_2\text{O, CO}_2, \text{CO, CH}_4)\]

\[
\text{Conc}_{\text{vol},\text{H}_2\text{O}}^\text{vol} = 100 - \text{Conc}_{\text{vol},\text{H}_2}^\text{vol} - \%_{\text{in}}^\text{vol,N_2}
\]

\[
\%_{\text{real}}^\text{vol,j} = \frac{\text{Conc}_{\text{vol},j}^\text{vol}}{\sum \text{Conc}_{\text{vol},j}^\text{vol} + \%_{\text{in}}^\text{vol,N_2}} \quad \text{(where } j = \text{H}_2\text{O, CO}_2, \text{CO, CH}_4)\]

From the obtained concentrations, it was possible to calculate yields and conversions for the 2\textsuperscript{nd} steps.

3\textsuperscript{rd} step – regeneration

The regeneration step was carried out in air (20 mL/min) at 450°C in order to increase the stability of the looping material and to overcome the deactivation problems, such as: a coke deposition/accumulation and an incomplete re-oxidation of M\textsuperscript{0} phase after the first two steps. The reaction time was varied according to the amount of the remained coke (the end of the regeneration step was correlated to the amount of produced CO\textsubscript{2} ≈ reached a value << 1 \%\textsubscript{vol}).

\textit{Chemical-Loop Reforming and Cycling Time variations}

\textit{I. Conventional Chemical-Loop process, named as “2 steps CLR”, consists of:}

1\textsuperscript{st} step – reduction - carried out with ethanol in N\textsubscript{2} flow at 450°C;

2\textsuperscript{nd} step – re-oxidation – carried out with water in N\textsubscript{2} flow at 450°C.

\textit{II. Modified Chemical-Loop process, named as “3 steps CLR” consists of:}

1\textsuperscript{st} step – reduction - carried out with ethanol in N\textsubscript{2} flow at 450°C;
2\textsuperscript{nd} step – re-oxidation – carried out with water in \( \text{N}_2 \) flow at 450\(^\circ\)C;

3\textsuperscript{rd} step – regeneration – carried out in air at 450\(^\circ\)C.

\textit{III. Cycling Time (CL) variations:}

- Short cycles: 1, 3, 5 and 6 min;
- Long cycles: 20 and 60 min.
3. MATERIALS PREPARATION

All the ferrites used have been prepared using the co-precipitation method described elsewhere.\(^\text{102}\)

*Co-precipitation*

**TYPE I SPINELS: MFe\(_2\)O\(_4\) (where Fe/M=2/1 or Fe/M\(^1\)/M\(^2\)=4/1/1)**

MFe\(_2\)O\(_4\) ferrospinelns with different atomic ratio Fe/M (where M=Co, Cu, Mn or Cu/Co, Cu/Mn, Co/Mn) were prepared by the co-precipitation method (Figure 3-1). Nitrate precursors were used for all of the synthesized materials. The mixed solutions of metal precursors containing 100mL of 1M Fe(NO\(_3\))\(_3\)·9H\(_2\)O, 100 mL of 0.5M M(NO\(_3\))\(_2\)·xH\(_2\)O (or 100 mL of 0.25M M\(_1\)(NO\(_3\))\(_2\)·xH\(_2\)O and 100 mL of M\(_2\)(NO\(_3\))\(_2\)·xH\(_2\)O solutions) were put into a separation funnel and then drop-by-drop added into the reaction vessel containing 0.5L of 2M NaOH aqueous solution at the temperature of 50°C under vigorous stirring with a constant speed. The suspensions were stirred for 2h at the constant temperature of 50°C adding NaOH 3M in order to maintain the pH above 13. The precipitates were separated by vacuum filtration by means of a Büchner funnel and then washed with about 1.5L of distilled water at room temperature (RT), to remove sodium and nitrates ions.

**TYPE II SPINELS: M\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) (where Fe/M=4/1 or Fe/M\(^1\)/M\(^2\)=8/1/1)**

MFe\(_2\)O\(_4\) ferrospinelns with different atomic ratio Fe/M (where M=Co, Cu, Mn, Mg, Ca or Cu/Co, Cu/Mn, Co/Mn) were prepared by the co-precipitation method (Figure 3-1). Nitrate precursors were used for all of the synthesized materials. The mixed solutions of metal precursors containing 100mL of 1M Fe(NO\(_3\))\(_3\)·9H\(_2\)O, 50 mL of 0.5M M(NO\(_3\))\(_2\)·xH\(_2\)O (or 50 mL of 0.25M M\(_1\)(NO\(_3\))\(_2\)·xH\(_2\)O and 50 mL of M\(_2\)(NO\(_3\))\(_2\)·xH\(_2\)O solutions) were put into a separation funnel and then drop-by-drop added into the reaction vessel containing 0.5L of 2M NaOH aqueous solution at the temperature of 50°C under vigorous stirring with a constant speed. The suspensions were stirred for 2h at the constant temperature of 50°C adding NaOH 3M in order to maintain the pH above 13. The precipitates were separated by vacuum filtration.
by means of a Büchner funnel and then washed with about 1.5L of distilled water at room temperature (RT), to remove sodium and nitrates ions.

*Thermal treatments*

All the washed samples (TYPE I and II) were dried at 120°C in air for 12 h, milled in agate mortar and then calcined in static air at 450°C for 8h with the heating rate of 10°C/min.

**NOTE:** A high surface area is important in order to make easier ferrites reduction, as explained by Cocchi and al\textsuperscript{103}. It has been shown that by increasing the calcination temperature, the surface area decreased continuously. Moreover, the annealing temperature cannot be lower than the reaction temperature. And, as reported by Trevisanut\textsuperscript{101}, the lower reaction temperature at which it was possible to obtain a fast enough reduction of MgFe\textsubscript{2}O\textsubscript{4}(M=Fe, Co, Ni) ferrites is T-450°C. Taking into account these statements, the calcination temperature of *TYPE I* and *TYPE II* ferrites was maintained at 450°C.

![Figure 3-1. Scheme of the ferrospinels preparation](image)
Bulk characterization of fresh materials

The section includes a discussion of the results obtained from several characterization techniques over fresh MFe$_2$O$_4$ (M-Co, Cu, Mn or Cu/Co, Cu/Mn, Co/Mn) samples: EDX analysis, XRD, N$_2$ adsorption, Raman Spectroscopy, TPR/TPO used to study bulk properties of freshly prepared ferrospinel.

4.1. Energy dispersive spectroscopy (EDX)

EDX is an addition characterization technique used for the elemental analysis or chemical characterization of the samples (the overall analytical accuracy is app. ± 2%). It is worth noting, that the EDX is a surface analysis technique, however it can be assimilated to a bulk analysis for nanoparticles smaller than the depth of penetration of the incident beam $x \sim 0.1 \times E^{-1.5} / \rho^{104}$ where $x$ is in μm, $E$ in keV and $\rho$ in kg m$^{-3}$. For $E$ 15 keV and $\rho \sim 6$ the penetration depth is about 1 μm, so the EDX analysis of particles up to 2μ can be considered representative of the bulk composition.

Table 4-1 shows theoretical and measured ratios between Fe/M (M-foreign metal: Co, Cu, Mn or Cu/Co, Cu/Mn, Co/Mn). In all the cases the real ratio of Fe/M is slightly different from the expected one. This difference can first of all come from a weighing error and an incomplete pouring of the metal precursor solutions or to the slight hydration of the samples powders. Moreover, according to EDX analysis there is also a presence of Na < 1%$_{w}$ (as a residual which comes from the synthesis procedure).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Theoretical ratio, Fe/M</th>
<th>Measured ratio, Fe/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>Fe/Cu - 2/1</td>
<td>Fe/Co –2.16/1</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>Fe/Co - 4/1</td>
<td>Fe/Co –3.85/1</td>
</tr>
<tr>
<td></td>
<td>Fe/Cu - 4/1</td>
<td>Fe/Cu– 4.21/1</td>
</tr>
</tbody>
</table>
### RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe<sub>2</sub>O<sub>4</sub>)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe/Co - 2/1</th>
<th>Fe/Co - 1.99/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;0.5&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Fe/Co - 4/1</td>
<td>Fe/Co - 4.39/1</td>
</tr>
<tr>
<td></td>
<td>Fe/Mn - 4/1</td>
<td>Fe/Mn - 4.02/1</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.3&lt;/sub&gt;Mn&lt;sub&gt;0.7&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Fe/Cu - 4/1</td>
<td>Fe/Cu - 5.25/1</td>
</tr>
<tr>
<td></td>
<td>Fe/Mn - 4/1</td>
<td>Fe/Mn - 4.04/1</td>
</tr>
<tr>
<td>MnFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2. **XRD and N<sub>2</sub> adsorption**

The structure of fine powders is defined from XRD patterns (Figure 4-1). Resulted patterns confirm the formation of a spinel oxide, as the main phase for all the samples. However, the presence of CuO with a reflection at 38.8° is detected for the Cu-modified sample (CuFe<sub>2</sub>O<sub>4</sub>)

---

**Figure 4-1.** XRD patterns of fresh MFe<sub>2</sub>O<sub>4</sub> samples calcined at 450°C for 8 h
ferrite). Using Rietveld refinement, CuO is present as 21% in the freshly prepared sample and this is taken into account for further calculations. Apparent broadening of the diffraction patterns observed for the Mn-incorporated samples (MnFe$_2$O$_4$, Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$) was attributed to a decrease in a particle size or as a fact of a lower crystallinity. Similar results were previously obtained with Mn-substituted in Co/Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ system (see PART II). In the Table 4-2 are listed results of a specific surface area (SSA), a crystallite size (calculated by Scherrer eq. and) and a particle size (calculations are based on N$_2$ adsorption (BET) data) of the fresh powders calcined at 450°C for 8 h.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>SSA$_{\text{fresh}}, \text{m}^2/\text{g}$</th>
<th>Crystallite size (Scherrer eq.), nm</th>
<th>Particle size ($d_{\text{BET}}$, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>60</td>
<td>6.9</td>
<td>18.3</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>67</td>
<td>10.4</td>
<td>16.5</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>69</td>
<td>12.0</td>
<td>16.2</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>141</td>
<td>3.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>112</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>165</td>
<td>-</td>
<td>6.9</td>
</tr>
</tbody>
</table>

All Mn-substituted ferrites exhibit a higher surface area even after the thermal treatment which first of all can be attributed to the presence of smaller particles (Table 4-2) along with the existence of an amorphous phase.
4.3. Raman Spectroscopy

Raman spectra of fresh materials calcined at 450°C are shown in Figure 4-2. Cu/Co-substituted ferrites (Figure 4-2, D-F) reveal 5 distinct Raman modes, predicted by the literature: $A_{1g}^{(1)}$ (690 cm$^{-1}$), $F_{2g}^{(3)}$ (560 cm$^{-1}$), $F_{2g}^{(2)}$ (472 cm$^{-1}$), $E_g$ (305 cm$^{-1}$). The literature is discrepant to the assignment of the Raman active modes within a spinel lattice. However, the highest frequency mode ($A_{1g}^{(1)}$) at 690 cm$^{-1}$ is usually assigned to the symmetric stretching of the M-O bond in a $T_d$ void$^{107,108,109}$. In addition to the 5 theoretically predicted modes, samples D and E exhibit an additional peak at $A_{1g}^{(2)}$ 616 cm$^{-1}$, which caused by disorder effects of $M^{2+}$ and $Fe^{3+}$ over the $T_d$ and $O_h$ sites$^{109}$. This shoulder for a CoFe$_2$O$_4$ spinel was also observed by Chandramohan and others$^{107}$. They correlated an increase in the intensity of $A_{1g}^{(2)}$ mode with lowering of inversion parameter in the following spinel, which also being supported by Mössbauer studies.

![Figure 4-2. Raman spectra of MFe$_2$O$_4$ ferrites: A-MnFe$_2$O$_4$, B-Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, C-Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, D-CoFe$_2$O$_4$, E-Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ and F-CuFe$_2$O$_4$.](image)

Looking at the spectra of A-C samples (Mn-substituted ferrites), the position of the $A_{1g}^{(1)}$ shifts to a lower frequency at about 661 cm$^{-1}$ along with a distinct broadening of the
following spectra. The similar behavior was observed for Co/Mn-incorporation. Hence, Mn$^{2+}$ ions are proposed to partially replace Fe$^{3+}$ ions in the Td sites, which may cause the change of the inversion degree towards the formation of the normal spinel. The low intensity of the peaks and partial energy shifts can be related also to a lack of a long range in the small dimension systems along with an effect due to high defectivity and a low crystallinity as confirmed by XRD.

4.4. Temperature programmed reduction/oxidation (TPR1/O/R2)

**TPR curves: signal-vs-T**

The reduction of the iron$^{(II,III)}$ oxide: Fe$_3$O$_4$→FeO→Fe strongly depends on the presence of another metal oxide in the resulted M-modified ferrite. According to the XRD and Raman results, discussed previously, the main phase obtained at the end of the preparation procedure was a Fe$_3$O$_4$-like spinel oxide phase with a generic formula of MFe$_2$O$_4$. Following the TPR profiles of M-modified ferrites, plotted in Figure 4-4, mainly two steps of the reduction processes can be distinguished: the reduction of iron oxide to metallic iron and the reduction process of other incorporated metal oxide to its metal. However, it’s difficult to distinguish each stage of the reduction since some steps seamlessly flow from one to another which finally causes an overlap. Nevertheless, the obtained results and its further elaboration based on the nature of the foreign metals (M$^{2+}$), their reduction potentials and the amount of consumed H$_2$ helped us to track back possible steps of the MFe$_2$O$_4$ reduction process, which are summarized in Figure 4-3.

![Reduction scheme of MFe$_2$O$_4$ ferrites](image)

Figure 4-3. Reduction scheme of MFe$_2$O$_4$ ferrites
Looking at the TPR profile of CuFe$_2$O$_4$, the first peak at 240°C can be attributed to a starting reduction of the initially present copper oxide (CuO$\sim$21%$_w$) to the metallic copper (Cu$^0$), which contributes to $\alpha$$\sim$16%. The second peak at $\sim$ 340°C was attributed to a primary stepwise reduction of the spinel with a final formation of Cu$^0$ and Fe$_3$O$_4$ phases ($\alpha$$\sim$27%), following the pass I (Figure 4-3); the further reduction of the Fe$_3$O$_4$ to FeO and FeO to Fe$^0_{\text{incm}}$ appears at higher temperatures with a total $\alpha$$\sim$70%. The reduction of Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ samples follows the pass III (Figure 4-3), where the first peak at lower temperature corresponds to the stepwise exclusion or/and reduction of the Mn-incorporated cations to form Mn (Cu$^0$), MO (MnO/CoO) and Fe$_3$O$_4$ phases. Further reduction of the Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite goes through the following stages: (1) Fe$_3$O$_4$$\rightarrow$FeO (+0.77 eV), (2) CoO$\rightarrow$Co$^0$ (-0.28 eV), (3) FeO$\rightarrow$Fe$^0_{\text{incm}}$ (-0.44 eV), reaching $\alpha$$\sim$65%. On the other hand, the reduction of Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrite can be schematized as follows: (1) Fe$_3$O$_4$$\rightarrow$FeO, (2) FeO$\rightarrow$Fe$^0_{\text{incm}}$, which corresponds to $\alpha$$\sim$65%. It turned out that it is difficult for MnO to be reduced to its metallic component Mn$^0$, due to its highly negative reduction potential (-1.18 eV)$^{106}$ and thus this step can occur only at very extreme temperatures (see $\Delta G^0_{\text{react}}$, Table 4-3). The reduction of the CoFe$_2$O$_4$, Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and MnFe$_2$O$_4$ samples follows the pass II in Figure 4-3. In a case of CoFe$_2$O$_4$, the first small peak at 400°C can be attributed to the primary spinel reduction with a stepwise formation of CoO and Fe$_3$O$_4$ phases (which corresponds to $\alpha$$\sim$8%), whereas in Mn-incorporated ferrites (MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$) this step starts at lower temperature. However, the total reduction extent of CoFe$_2$O$_4$ ($\alpha$$\sim$86%) was much higher than of the Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (61%) and MnFe$_2$O$_4$ (45%) samples and can be explained by the formation of the hardly reducible phase of MnO (or in the form of Mn$_x$Fe$_y$O oxide).
### RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

#### COMPLETE REDUCTION SCHEME OF MFe$_2$O$_4$ FERROSPINELS

<table>
<thead>
<tr>
<th>Spinel Type</th>
<th>Complete Reduction Scheme</th>
<th>At the end of TPR1:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</strong></td>
<td>$\text{Cu}<em>{0.40}\text{Mn}</em>{0.52}\text{Fe}_{2.08}\text{O}_4 + 0.71 \text{H}_2 \rightarrow 0.4 \text{Cu} + 0.52 \text{MnO} + 0.69 \text{Fe}_3\text{O}_4 + 0.71 \text{H}_2\text{O}$ ($\alpha \sim 18%$) $0.69 \text{Fe}_2\text{O}_3 + 0.69 \text{H}_2 \rightarrow 2.08 \text{FeO} + 0.69 \text{H}_2\text{O}$ ($\alpha \sim 35%$) $0.77 \text{FeO} + 0.77 \text{H}<em>2 \rightarrow 0.77 \text{Fe} + 0.77 \text{H}<em>2\text{O}$ ($\alpha \sim 54%$) <strong>At the end of TPR1:</strong> incomplete reduction of FeO and MnO phases: Mn$</em>{0.29}$Fe$</em>{0.72}$O</td>
<td>incomplete reduction of FeO and MnO phases: Mn$<em>{0.29}$Fe$</em>{0.72}$O</td>
</tr>
<tr>
<td><strong>CuFe$_2$O$_4$ (CuO$^+$ $\sim$ 21 %$_w$)</strong></td>
<td>$\text{CuO}^+ + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ ($\alpha \sim 16%$) $\text{CuO} + \text{H}_2\text{O} \rightarrow \text{Cu} + \text{H}_2\text{O}$ ($\alpha \sim 21%$) $\text{CuO} + \text{H}_2\text{O} \rightarrow \text{Cu} + \text{H}_2\text{O}$ ($\alpha \sim 35%$) $0.87 \text{Fe}_2\text{O}_3 + 0.87 \text{H}_2 \rightarrow 2.61 \text{FeO} + 0.87 \text{H}_2\text{O}$ ($\alpha \sim 45%$) $1.17 \text{FeO} + 1.17 \text{H}_2 \rightarrow 1.17 \text{Fe} + 1.17 \text{H}_2\text{O}$ ($\alpha \sim 70%$) <strong>At the end of TPR1:</strong> incomplete reduction of segregated CuO phase</td>
<td><strong>At the end of TPR1:</strong> incomplete reduction of segregated CuO phase</td>
</tr>
<tr>
<td><strong>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</strong></td>
<td>$\text{Cu}<em>0.48\text{Co}</em>{0.52}\text{Fe}_2\text{O}_4 + 0.81 \text{H}_2 \rightarrow 0.48 \text{Cu} + 0.52 \text{CoO} + 0.67 \text{Fe}_3\text{O}_4 + 0.81 \text{H}_2\text{O}$ ($\alpha \sim 20%$) $0.67 \text{Fe}_2\text{O}_3 + 0.67 \text{H}_2 \rightarrow 2 \text{FeO} + 0.67 \text{H}_2\text{O}$ ($\alpha \sim 37%$) $0.52 \text{CoO} + 0.52 \text{H}_2 \rightarrow 0.52 \text{Co} + 0.52 \text{H}_2\text{O}$ ($\alpha \sim 50%$) $0.6 \text{FeO} + 0.6 \text{H}_2 \rightarrow 0.6 \text{Fe} + 0.6 \text{H}_2\text{O}$ ($\alpha \sim 65%$) <strong>At the end of TPR1:</strong> incomplete reduction of FeO phase</td>
<td>incomplete reduction of FeO phase</td>
</tr>
<tr>
<td><strong>CoFe$_2$O$_4$</strong></td>
<td>$\text{CoFe}_2\text{O}_4 + 0.33 \text{H}_2 \rightarrow \text{CoO} + 0.67 \text{Fe}_3\text{O}_4 + 0.33 \text{H}_2\text{O}$ ($\alpha \sim 8%$) $0.67 \text{Fe}_2\text{O}_3 + 0.67 \text{H}_2 \rightarrow 2 \text{FeO} + 0.67 \text{H}_2\text{O}$ ($\alpha \sim 25%$) $\text{CoO} + \text{H}_2 \rightarrow \text{Co} + \text{H}_2\text{O}$ ($\alpha \sim 50%$) $1.44 \text{FeO} + 1.44 \text{H}_2 \rightarrow 1.44 \text{Fe} + 1.44 \text{H}_2\text{O}$ ($\alpha \sim 86%$) <strong>At the end of TPR1:</strong> incomplete reduction of FeO phase</td>
<td>incomplete reduction of FeO phase</td>
</tr>
<tr>
<td><strong>Co$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</strong></td>
<td>$\text{Co}<em>{0.47}\text{Mn}</em>{0.53}\text{Fe}_2\text{O}_4 + 0.32 \text{H}_2 \rightarrow 0.47 \text{Co} + 0.5 \text{MnO} + 0.68 \text{Fe}_3\text{O}_4 + 0.32 \text{H}_2\text{O}$ ($\alpha \sim 8%$) $0.68 \text{Fe}_2\text{O}_3 + 0.68 \text{H}_2 \rightarrow 2.03 \text{FeO} + 0.68 \text{H}_2\text{O}$ ($\alpha \sim 25%$) $0.47 \text{CoO} + 0.47 \text{H}_2 \rightarrow 0.47 \text{Co} + 0.47 \text{H}_2\text{O}$ ($\alpha \sim 36%$) $0.99 \text{FeO} + 0.99 \text{H}<em>2 \rightarrow 0.99 \text{Fe} + 0.99 \text{H}<em>2\text{O}$ ($\alpha \sim 61%$) <strong>At the end of TPR1:</strong> incomplete reduction of FeO and MnO phases: Mn$</em>{0.33}$Fe$</em>{0.67}$O</td>
<td>incomplete reduction of FeO and MnO phases: Mn$<em>{0.33}$Fe$</em>{0.67}$O</td>
</tr>
<tr>
<td><strong>Mn$<em>2$Fe$</em>{0.5}$O$_4$</strong></td>
<td>$\text{Mn}<em>{1.04}\text{Fe}</em>{1.96}\text{O}_4 + 0.35 \text{H}_2 \rightarrow 1.04 \text{MnO} + 0.65 \text{Fe}_3\text{O}_4 + 0.35 \text{H}_2\text{O}$ ($\alpha \sim 8%$) $0.65 \text{Fe}_2\text{O}_3 + 0.65 \text{H}_2 \rightarrow 1.96 \text{FeO} + 0.65 \text{H}_2\text{O}$ ($\alpha \sim 25%$) $0.82 \text{FeO} + 0.82 \text{H}<em>2 \rightarrow 0.82 \text{Fe} + 0.82 \text{H}<em>2\text{O}$ ($\alpha \sim 45%$) <strong>At the end of TPR1:</strong> incomplete reduction of FeO and MnO phases: Mn$</em>{0.48}$Fe$</em>{0.52}$O</td>
<td><strong>At the end of TPR1:</strong> incomplete reduction of FeO and MnO phases: Mn$<em>{0.48}$Fe$</em>{0.52}$O</td>
</tr>
</tbody>
</table>

**Notes:**
- $\alpha$ denotes the degree of reduction.
- The reduction is shown for each spinel type with its specific reaction equations and final states.
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe₂O₄)

Figure 4.4. TPR profiles of MFe₂O₄ ferrites with temperature program from 50 to 800°C (+isotherm at T-800°C for 40 min)
**TPR curves: α-vs-T**

Different modifications in the composition of bare-Fe$_3$O$_4$ to MFe$_2$O$_4$ (M-Cu, Co, Ni, Mn, Mg, Ca, etc.) have been done by many research groups in order to change its redox properties. Moreover, the so called “promoting effect” of Cu$^{2+}$ was also seen $^{116,117,74,118}$, however a real role of copper ions and the reduction mechanism has not been clearly elucidated. Thus, the primary idea was to focus our study on a deep understanding of TPR profiles with a further data elaboration for possible clarification of MFe$_2$O$_4$ reduction mechanism.

![Graph showing TPR curves](image)

Conventionally, the shape of an ($\alpha$ vs time) isotherm can reveal information on the mechanism of solid state reactions$^{119}$. And, according to A. Jones, the reduction of CuO produces an S-shape (sigmoidal) reduction isotherm familiar for a “nucleation and autocatalytic” reduction model, where the reduction consists of three distinct stages: 1. induction, 2. autocatalysis and 3. decreasing rate$^{120}$. However, some oxides may be reduced via spontaneous nucleation over an entire surface which is usually characterized by a continuously decreasing rate. If the nucleation is very fast, the real formation of separated...
and independent nuclei cannot be distinguished leading to a total coverage of the solid oxide particle with a thin layer of metallic product, and typical for Mn$_x$O$_y$ → Mn redox system\textsuperscript{121}. Thus, we decided that the best depiction of the reduction models of MFe$_2$O$_4$ ferrites can be described being based on these two mechanisms.

Figure 4-5 shows $\alpha$-versus-$T$ reduction curves of MFe$_2$O$_4$ samples. Increasing the temperature of the reduction markedly increased the reduction rate of all oxides regardless of the nature of incorporated metal M and this in turn can be justified by Arrhenius equation (exponential relation between $K$ and $T$). However, looking at the reduction curves of Cu-incorporated ferrites a peculiar behavior is observed that cannot be explained only by an increase in the temperature. All three samples (CuFe$_2$O$_4$, Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ and Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$) produce the S-shaped (sigmoidal) reduction curve with a strong acceleration of the reduction rate above 160-200$^\circ$C, which was associated with a self-catalyzed nucleation (autocatalysis). Apparently, nuclei catalyze further nuclei formation, due to branching of nuclei or to the catalytic role of the Cu metal in H$_2$ dissociation. According to this, an effect of Cu$^0$ can be described as follows: Cu$^0$ formed in the early stage of the reduction (Cu$^{2+}$→Cu$^{0*}$) is further catalyzing the reduction of a newly reformed Fe-enriched spinel (with generic formula - M$_{1-x}$Fe$_{(2+x)}$O$_4$). The reduction occurs on the basis of hydrogen spill over effect, where Cu$^0$ plays role of a catalyst which is needed to dissociate H$_2$ into 2H atoms. Essentially, hydrogen atoms would migrate from a hydrogen-rich (Cu$^0$) to a hydrogen-poor (spinel) surface (see Figure 4-6, A). On the other hand, we cannot ignore thermodynamic aspects of the following reaction; and from an enthalpy point of view (Table 4-3) the reduction of CuO to Cu$^0$ is an exothermal reaction with released energy of about 84 kJ/mol$_{\text{CuO}}$ (CuO+H$_2$=Cu+H$_2$O, $\Delta H^0_{\text{react}}$=-84.53 kJ/mol$_{\text{CuO}}$). Using a heat equation ($Q=C_p\cdot m\cdot \Delta T$) it is possible to calculate an approximate value of the temperature rise ($T_{\text{rise}}=768^\circ$C if 100% Cu$^{2+}$ ions being reduced, however even if 50% of Cu$^{2+}$ ions are reduced the $T_{\text{rise}}=384^\circ$C, if 10% of Cu$^{2+}$ $T_{\text{rise}}=77^\circ$C, which is still very high). Moreover, we should take into consideration also the flowing gas mixture (5% of H$_2$ in Ar, $v=30$ ml/min), in that case the $T_{\text{rise}}=118^\circ$C, when 100% of Cu$^{2+}$ ions were reduced, or $T_{\text{rise}}=12^\circ$C when only 10% of Cu$^{2+}$ reduced. However, self-heating effects would result if too large amount of the sample was used. Thus, considering that experiments were carried
out under the small scale (with the sample mass of about 100 mg) and the self-heating effect in this case can be neglected.

Coming back to $\alpha$-versus-$T$ curves, the reduction of the MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ samples produces elongated curves without a strong acceleration of the reaction rate which led us to the idea of a different model, we called an “egg-shell” model (see Figure 4-6, B). Like, if the ferrite reduction goes through a total coverage of the solid oxide particle with a thin layer of newly formed product. Hence, the reduction of MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites can be better described by a spontaneous reduction over the entire surface which occurs immediately on the contact with hydrogen and lead to the expelling of Mn$^{2+}$ cations out of the spinel structure with a formation of the new phases: a Fe-rich reformed spinel ($M_{1-x}Fe_{2+x}O_4$) and a non-reducible layer of MnO oxide (since: MnO$\rightarrow$Mn$^0$, $\epsilon$=1.18 eV)\textsuperscript{106}, like an “egg-shell” (or in the form of a thermodynamically stable oxide solid solution - Mn$_n$Fe$_y$O, supported by ex-situ XRD study). This elucidate the elongated shape of the reduction curve, since the initially formed compact MnO/Mn$_n$Fe$_y$O layer may act as a “shielding” layer, causing an aggravation of H$_2$ diffusion into the bulk leading to a starvation and a decrease of the total reduction rate of the core (reformed spinel Mn$_{1-x}Fe_{2+x}O_4$).

<table>
<thead>
<tr>
<th>REACTION</th>
<th>$\Delta H^0_{\text{react}}$, kJ/mol</th>
<th>$\Delta G^0_{\text{react}}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO$+$H$_2$=Cu$+$H$_2$O</td>
<td>exothermic, $\Delta H^0_{\text{react}}$=-84.53 kJ/mol$_{\text{CuO}}$</td>
<td>-99.05</td>
</tr>
<tr>
<td>Co$_3$O$_4$+H$_2$=3CoO$+$H$_2$O</td>
<td>exothermic, $\Delta H^0_{\text{react}}$=-45.63 kJ/mol$_{\text{Co3O4}}$</td>
<td>-76.26</td>
</tr>
<tr>
<td>CoO$+$H$_2$=Co$+$H$_2$O</td>
<td>exothermic, $\Delta H^0_{\text{react}}$=-3.89 kJ/mol$_{\text{CoO}}$</td>
<td>-14.38</td>
</tr>
<tr>
<td>Fe$_2$O$_3$+3H$_2$=2Fe$+$3H$_2$O</td>
<td>endothermic, $\Delta H^0_{\text{react}}$=+98.72 kJ/mol$_{\text{Fe2O3}}$</td>
<td>56.55</td>
</tr>
<tr>
<td>3Fe$_2$O$_3$+H$_2$=2Fe$_3$O$_4$+H$_2$O</td>
<td>exothermic, $\Delta H^0_{\text{react}}$=-2.086 kJ/mol$_{\text{Fe2O3}}$</td>
<td>-14.84</td>
</tr>
<tr>
<td>Fe$_3$O$_4$+4H$_2$=3Fe$+$4H$_2$O</td>
<td>endothermic, $\Delta H^0_{\text{react}}$=+151.1 kJ/mol$_{\text{Fe3O4}}$</td>
<td>101.04</td>
</tr>
<tr>
<td>Reaction</td>
<td>Endothermic</td>
<td>( \Delta H_{\text{react}}^0 )</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>( \text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{FeO} + \text{H}_2\text{O} )</td>
<td>Endothermic</td>
<td>+60.69 kJ/mol</td>
</tr>
<tr>
<td>( \text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} )</td>
<td>Endothermic</td>
<td>+30.134 kJ/mol</td>
</tr>
<tr>
<td>( \text{MnO} + \text{H}_2 \rightarrow \text{Mn} + \text{H}_2\text{O} )</td>
<td>Endothermic</td>
<td>+143.39 kJ/mol</td>
</tr>
</tbody>
</table>

Figure 4-6. Schematic representation of H\(_2\)-reduction over: A-CuFe\(_2\)O\(_4\) as “nucleation/autocatalytic” model and B-MnFe\(_2\)O\(_4\) as an “egg-shell” model.
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe₂O₄)
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)
In addition to the conventional TPR measurements, discussed in Paragraph 4.4, \( \text{MFe}_2\text{O}_4 \) ferrospinels were tested in the TPR1-TPO-TPR2 sequence, which gave the important information on resulted interior redox properties of the binary/ternary complex systems.

Table 4-4 shows the integrated values of consumed \( \text{H}_2/\text{O}_2 \) during TPR1/TPO/TPR2 experiments at 800\(^\circ\)C (note: calculations are made based on the actual \( \text{H}_2/\text{O}_2 \) consumption with respect to the initially loaded mass, cm\(^3\)/g). In order to grasp the reason of the decreasing values for \( \text{H}_2 \) consumption during the second reduction (TPR2), see Table 4-4, it was decided to calculate the actual degrees of reduction (TPR1)/oxidation (TPO)/reduction (TPR2) starting from initial moles of oxygen in the solid at the beginning of the experiment, as depicted in Figure 4-7 (note: an oxidation degree (O) was calculated starting from the experimentally obtained moles of consumed oxygen divided on the initial value, which assumed to be the max value whenever the material is being fully re-oxidized to its primary state – \([n_{\text{Ox} \text{TPO}}/n_{\text{Ox TO}}] \cdot 100\); whereas a reduction degree (R) during the TPR1/TPR2 experiments was calculated based on the amount of removed oxygen divided on its initial amount in a fresh sample – \([n_{\text{Ox} \text{TPR1}} (or n_{\text{Ox} \text{TPR2}})/n_{\text{Ox TO}}] \cdot 100\). Considering the obtained results, several statements can be made:

**TPR1:**

- Co/Cu-incorporation leads to a higher reduction extent, i.e. is more attractive in terms of potentially higher reducibility: \( \text{CoFe}_2\text{O}_4 \) (R-86%), \( \text{CuFe}_2\text{O}_4 \) (R-65%) and

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Integrated values for ( \text{H}_2/\text{O}_2 ), cm(^3)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TPR1</td>
</tr>
<tr>
<td>( \text{CoFe}_2\text{O}_4 )</td>
<td>357</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.5}\text{Co}</em>{0.5}\text{Fe}_2\text{O}_4 )</td>
<td>267</td>
</tr>
<tr>
<td>( \text{Co}<em>{0.5}\text{Mn}</em>{0.5}\text{Fe}_2\text{O}_4 )</td>
<td>258</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.5}\text{Mn}</em>{0.5}\text{Fe}_2\text{O}_4 )</td>
<td>229</td>
</tr>
<tr>
<td>( \text{CuFe}_2\text{O}_4 )</td>
<td>274</td>
</tr>
<tr>
<td>( \text{MnFe}_2\text{O}_4 )</td>
<td>192</td>
</tr>
</tbody>
</table>
Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (R-71%); whereas, on the contrary, Mn-incorporation leads to a lower intrinsic reducibility of the resulted ferrites: MnFe$_2$O$_4$ (R-46%), Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (R-61%) and Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (R-54%)

**TPO:**

- Mn/Cu-incorporation leads to a higher oxidation extent, i.e. is more attractive for the performing an easier re-oxidation: MnFe$_2$O$_4$ (O-15%), Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (O-22%), Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (O-20%), CuFe$_2$O$_4$ (O-20%) and Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (O-16%); while Co-incorporation have an opposite effect: CoFe$_2$O$_4$ (O-6%)

**TPR2:**

- In connection with the previous two statements, derived from the TPR1 and TPO results: Co/Cu-incorporation enhances the reduction extent whereas Mn/Cu-incorporation enhances the oxidation extent implies that ternary ferrospinel, composed of Cu/Mn (Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$), Co/Mn (Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$) or Cu/Co (Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$) together with the only Cu-incorporated sample - CuFe$_2$O$_4$, showed better results for the 2nd consecutive reduction (TPR2) with the values that are comparable to the ones obtained during the 1st reduction (TPR1): Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (R-40%), Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (R-42%), Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (R-32%) and CuFe$_2$O$_4$ (R-40%).

**To summarize:** In view of the prospective to use M-ferrites as oxygen carrier materials, where the reduction as well as the oxidation degree are both important parameters that have a direct impact on the overall conversion and efficiency, utilization the material with equilibrated redox properties, such as Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ or CuFe$_2$O$_4$, can be more profitable for the large-scale applications.

**4.5. Ex-situ XRD study of MFe$_2$O$_4$ ferrites**

The discussion is focused on the deep understanding of the C$_2$H$_5$OH-reduction process of the MFe$_2$O$_4$ ferrites via stepwise reduction of the solids with the further XRD characterization including Rietveld refinement results.
Ex-situ XRD study of the reduced samples → ethanol reduction

The H$_2$-reduction of Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites, discussed in the previous paragraph, has shown remarkable differences in the reaction models. The same idea was taken to explain the reduction of these samples with ethanol, which corresponds to the 1$^{\text{st}}$ step of the chemical-loop reforming process. The ex-situ study of XRD patterns, obtained after 1, 3, 5 and 20 min of ethanol exposure, was performed in order to justify this statement.

Essentially, a reduction cascade of the MnFe$_2$O$_4$ ferrite (Figure 4-8 and Figure 4-9) was chosen as a reference for the “egg-shell” model(Figure 4-14, B). The results, obtained after feeding ethanol for 1 min, reveal the appearance of a new Mn$_x$Fe$_y$O oxide along with a remaining “reformed” spinel phase (Mn$_{1-x}$Fe$_{2-x}$O$_4$). Moreover, with increasing the reduction time from 1 to 20 min the relative amount of the spinel phase continued to decrease (from 92 to 67 \%$_w$) whereas that of the Mn$_x$Fe$_y$O increased (from 8 to 33 \%$_w$) without an appearance of the other phases. This apparently shows that the reduction of the MnFe$_2$O$_4$goes through the formation of Mn$_x$Fe$_y$O phase, which is an important proof of the previously discussed TPR results where we proposed the reduction mechanism which goes through the formation of hardly reducible and thermodynamically stable layer of Mn$_x$Fe$_y$O oxide.
Figure 4-8. Stepwise (1, 3, 5 and 20 min) reduction of MnFe$_2$O$_4$
The stepwise reduction of Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (Figure 4-10 and Figure 4-11) clearly indicates that a primarily formed phase during the 1st min of ethanol exposure was Cu$^0$ (with app. 11%$_w$). Increasing the reaction time to 3 min resulted in the formation of the second reduced phase – an oxide solid solution Mn$_x$Fe$_y$O, with app. 12%$_w$. Subsequent increase of the reduction time to 5 min led to a decrease of the spinel relative amount to 63%$_w$ whereas the one of Mn$_x$Fe$_y$O increased to 25%$_w$, while Cu$^0$ phase remained practically unchanged, app. 12%.$w$. Further step up in the reduction time (up to 20 min) resulted in the formation of strongly reduced species like iron carbides (Fe$_5$C$_2$ and Fe$_3$C), with total amount of 55%$_w$. On this basis, we may point out that the reduction of Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ at first proceeds with the formation of Cu$^0$ and iron-rich reformed spinel (Cu$_{0.5-x}$Mn$_{0.5}$Fe$_{2+x}$O$_4$), where Cu$^0$ may play its role as a catalyst for the deeper reduction with a formation of Mn$_x$Fe$_y$O and Fe-carbides, as also been supported by TPR study.
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe₂O₄)

1 min red
Cu₃Cu₂Mn₆Fe₂O₁₄

Appearance of Cu⁰ as primarily reduced phase

3 min red
Cu₁₃Mn₄Fe₂O₁₄

5 min red
Cu₁₃Mn₄Fe₂O₁₄

Spinel 89.55%
Cu₃Mn₄Fe₂O₁₄ 10.85%

Spinel 96.10%
Cu₃Mn₄Fe₂O₁₄ 23.73%
Mn₃Fe₂O 32.19%

Spinel 63.41%
Cu₃Mn₄Fe₂O₁₄ 21.87%
Mn₃Fe₂O 24.78%
The reduction cascade of the Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrite is shown in Figure 4-12 and Figure 4-13. It is worth noting, that incorporation of Co-cations may stabilize iron in the ferric state in an even higher proportion, exceeding the nominal 1:2 ratio$^{74}$; this in turn determines the reduction mechanism and, as a consequence, phases which are formed during the reduction step. From the obtained results, the reduction of Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ have the same nature as the one of MnFe$_2$O$_4$; which primarily gives rise to app. 15%$_w$ of Mn$_x$Fe$_y$O oxide and 85%$_w$ of Fe-enriched spinel with its further evolution to 42 and 58%$_w$, respectively. The formation of Mn$_x$Fe$_y$O acts as a “shielding” layer and prevents a deep reduction of the following ferrite. This also can explain such high difference in the reduction degree ($\alpha$) between
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Co$_{0.3}$Mn$_{0.5}$Fe$_2$O$_4$ (10%) and Cu$_{0.3}$Mn$_{0.5}$Fe$_2$O$_4$ (73%) whereas samples without Mn-incorporation showed the same $\alpha$: CoFe$_2$O$_4$ (82%) and CuFe$_2$O$_4$ (82%) (Figure 4-15).
RESULTS AND DISCUSSION, PART I:

Figure 4-12. Stepwise (1, 3, 5 and 20 min) reduction of Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$

Figure 4-13. The evolution of phases during the Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ stepwise reduction; R – reduction extent, %

Figure 4-15 and Table 4-5 summarize the results on the Rietveld refinement for all MFe$_2$O$_4$ samples after ethanol reduction within 20 min. By looking at the reduction degree values, an introduction of Cu$^{2+}$ ions into the Co/Fe system shows its strong promoting effect on the reduction of Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ($\alpha=100\%$), caused by a synergetic effect of Cu-Co couple (while by itself the reduction degree of CuFe$_2$O$_4$ and CoFe$_2$O$_4$ is equal to 82%). On the contrary, even though the highest surface area was shown by MnFe$_2$O$_4$, Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ catalysts (SSA values of the fresh samples reported in Table 4-2), the Mn-incorporation illustrates an opposite inhibiting effect on the MFe$_2$O$_4$-reduction, causing its drop from 82% (CoFe$_2$O$_4$) to 10% (Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$) and from 82% (CuFe$_2$O$_4$) to 73% (Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$). This suggests that the difference in the reducibility of the resulted M-
modified ferrospinel is related to the nature of the M-incorporated cation and its intrinsic reactivity.

Figure 4-14. Schematic representation of C\(_2\)H\(_2\)OH-reduction over: A-CuFe\(_2\)O\(_4\), as “nucleation/autocatalytic” model and B-MnFe\(_2\)O\(_4\), as an “egg-shell” model

Table 4-5. Rietveld refinement data of MFe\(_2\)O\(_4\) ferrites after 20 min reduction with ethanol

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>Degree of reduction ((\alpha)), %</th>
<th>Phase composition after 20 min ethOH (*from RV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe(_2)O(_4)</td>
<td>8%</td>
<td>SPINEL – 67.16% w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(<em>{x})Fe(</em>{y})O – 32.84% w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SPINEL – 16.09% w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn(<em>{x})Fe(</em>{y})O – 19.95% w</td>
</tr>
<tr>
<td>Cu(<em>{0.5})Mn(</em>{0.5})Fe(_2)O(_4)</td>
<td>73%</td>
<td>Fe(_{5})C(_2) – 41.76% w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe(_{3})C – 13.05% w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu – 9.15% w</td>
</tr>
<tr>
<td></td>
<td>SPINEL – 57.69%&lt;sub&gt;ω&lt;/sub&gt;</td>
<td>Mn&lt;sub&gt;x&lt;/sub&gt;Fe&lt;sub&gt;y&lt;/sub&gt;O – 42.31%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;0.5&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.5&lt;/sub&gt;Co&lt;sub&gt;0.5&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>82%</td>
<td></td>
</tr>
<tr>
<td>CuFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>82%</td>
<td></td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.5&lt;/sub&gt;Co&lt;sub&gt;0.5&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>100%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cu – 20.61%&lt;sub&gt;ω&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe&lt;sub&gt;5&lt;/sub&gt;C – 29.45%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;C – 22.27%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Fe – 4.75%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CoFe&lt;sub&gt;alloy&lt;/sub&gt; – 54.03%&lt;sub&gt;ω&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPINEL – 22.65%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Fe&lt;sub&gt;5&lt;/sub&gt;C – 17.34%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>FeC&lt;sub&gt;0.045&lt;/sub&gt; – 5.98%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Cu – 12.34%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Fe&lt;sub&gt;5&lt;/sub&gt;C – 40.08%&lt;sub&gt;ω&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;C – 30.87%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>CoFe&lt;sub&gt;alloy&lt;/sub&gt; – 16.71%&lt;sub&gt;ω&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
Figure 4-15. The evolution of phases during the MFe$_2$O$_4$ stepwise reduction; R – reduction extent, %

4.6. Ex-situ Mössbauer study

Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ 20 min ethOH
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)
RESULTS AND DISCUSSION, PART I:

Figure 4-16. $^{57}$Fe Mössbauer absorption spectra of the MFe$_2$O$_4$ ferrites recorded at 25 °C after 20 min C$_2$H$_5$OH-reduction at 450°C; solid lines are derived from the least-square fits

Mössbauer spectra on the MFe$_2$O$_4$ ferrites reduced with ethanol at 450°C for 20 min have been recorded in order to support the statements made on the basis of the ex-situ XRD studies and to gain new quantitative and compositional information (Figure 4-16). Experimental data were fitted using Lorentzian functions and the hyperfine parameters derived from the fittings are listed in Table 4-6.

The spectrum of Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite (with α~100%) was fitted with 4 sextets and one doublet. The first sextet ($\delta$-0.04 mm/s, H-35.9 T and Rel.In.-10%at) was attributed to Fe$^0$ in the CoFe$_{\text{alloy}}$ phase, which was also detected by XRD. The other 3 sextets correspond to the two iron carbides (Fe$_3$C-cementite and Fe$_5$C$_2$-Hagg carbide), formed as the main phases (84%at) during the reduction process. The best fit of the experimental spectrum was obtained with two sextets for Fe$_3$C$_2$ ($\delta$-0.19 mm/s, H-18.9 T and $\delta$-0.17 mm/s, H-11.2 T) and one shared sextet ($\delta$-0.21 mm/s, H-21.0 T) for Fe$_5$C$_2$+Fe$_3$C components. The obtained parameters of the corresponding sextets are in a good agreement with those reported literature$^{122-124}$. The doublet ($\delta$ 0.18 mm/s; $\Delta$ 1.05 mm/s) representing just6%at of the total spectrum, was ascribed to the presence of Fe$^{3+}$ phase in the form of carburized Fe oxide (or Co/Fe oxide) resulting from the incomplete transformation of the ferrite (it should be recall
that X-ray diffraction is not extremely sensitive and up to 5% of the remained/formed phase could not be detected).

The experimental spectrum of CuFe$_2$O$_4$ ferrite (with $\alpha \sim 82\%$) was fitted with 5 sextets. Spinel component (24%$_{\text{at}}$) with generic formula: Cu$_{(1-x)}$Fe$_{(2+x)}$O$_4$ composed of 2 sextets with the corresponding distribution of Fe-cations in between T$_d$ and O$_h$ sites: IS-0.25 mm/s, CH-49 T and $\delta$-0.67 mm/s, H-45.9 T, respectively. Another 3 sextets are similar to those discussed above and were attributed to the existence of a relatively high amount of Fe$_x$C$_y$ phases (Fe$_3$C+Fe$_3$C$_2$ $\sim 76\%_{\text{at}}$).

Mössbauer spectrum of CoFe$_2$O$_4$ sample (with $\alpha \sim 82\%$) was fitted with 6 sextets. The first two sextets (Fe in T$_d$ sites: $\delta$-0.25 mm/s and H-48.4 T; Fe in O$_h$ sites: $\delta$-0.55 mm/s and H-44.9 T) represent a remained spinel component – Co$_{1-x}$Fe$_{2+x}$O$_4$ (10%$_{\text{at}}$) resulted from the incomplete reduction, as supported by ex-situ XRD study. The third sextet ($\delta$-0.02 mm/s and H-35.0 T) with a relatively high contribution to the total spectrum (51%$_{\text{at}}$) was attributed to Fe$^0$ and should correspond to CoFe$_{\text{alloy}}$ and FeC$_{0.045}$ phases, see Table 4-6. The three remained sextets were assigned to Hagg-carbide (Fe$_5$C$_2$), representing 39%$_{\text{at}}$ with the following hyperfine parameters: $\delta$-0.17 mm/s and H-20.5 T, $\delta$-0.18 mm/s and H-18.5 T, $\delta$-0.17 mm/s and H-9.8 T, which corresponds to the three types of Fe in the unit cell of Fe$_3$C$_2$.\textsuperscript{122}

Experimental data of the Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ sample (with $\alpha \sim 73\%$) were fitted with 5 sextets and 2 doublets. Spinel component (24%$_{\text{at}}$) composed of 2 sextets: Fe in T$_d$ sites with $\delta$-0.30 mm/s and H-48.8 T; Fe in O$_h$ sites with $\delta$-0.49 mm/s and H-45.6 T. Another 3 sextets are similar to those discussed above and were attributed to the existence of a relatively high amount of Fe$_x$C$_y$ phases (Fe$_3$C+Fe$_3$C$_2$ $\sim 53\%_{\text{at}}$). Remaining two doublets which represent ferric (Fe$^{3+}$ as 11%$_{\text{at}}$) and ferrous (Fe$^{2+}$ as 12%$_{\text{at}}$) iron oxides characterized by an $\delta$:Fe$^{3+}$- 0.28 mm/s; Fe$^{2+}$- 1.10 mm/s and a $\Delta$: Fe$^{3+}$- 0.78 mm/s; Fe$^{2+}$- 0.62 mm/s and were attributed to the presence of the Mn$_x$Fe$_y$O oxide solid solution (a small amount of Fe$^{3+}$ in FeO (is generally present in FeO) was also seen by Johnson\textsuperscript{125}). Eventually, the obtained results support the ex-situ XRD study and a lower $\alpha$-value obtained over Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ sample in comparison to CuFe$_2$O$_4$ and CoFe$_2$O$_4$ones, which in turn explained by the direct effect of Mn-incorporation, leading to the formation scarcely reducible phase - Mn$_x$Fe$_y$O).
Mössbauer spectroscopy results on the $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ (with $\alpha \approx 10\%$) and $\text{MnFe}_2\text{O}_4$ (with $\alpha \approx 8\%$) ferrites once again confirmed the apparent differences observed between the Mn, Mn/Co- and Co, Cu, Cu/Co, Cu/Mn-incorporated samples. Corresponding spectra were all fitted with 2 sextets and 2 doublets. Two sextets were used to fit the remained spinel component (in the form of $\text{M}_{1-x}\text{Fe}_{2+x}\text{O}_4$): $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ with 65%\textsubscript{at} (Fe in Td sites: $\delta$-0.29 mm/s, H-49.3 T; Fe in Oh sites: $\delta$-0.45 mm/s, H-46.5 T) and $\text{MnFe}_2\text{O}_4$ with 68%\textsubscript{at} (Fe in Td sites: $\delta$-0.28 mm/s, H-48.7 T; Fe in Oh sites: $\delta$-0.44 mm/s, H-45.6 T). The two doublets ($\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$: $\delta$-0.28 mm/s, $\Delta$-0.87 mm/s and $\delta$-1.04 mm/s, $\Delta$-0.97 mm/s; $\text{MnFe}_2\text{O}_4$: $\delta$-0.23 mm/s, $\Delta$-0.57 mm/s and $\delta$-1.09 mm/s, $\Delta$-0.64 mm/s) were attributed to the same ferric ($\text{Fe}^{3+}$) and ferrous ($\text{Fe}^{2+}$) iron oxides, respectively, as detected in $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ sample. From the obtained results, it is clear that the reduction of $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{MnFe}_2\text{O}_4$ samples is of the same nature and follows a proposed “egg-shell” model, with only the formation of two new phases: a Fe-rich reformed spinel ($\text{M}_{1-x}\text{Fe}_{2+x}\text{O}_4$) and a thermodynamically stable hardly reducible layer of $\text{Mn}_x\text{Fe}_y\text{O}$ oxide solid solution. These results are in agreement with those of TPR and ex-situ XRD studies.

Table 4-6. Hyperfine parameters derived from the fittings of the $^{57}\text{Fe}$ Mössbauer absorption spectra over $\text{MFe}_2\text{O}_4$ ferrites after 20 min $\text{C}_2\text{H}_5\text{OH}$-reduction at 450°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>H (T)</th>
<th>Rel. Int. (%)</th>
<th>Phase attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CuFe}_2\text{O}_4$ after 20 min reduction</td>
<td>0.25</td>
<td>0.00</td>
<td>49.0\textsubscript{td}</td>
<td>8</td>
<td>spinel</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>0.00</td>
<td>45.9\textsubscript{Oh}</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.00</td>
<td>21.1</td>
<td>48</td>
<td>$\text{Fe}_5\text{C}_2 + \text{Fe}_3\text{C}$</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>0.00</td>
<td>10.7</td>
<td>12</td>
<td>$\text{Fe}_5\text{C}_2$</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>0.00</td>
<td>19.1</td>
<td>16</td>
<td>$\text{Fe}_5\text{C}_2$</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.5}\text{Co}</em>{0.5}\text{Fe}_2\text{O}_4$ after 20 min reduction</td>
<td>0.04</td>
<td>0.00</td>
<td>35.9</td>
<td>10</td>
<td>$\text{Fe}^6$ (alloy)</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>0.00</td>
<td>18.9</td>
<td>17</td>
<td>$\text{Fe}_5\text{C}_2$</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>0.00</td>
<td>11.2</td>
<td>13</td>
<td>$\text{Fe}_5\text{C}_2$</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.00</td>
<td>21.0</td>
<td>54</td>
<td>$\text{Fe}_5\text{C}_2 + \text{Fe}_3\text{C}$</td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>1.05</td>
<td>-</td>
<td>6</td>
<td>$\text{Fe}^{3+}$</td>
</tr>
</tbody>
</table>
4.7. Reactivity tests and characterization of the cycled materials

This chapter contains a further discussion on the redox properties of MFe₂O₄ ferrites and its usage as looping materials (LM) in the ethanol chemical-loop reforming (CLR), which consists of 2 steps: 1st step - reduction of LM$_{\text{fresh}}$ with ethanol at T-450°C; 2nd - re-oxidation of LM$_{\text{red}}$ with water steam. The choice of reaction conditions and cycling time was adopted according to the study of Cocchi (reducing agent: methanol, T$_{\text{red}}$ – 300 and 420°C/T$_{\text{re-ox}}$ – 420°C, looping materials: Fe₃O₄, CoFe₂O₄ and NiFe₂O₄) and Trevisanut (reducing agent: ethanol, T$_{\text{red}}$– 400 and 450°C/T$_{\text{re-ox}}$ – 450°C, looping materials: Fe₃O₄, CoFe₂O₄ and NiFe₂O₄). Important to note, that the essential aim of the reduction step was to maximize the reduction extent with a minimum deactivation (an effect of coke accumulation and incomplete M⁰ re-oxidation) of the looping material along with an improving of its cycling...
stability. Hence, previously obtained results suggested the best reaction conditions to be as follows: 1\textsuperscript{st} step – ethanol reduction at $T_{\text{red}}$=450°C and 2\textsuperscript{nd} step – water re-oxidation at $T_{\text{re-ox}}$=450°C. Cycling time was chosen on the same basis with the final optimum duration of both steps as 20 min per each cycle. Moreover, the composition of MFe$_2$O$_4$ ferrospinels was also varied in between Co, Mn, Cu and its combination Cu/Co, Cu/Mn and Co/Mn. The aim of the following modifications was to pursue a better performance (like a \textit{cycling stability} $(Y_{\text{int}}^\text{H}_2)=f(\text{cycles})=\text{const}$) of the M-incorporated ferrites in comparison to a pristine Fe$_3$O$_4$, as a primarily accepted LM for the CLR, proposed first by Nakamura.

In addition, as reported by Trevisanut\textsuperscript{101}, it is impossible to avoid a coke deposition in the anaerobic reduction conditions, which accumulates after each complete cycle leading to an inevitable deactivation. This in turn led us to an idea of the “modified ethanol CLR”, which now consists of 3 steps: 1\textsuperscript{st} step - reduction of LM$^\text{fresh}$ with ethanol at T=450°C; 2\textsuperscript{nd} - re-oxidation of LM$^\text{red}$ with water steam; 3\textsuperscript{rd} step - regeneration of coked LM$^\text{re-ox}$ with air at T=450°C. The obtained results are compared to a conventional 2 steps CLR process.
1st step: 20 min reduction with ethanol

Figure 4-17. Conversion and Yields to the main products obtained for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ during the 20 min cycling at T-450°C

Figure 4-17, Figure 4-19 to Figure 4-23 show conversion and yields for the main products (yield >5%), obtained during the ethanol reduction step performed at 450°C for 20 min. The general statement which can be applied to all the MFe$_2$O$_4$ (as LM): the amount of each product is greatly affected by the degree of metal oxide reduction. Thus, Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite (Figure 4-17) starting from the first minutes of the reaction showed 100% of conversion followed by its decrease down to 95%, while the extent of a spinel reduction increased from 0 to 100% (see Table 4-5). One of the main products of ethanol conversion was hydrogen, with an initial yield of about 50%, which increased up to 74%. The similar trend, as the one for hydrogen, was observed for CO with its max yield about 20%. Looking at CO$_2$ and H$_2$O profiles, one may notice a similar decreasing trend (starting yields: CO$_2$-32% and H$_2$O-18%, final yields: CO$_2$-12% and H$_2$O-4%). Thus, taking into account the elaborated results, we suggest that the main reactions during spinel reduction involved the partial and total oxidation of ethanol:

1. $\text{C}_2\text{H}_5\text{OH} + \text{MeO}_x \rightarrow 2 \text{CO} + 3 \text{H}_2 + \text{MeO}_{(x-1)}$
2. $\text{C}_2\text{H}_5\text{OH} + 3 \text{MeO}_x \rightarrow 2 \text{CO}_2 + 3 \text{H}_2 + 3 \text{MeO}_{(x-1)}$
3. $\text{C}_2\text{H}_5\text{OH} + 6 \text{MeO}_x \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} + 6 \text{MeO}_{(x-1)}$
In addition, the formation of water involves several possible reactions:

(4) \( H_2 + MeO \rightarrow H_2O + Me \)

(5) \( C_2H_5OH \rightarrow 2C + 2H_2 + H_2O \)

Acetone formation, which declined with time from 32 to 2%, as reported previously\(^{126}\), can be a result of an aldol condensation of the intermediately formed acetaldehyde, with further isomerization of the aldol into hydroxyketone followed by a reverse reaction to form acetone and formaldehyde (converted into CO and H\(_2\)). Either, as recently proposed by Rodrigues et al., by ketonization of carboxylates (acetates) which are obtained by dehydrogenation of this alcohol followed by oxidation\(^{127}\). In fact, the formation of acetates over Cu\(_{0.6-x}\)Mn\(_x\)Fe\(_{2.4}\)O\(_y\) and Co\(_{0.6-x}\)Mn\(_x\)Fe\(_{2.4}\)O\(_y\) samples was confirmed by DRIFTS study\(^{106}\).

Increasing yields for an acetaldehyde (from 1 to 15%) over the continuously reducing sample indicates that dehydrogenation/deoxyhydrogenation of ethanol also occurred:

(6) \( C_2H_5OH \rightarrow C_2H_4O + H_2 \)

(7) \( C_2H_5OH + MeO_x \rightarrow C_2H_4O + H_2 + Me \)

Coke and heavy compounds (mainly aromatics) are formed at the very beginning of the reaction time (~1%), with a progressive increase in yield to 39%. The generation of coke was likely due to the dehydrogenation and total deoxygenation of ethanol:

(8) \( C_2H_5OH \rightarrow C + CO + 3H_2 \)

(9) \( C_2H_5OH \rightarrow 2C + H_2O + 2H_2 \)

Moreover, a disproportionation of CO (Boudouard reaction) can also lead to the coke deposition:

(10) \( 2CO \rightarrow CO_2 + C \)

Several heavy compounds, with 4 and more C atoms, were also detected during the reduction step (Figure 4-17):

- Butenes
- Benzene
- 2-Pentanone
• 4-Penten-2-one and isomers
• Xylenes
• C₈ and C₉ aromatics

Figure 4-18. General scheme of pentanones/heptanones formation starting from ethanol

Figure 4-19. Conversion and Yields to the main products obtained for CuFe₂O₄ during the 20 min cycling at T-450°C

Looking at the conversion and yields evolution over CuFe₂O₄ ferrite (Figure 4-19), the results demonstrate similar trends in the products distribution and, as a consequence, similar
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe₂O₄)

reduction paths which involve the same set of reactions (eq. 1 to 10). The reduction of CuFe₂O₄ sample started with 95 % of ethanol conversion which approached to 92% after 20 min of reduction time, while degree of reduction reached 82%. As for the previously discussed ferrite, hydrogen was one of the main products of the ethanol conversion, with the following increasing trend: from 57 to 75%. However, H₂O and CO₂ have decreasing trends from 9 to 3% and 23 to 12%, respectively. This may indicate that the total oxidation is more favourable at the beginning of the reduction process (eq.3) over a less reduced material. Acetaldehyde was observed only after 5 min of tos (time-on-stream) with the increasing trend from 2 to 9%, eq. 6 and 7. Acetone was formed at the beginning with the yield of 31% and then its amount decreased to 5%. The overall reactions for the formation of acetone via aldol condensation may be expressed as follows:

(11) 2 CH₃CHO ⇌ CH₃-CH(OH)-CH₂-CHO (aldol condensation)

(12) CH₃-CH(OH)-CH₂-CHO ⇌ CH₃-CO-CH₂-CH₂OH (intramolecular disproportion-isomerization)

(13) CH₃-CO-CH₂-CH₂OH ⇌ CH₃-CO-CH₃ + H₂CO (retro-aldol condensation)

(14) H₂CO → CO + H₂ (decomposition of formaldehyde)

or via ketonization from the acetates bounded to the surface:

(15) 2CH₃COOH → CH₃COCH₃ + CO₂ + H₂O (via ketonization)

Coke and heavy compounds (mainly aromatics) are also formed with the comparably high yield as for the Cu₀.₅Co₀.₅Fe₂O₄ sample (increasing from 7 to 38%).
Results obtained with the CoFe$_2$O$_4$ ferrite are very similar to those obtained with the Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ and CoFe$_2$O$_4$ samples (Figure 4-20, eq.1-15). The conversion, starting from the beginning, reached its max (app. 100%) and was stable during the reduction time, yielding to 82% of the material reduction. The formation of CO and H$_2$O, H$_2$ as the main products led to the same conclusion on the prevailing reactions of the total and partial ethanol oxidation (eq. 1-3). The main difference between the previous two samples was observed in the amount of produced acetaldehyde (in this case the yield is very small, ≤1% during all 20 min of tos) and coke+HC (increased from 4 to 60%).
The conversion and yields during the reduction of the Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrite are shown in Figure 4-21. An addition of Mn-cations into Cu/Fe system just slightly affected the catalytic performance of the resulted material (in comparison to Cu/Fe system – CuFe$_2$O$_4$). Thus, during 20 min of tos the sample was reduced just about 73%; the conversion starting from the very beginning approached to 99% and was stable till the end of the reduction step. The formation of products (eq. 1-15) showed the following trend distributions: H$_2$ increased from 50 to 81%, CO$_2$ varying from 18 to 16% (with the max value of 26%), CO decreased from 20 to 13%, H$_2$O decreased from 9 to 2%, acetone decreased from 36 to 1% and acetaldehyde was detected just in traces.
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Figure 4-22 and Figure 4-23 show the conversion of ethanol and the yields to the various products obtained over MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites. The data demonstrate an apparent difference in the reducibility and the “catalytic activity” of these ferrites in comparison to the four previously discussed samples. Specifically, we could distinguish two different zones, during which the spinel first underwent a progressive reduction followed by “pseudo-steady-state”. Taking into account the ex-situ XRD study of the MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites performed at different reduction stages (1, 3, 5 and 20 min of tos), the formation of just two phases Mn$_x$Fe$_y$O and Mn$_{1-x}$Fe$_{2+y}$O$_4$ helped us to explain their peculiar behavior.

Looking first at the Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ graph (Figure 4-22), the conversion of ethanol during 20 min of tos slightly decreased from 100 to 98%, giving its max reduction degree of just 10% (while by itself CoFe$_2$O$_4$ during the same 20 min of tos was almost completely reduced – 82%). At the same time, the conversion of ethanol over MnFe$_2$O$_4$ decreased from 100 to 96% (Figure 4-23). The evolution of the product yields over these two samples showed the same time depending trend variations, viz. in approximately 5 min (zone I) the yields to all the products varied the most, while the reduction degree approached to 6 % for MnFe$_2$O$_4$ and 8% for Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (corresponds to the reduction speed of 0.8 %/min). Thereafter a
zone II started (from 5 to 20 min of tos, Δt=15 min), where all the yields were stable in time without any big changes, while the total reduction extent reached 8% for MnFe$_2$O$_4$ and 10% for Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (corresponds to Δα=2% and the reduction speed of 0.13%/min). In comparison to Co, Cu, Cu/Co and Cu/Mn ferrites, the reduction of MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ samples demonstrates different trends in the products distribution. Namely ethane, ethylene and acetone were formed continuously within 20 min of tos with much higher yields of about 14, 15 and 39% for MnFe$_2$O$_4$/12, 13 and 33% for Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$, respectively:

![Figure 4-23. Conversion and Yields to the main products obtained for MnFe$_2$O$_4$ during the 20 min cycling at T-450°C](image)

(16) $2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CH}_3 + \text{CH}_3\text{CHO} + \text{H}_2\text{O}$

(17) $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$

(18) $\text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2$

According to the TPR and ex-situ XRD results (discussed previously), the reduction of the following samples is described by a spontaneous reduction over the entire surface which occurs immediately on the contact with the reducing stream and leads to the expelling of Mn$^{2+}$ cations out of the spinel structure. The formation of new phases resembles more to a core-shell catalytic system, comprised of Fe-enriched spinel core (Mn$_{1-x}$Fe$_{2+x}$O$_4$) covered with a Mn$_x$Fe$_y$O shell (Mn$_{1-x}$Fe$_{2+x}$O$_4$@Mn$_x$Fe$_y$O). According to this, a significant slowdown of
the reduction speed from 0.8 to 0.13%/min was attributed to an accumulation of Mn$_x$Fe$_y$O phase, which has a high thermodynamic stability and as a consequence ascarce attitude towards the reduction to the metallic component, where the further diffusion of the reducing stream into the bulk (core) may be more problematic. Moreover, the “core@shell” model may also explain the formation of acetone directly from the ethanol via ketonization of acetates (eq.15), where the formed shell of Mn$_x$Fe$_y$O acts as a catalyst while Mn$_{1-x}$Fe$_{2+x}$O$_4$ core delivers oxygen (O$_L$) to restore the pre-reduced shell. It is worth noting, that DRIFTS study performed earlier over Co$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrospinels confirmed the formation of acetates and carbonates as important surface intermediates. Moreover, only in the case of Mn$_{0.6}$Fe$_{2.4}$O$_y$ sample there was no evidence of the acetate species to be transformed into carbonates one, which may also justify the high acetone yields over Mn$_{0.6}$Fe$_{2.4}$O$_y$ as well as for MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ samples.

Coke and heavy compounds were formed in a much smaller amount MnFe$_2$O$_4$ (from 16 to 8%) and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (from 21 to 12%); the total integrated yields to coke for all MFe$_2$O$_4$ ferrites are plotted in Figure 4-24 (see also CHNS analysis).

![Figure 4-24. Integrated yields of coke and heavy compounds formed within 20 min over MFe$_2$O$_4$ ferrites](image)

**Determination of carbon content (CHNS analysis): after 1$^{st}$ reduction step with ethanol**

In order to evaluate the amount of coke formed during the reduction step with ethanol (within 20 min), an elemental analysis (CHNS) on the different materials was carried out. Table 4-7 summarizes the results of CHNS analysis over MFe$_2$O$_4$ ferrospinels. According to the obtained results, the highest amount of coke accumulated during the ethanol reduction...
was detected over Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ and CoFe$_2$O$_4$ samples and it declines in the following order: Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$>CoFe$_2$O$_4$>CuFe$_2$O$_4$>Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$>Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$>MnFe$_2$O$_4$.

Table 4-7. CHNS results over MFe$_2$O$_4$ ferrites after 20 min reduction

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{w%}$ (after 20 min reduction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>6.9</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>16.3</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>11.6</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>1.5</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>6.1</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>1.7</td>
</tr>
</tbody>
</table>

2nd step: 20 min re-oxidation with water

Figure 4-25. Yields to H$_2$ and CO$_x$ obtained for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ during the re-oxidation step at T-450°C within 20 min of tos
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Figure 4-26. Yields to H$_2$ and CO$_x$ obtained for CuFe$_2$O$_4$ during the re-oxidation step at T-450°C within 20 min of tos.

Figure 4-27. Yields to H$_2$ and CO$_x$ obtained for CoFe$_2$O$_4$ during the re-oxidation step at T-450°C within 20 min of tos.
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Figure 4-28. Yields to H$_2$ and CO$_x$ obtained for Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ during the re-oxidation step at T-450°C within 20 min of tos

Figure 4-29. Yields to H$_2$ and CO$_x$ obtained for Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ during the re-oxidation step at T-450°C within 20 min of tos
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

After the 1$^{st}$ step with ethanol, the reduced material was then re-oxidized with water steam at 450°C during the same tos of 20 min, which corresponds to the 2$^{nd}$ step of the CLR process. The out flowing gas mixture was first passed through a water trap, in order to avoid a high-water concentration which could be pernicious for the micro-GC columns. The GC method, created to quantify all the compounds present in the gas mixture, allowed us to carry out an analysis every 1.5 min. The reactions conditions described in Paragraph 2.11.

Figure 4-25 to Figure 4-30 report the yields to H$_2$, CO$_2$ and CO versus time (yields have been calculated based on the H (for H$_2$) or O (CO$_x$) content in products, with respect to the water fed – described in Paragraph 2.11.), whereas Figure 4-31 compares the overall integrated yields to H$_2$, CO and CO$_2$ formed during 20 min over MFe$_2$O$_4$ ferrites. It is important to notice, that the increasing trends (within 0-5 min) shown in the Figure 4-25 to Figure 4-30 most probably arise from the following fact: the stream, containing unconverted steam and products, needs a few minutes to reach the catalyst and then the on-line GC instrument after the start-up of the reaction. A common feature, which observed for almost all the samples, was a complete re-oxidation of the material in the chosen timeframe of 20 min (excluding only CoFe$_2$O$_4$ and Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ samples, where the H$_2$-yield was still decreasing indicating an incomplete re-oxidation).

![Graph](image-url)

Figure 4-30. Yields to H$_2$ and CO$_x$ obtained for MnFe$_2$O$_4$ during the re-oxidation step at T-450°C within 20 min of tos
The highest hydrogen yields were detected for all three samples which contain Cu-cations as one of the incorporated metals: CuFe\(_2\)O\(_4\) (52%), Cu\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\) (47%), and Cu\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\) (37%); whereas a lower amount of hydrogen produced during the re-oxidation process, was obtained over Co, Mn and Mn/Co-incorporated samples: CoFe\(_2\)O\(_4\) (24%), Co\(_{0.5}\)Mn\(_{0.5}\)Fe\(_{2.4}\)O\(_y\) (6%) and MnFe\(_2\)O\(_4\) (4%). These data lie in parallel with the previously discussed results and can be explained, taking into account the values of the reduction extent (\(\alpha\)), calculated on the basis of Rietveld refinement; the increasing order of \(\alpha\): Cu\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\)-100%> CuFe\(_2\)O\(_4\)=CoFe\(_2\)O\(_4\)-82%> Cu\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\)-73%> Co\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\)-10%> MnFe\(_2\)O\(_4\)-8%, corresponds quite well to the increasing order for H\(_2\)-yields: CuFe\(_2\)O\(_4\)-52%> Cu\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\)-47%> Cu\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\)-37%> CoFe\(_2\)O\(_4\) (24%)> Co\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\)-6%> MnFe\(_2\)O\(_4\)-4%, with the exception of only two catalysts - CoFe\(_2\)O\(_4\) and Cu\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\) which indeed was expected since the re-oxidation never reached the end.

Apart of the produced hydrogen, the common feature for all the samples was the formation of CO\(_x\) (CO\(_2\) and CO) during the re-oxidation step (Figure 4-25 to Figure 4-31), because of the gasification of carbonaceous residues, previously formed during the reduction step. The main reactions occur during the re-oxidation process are defined as following:

19) \(\text{Me} + \text{H}_2\text{O} \rightarrow \text{MeO} + \text{H}_2\)

20) \(3 \text{MeO} + \text{H}_2\text{O} \rightarrow \text{Me}_3\text{O}_4 + \text{H}_2\)

21) \(\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\)

22) \(\text{C} + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}_2\)

The formation of CO\(_x\) was observed with all MFe\(_2\)O\(_4\) ferrites, though the total amount of CO\(_2\)+CO was significantly different. According to the obtained results, Mn-containing catalysts produced less CO\(_x\) which resulted from a lower amount of deposited carbon during the reduction step, this results agreed with the calculated values of Coke+HC and CHNS analysis (Table 4-7).
It is worth noting, that the initial reason for altering composition of the original looping material-Fe$_3$O$_4$ was to achieve a better efficiency and a cycling stability, which was defined as the main drawback by Trevisanut et al$^{101}$. From the Figure 4-31 one may notice that pristine Fe$_3$O$_4$ by itself is a reasonably efficient LM with the H$_2$-yield of 33%, although it turned out that Cu-incorporated samples surpassed the overall yield to H$_2$. From this point, we decided to compare the cycling stability of Fe$_3$O$_4$ with CuFe$_2$O$_4$ (52%) and Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (47%) samples, which gave the max yields to hydrogen (see Paragraph 4.9).
Ex-situ XRD results: “2 step CLR” – 1 complete cycle (20 min red/20 min re-ox)
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Figure 4-32: XRD patterns after 1 complete cycle of the "2 steps CLR" performed on MFe$_2$O$_4$ ferrites

One of the key points to obtain an efficient CLR process lies in the use of potentially stable (the ability to reform a spinel phase after each complete cycle with minimum segregation) and highly active (with no significant loss in the redox performance with cycling) materials. By mean of the ex-situ XRD study, performed on the used MFe$_2$O$_4$ materials, identification of the reformed phases after 1 complete cycle reveals important information on the stability...
of the spinel phase itself and a relevance of the use of only H₂O steam to restore the original state of the looping material.

Figure 4-32 shows the XRD results taken on the cycled samples after 1 complete cycle. It can be seen, that all tested materials underwent some morphological changes and were significantly affected by sintered temperature (narrowing of the XRD patterns), segregation (presence of M and MO phases in addition the spinel one).

Performing the 2nd re-oxidation step with water steam at 450°C led to the formation of the following phases: Cu₀.₅Co₀.₅Fe₂O₄ (reformed spinel, CoFe alloy and metallic Cu⁰), CuFe₂O₄ (reformed spinel and metallic Cu⁰), CoFe₂O₄ (reformed spinel and CoFe alloy), Cu₀.₅Mn₀.₅Fe₂O₄ (reformed spinel, metallic Cu⁰ and MnₓFeₙO), Co₀.₅Mn₀.₅Fe₂O₄ (reformed spinel and MnₓFeₙO) and MnFe₂O₄ (reformed spinel and MnₓFeₙO). The following results indicate that all of the looping materials were affected by segregation phenomena in addition to the sintering one. Nevertheless, the presence of the reformed spinel phase (a main 100% reflection of (311) plane at 35.5° 2θ) in all re-oxidized MFe₂O₄ samples indicate the possibility to partly re-obtain the original state of the looping material. However, the evidence of the incomplete re-oxidation of the metallic component - M⁰ (mainly as CoFe alloy and Cu⁰) to M¹⁺ indicated that the use of H₂O steam as the only oxidant at T-450°C was insufficient. One of the possible solutions to overcome this problem is to add the 3rd step (O₂-feeding to complete re-oxidation and to clean the looping material from the remained coke), discussed in the next paragraph.

4.8. Characterization of cycled looping materials: 3 steps CLR - 1 complete cycle (20 min red/20 min re-ox/30 min air)

XRD and BET results after 1 complete cycle

The structure of the materials after 1 complete cycle in the “3 step CLR” with air regeneration is defined from XRD patterns (Figure 4-33). Resulted patterns confirm the formation of the spinel oxide, as the main phase for all the regenerated samples. Using Rietveld refinement we managed to quantify the amount of the supplementary phases formed during the regeneration step with air: Cu₀.₅Co₀.₅Fe₂O₄ (spinel-98.52% and CuO-1.48%), CuFe₂O₄ (spinel-80.44% and CuO-19.56%, note that the starting material contained
21\% of CuO), CoFe$_2$O$_4$ (spinel-83,36\% and Co$_3$O$_4$-16,64\%), Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (spinel- 100\%), Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ (spinel-100\%) and MnFe$_2$O$_4$ (no RV refinement was done, however the small intensity reflection from MnO$_2$ in addition to the spinel phase was observed).

In the Table 4-8 are listed results for SSA, crystallite size (calculated by Scherrer eq.) and particle size (calculations are based on N$_2$ adsorption (BET) data) of fresh and regenerated samples. Apparent increase of the crystallite/particle size (as a consequence decrease of the SSA) observed for all MFe$_2$O$_4$ ferrites is a result of the sintering temperature effect.

\[
\text{Table 4-8. Specific surface area (SSA) and crystallite/particle size results}
\]

<table>
<thead>
<tr>
<th>Sample name</th>
<th>SSA$_{\text{fresh}}$, m$^2$/g</th>
<th>SSA$_{\text{reg}}$, m$^2$/g</th>
<th>Crystallite size (Scherrer eq.)$_{\text{fresh}}, \text{nm}$</th>
<th>Crystallite size (Scherrer eq.)$_{\text{reg}}, \text{nm}$</th>
<th>Particle size (d$<em>{\text{BET}}$)$</em>{\text{fresh}}, \text{nm}$</th>
<th>Particle size (d$<em>{\text{BET}}$)$</em>{\text{reg}}, \text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>60</td>
<td>12</td>
<td>7.2</td>
<td>34.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(22)</td>
<td>(18.6)</td>
<td>18.3</td>
<td>91.3</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>67</td>
<td>17</td>
<td>10.9</td>
<td>35$^m$</td>
<td>16.5</td>
<td>65.1</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>69</td>
<td>29</td>
<td>12.0</td>
<td>32$^m$</td>
<td>16.2</td>
<td>38.5</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS ($\text{MFe}_2\text{O}_4$)

**Determination of carbon content (CHNS analysis) after 1 complete cycle**

One of the reasons that the looping material undergoes deactivation is related to the coke deposition and its further accumulation during cycling using conventional “2 steps CLR”. From that point it was important to overcome it using modified process, so called “3 steps CLR”. Table 4-9 summarizes the results of CHNS analysis over $\text{MFe}_2\text{O}_4$ ferrospinels. The amount of remained carbon after carrying the 3rd step with air was neglectable, leading us to the conclusion that an addition of the 3rd step to the conventional process has its beneficial effect on the coke removal in addition to the possibility to restore the original state of the looping material which confirmed previously by XRD results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C$_{\text{w} %}$</th>
<th>(after regeneration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CuFe}_2\text{O}_4$</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>$\text{CoFe}_2\text{O}_4$</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$\text{Cu}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$\text{MnFe}_2\text{O}_4$</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

CuO phase

$^m$-medium value (at app.30.1 and 62.5 2°)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C$_{\text{w} %}$</th>
<th>(after regeneration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>141</td>
<td>30</td>
</tr>
<tr>
<td>$\text{Cu}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>112</td>
<td>14</td>
</tr>
<tr>
<td>$\text{MnFe}_2\text{O}_4$</td>
<td>165</td>
<td>26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>C$_{\text{w} %}$</th>
<th>(after regeneration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>141</td>
<td>30</td>
</tr>
<tr>
<td>$\text{Cu}_0.5\text{Mn}_0.5\text{Fe}_2\text{O}_4$</td>
<td>112</td>
<td>14</td>
</tr>
<tr>
<td>$\text{MnFe}_2\text{O}_4$</td>
<td>165</td>
<td>26</td>
</tr>
</tbody>
</table>

$^m$-medium value (at app.30.1 and 62.5 2°)
4.9. 2 steps CLR vs 3 steps CLR: cycling of looping materials (3 cycles-20 min)

Figure 4-34. Yields to $\text{H}_2$ and $\text{CO}_x$ obtained for $\text{Fe}_3\text{O}_4$ during the re-oxidation step at $T=450^\circ\text{C}$ within 3 cycles-20 min in the “2 steps CLR” process.

Figure 4-35. Yields to $\text{H}_2$ and $\text{CO}_x$ obtained for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ during the re-oxidation step at $T=450^\circ\text{C}$ within 3 cycles-20 min for each step (equal to the total time of 60 min for the first step) in the “2 steps CLR” process.
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Figure 4-36. Yields to H$_2$ and CO$_x$ obtained for CuFe$_2$O$_4$ during the re-oxidation step at T-450°C within 3 cycles·20 min for each step (equal to the total $t_{os}$ of 60 min for the first step) in the “2 steps CLR” process.

Figure 4-34 to Figure 4-36 show integrated values for the produced H$_2$ and CO$_x$ obtained during the 3 complete 2-steps CLR cycles of 20 min for each step (equal to the total $t_{os}$ of 60 min for the first step), where bare-Fe$_3$O$_4$ was taken as a reference. From the results it is clear, that both M modified samples (Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ and CuFe$_2$O$_4$) and Fe$_3$O$_4$ exhibited a decrease in the total amount of produced H$_2$ with each performed cycle, however magnetite showed the most extreme decreasing trend: Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ – 1$^{st}$ (47%), 2$^{nd}$ (41%) and 3$^{rd}$ (36%); CuFe$_2$O$_4$ – 1$^{st}$ (52%), 2$^{nd}$ (43%) and 3$^{rd}$ (36%); Fe$_3$O$_4$ – 1$^{st}$ (33%), 2$^{nd}$ (27%) and 3$^{rd}$ (15%). Moreover, the ratio between moles of produced H$_2$ and CO+CO$_2$ indicates that selectivity to H$_2$ is continuously declining whereas the CO$_x$ amount is growing which also specifies in a higher contribution of the coke gasification reactions to the total amount of produced hydrogen.

Thus, the obtained results confirm a previously made statement that the looping material tends to deactivate and its nature derives from the following: 1. deep modification of the starting material via sintering and segregation phenomena; 2. continuous “coking” of the material with each performed cycle due to impossibility to achieve a total removal of it in the conventional 2 steps CLR process; 3. incomplete re-oxidation of the metallic component (M$^0$) using just H$_2$O as an oxidant (supported by XRD and CHNS results).
Such conclusions incited us to make changes to the 2 steps CLR process, using instead 3 steps “modified ethanol CLR”, which consists of: 1st step - reduction of LM\textsuperscript{fresh} with ethanol at T-450°C; 2nd - re-oxidation of LM\textsuperscript{red} with water steam; 3rd step - regeneration of coked LM\textsuperscript{re-ox} with air at T-450°C.

Figure 4-37 and Figure 4-38 report the results obtained with Cu\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} and CuFe\textsubscript{2}O\textsubscript{4} ferrites in the “3 steps CLR” process (with the regeneration in air); materials were selected on the basis of the higher H\textsubscript{2} production, as already has been mentioned. The plotted results indicate that the amount of produced hydrogen during the 1st cycle was almost identical to its amount during the 2nd and the 3rd cycle: Cu\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} – 1st (47%), 2nd (45%) and 3rd (44%); CuFe\textsubscript{2}O\textsubscript{4} – 1st (52%), 2nd (54%) and 3rd (53%). Whereas, the ratio H\textsubscript{2}/CO+CO\textsubscript{2} and CO\textsubscript{2}/CO during 3 consecutive cycles remains practically unchanged indicating that the selectivity to H\textsubscript{2} is constant with no additional contribution of H\textsubscript{2} produced due to the gasification of coke. This in turn shows that the modified “3 steps CLR” process shows an improved cycling stability of the looping materials in comparison to the conventional “2 steps CLR”.

![Graph showing the yields of H\textsubscript{2} and CO\textsubscript{2} for Cu\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} during the re-oxidation step at T-450°C within 3 cycles-20 min for each step (equal to the total tos of 60 min for the first step) in the “3 steps CLR” process.]

<table>
<thead>
<tr>
<th>Cycles</th>
<th>H\textsubscript{2}/(CO+CO\textsubscript{2})</th>
<th>CO\textsubscript{2}/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.5</td>
<td>3.1</td>
</tr>
<tr>
<td>2</td>
<td>6.7</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>7.2</td>
<td>3.3</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION, PART I: **TYPE I SPINELS (MFe$_2$O$_4$)**

**Figure 4-38.** Yields to H$_2$ and CO$_x$ obtained for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ during the re-oxidation step at T-450°C within 3 cycles·20 min for each step (equal to the total tos of 60 min for the first step) in the “3 steps CLR” process

![Graph showing yields to H$_2$, CO$_2$, and CO over cycles](image)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>H$_2$/CO$_2$/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3/5.9</td>
</tr>
<tr>
<td>2</td>
<td>3.4/5.2</td>
</tr>
<tr>
<td>3</td>
<td>3.9/4.4</td>
</tr>
</tbody>
</table>

**Ex-situ XRD study: 2 steps CLR vs 3 steps CLR: cycling of looping materials (3 cycles·20 min)**

In order to understand the main difference between the “2 steps CLR” and “3 steps CLR” processes, ex-situ XRD study was carried out on the cycled materials (Figure 4-39 to Figure 4-42). Performed 3 complete cycles of the “2 steps CLR” at 450°C led to the formation of the following phases: Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (reformed spinel, CoFe alloy, metallic Cu$^0$ and alpha Fe$^0$) and CuFe$_2$O$_4$ (reformed spinel and metallic Cu$^0$). Recalling previously discussed XRD results after 1 complete cycle the phases were detected as follows: Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (reformed spinel, CoFe alloy and metallic Cu$^0$) and CuFe$_2$O$_4$ (reformed spinel and metallic Cu$^0$ with much lower intensity peak). Thus, the deactivation of the looping material together with the decreasing yield to H$_2$ first of all can be attributed to the incomplete re-oxidation of the metallic component (M$^0$) which tends to accumulate in its higher amount with each subsequent cycle resulting in the less and less available MFe$_2$O$_4$/MO form to be further reduced.

Looking at the same 3 complete cycles in the “3 steps CLR” process at 450°C the detected phases were identified as follows: Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (reformed spinel) and CuFe$_2$O$_4$ (reformed
spinel and CuO) which appears to be exactly the same phases of the primary starting materials. And as the matter of fact, it can explain the improved stability of the looping material by adding the 3rd regeneration step (with air).

Figure 4-39. XRD patterns for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite taken after 3 complete cycles during the “2 steps CLR” process

Figure 4-40. XRD patterns for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ferrite taken after 3 complete cycles during the “3 steps CLR” process
RESULTS AND DISCUSSION, PART I: TYPE I SPINELS (MFe$_2$O$_4$)

Figure 4-41. XRD patterns for CuFe$_2$O$_4$ ferrite taken after 3 complete cycles during the “2 steps CLR” process.

Figure 4-42. XRD patterns for CuFe$_2$O$_4$ ferrite taken after 3 complete cycles during the “3 steps CLR” process.
4.10. Conclusions on the study of MFe$_2$O$_4$ ferrospinels

This part of the work is focused on the study of TYPE I – MFe$_2$O$_4$ ferrospinels as O$^2-$/electrons carriers, where the composition was varied in between transition metals: Co, Mn, Cu and their combinations: Cu/Co, Cu/Mn, Co/Mn. Particular interest represented a deep study of the H$_2$/C$_2$H$_5$OH-reduction profiles in order to understand the main difference in the reducibility among the samples and its nature. On the basis of TPR studies, all Cu-incorporated samples CuFe$_2$O$_4$, Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ and Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ were proposed to reduce via so called “autocatalytic” model, where the primarily formed Cu$^0$ nucleus (Cu$^{2+}$→Cu$^0$) is further catalyzing the reduction of a newly reformed Fe-enriched spinel (with generic formula - M$_{1-x}$Fe$_{(2+x)}$O$_4$). The reduction occurs on the basis of hydrogen spill over effect, where Cu$^0$ plays the role of a catalyst which is needed to dissociate H$_2$ into 2H atoms. Whereas, the reduction of MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites appeared to be more complicated and was described by a spontaneous reduction over the entire surface which occurs immediately on the contact with hydrogen and lead to the expelling of Mn$^{2+}$ cations out of the spinel structure with a formation of the new phases: a Fe-rich reformed spinel (M$_{1-x}$Fe$_{(2+x)}$O$_4$) and a hardly-reducible layer of Mn$_x$Fe$_y$O oxide solid solution, like an “egg-shell”.

Using ex-situ XRD approach, we followed C$_2$H$_5$OH-reduction of the MnFe$_2$O$_4$, Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites which corresponds to the 1$^{st}$ step of the chemical-loop reforming process. For MnFe$_2$O$_4$ and Co$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ ferrites, the data clearly indicated that after feeding ethanol for 1 min the formation of a new Mn$_x$Fe$_y$O phase was observed. With increasing the reduction time from 1 to 20 min the spinel relative amount continued decreasing whereas that of the Mn$_x$Fe$_y$O increased without the appearance of other phases, which is an important proof of the “egg-shell” reduction model. Instead, the stepwise reduction of Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ clearly indicated that a primarily formed phase during the 1$^{st}$ min of ethanol exposure was Cu$^0$, and the further increase of the reaction time led to a deeper reduction with the formation of Fe-carbides, thus pointing out to the “autocatalytic” reduction model. Besides, the introduction of Cu$^{2+}$ ions into the Co/Fe system showed its strong promoting effect on the reduction of Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ ($\alpha=100\%$), caused by a synergetic effect of Cu-Co couple (while by itself the reduction degree of CuFe$_2$O$_4$ and CoFe$_2$O$_4$ is equal to 82%).
Moreover, all of the MFe$_2$O$_4$ ferrites were tested as looping materials in the “2 steps CLR” process. The obtained results showed that CuFe$_2$O$_4$, Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$, Cu$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ and CoFe$_2$O$_4$ within 20 min of ethanol reduction reached almost complete reduction, and as a consequence the higher yields to H$_2$ produced during the re-oxidation step with steam. However, with each performed cycle the material tends to deactivate as the result of: 1. deep modification of the starting material via sintering and segregation phenomena; 2. continuous “coking” of the material with each performed cycle due to impossibility to achieve a total removal of it in the conventional CLR process; 3. incomplete re-oxidation of the metallic component (M$^0$) using just H$_2$O as an oxidant. On the other hand, modifying the conventional 2 steps process by adding the 3$^{rd}$ step with air helped us to overcome these problems.
5. RESULTS AND DISCUSSION, PART II: TYPE II SPINELS \( (M_{0.6}Fe_{2.4}O_y) \)

**Bulk characterization of fresh materials**

The section includes a discussion of the results obtained from several characterization techniques over fresh \( M_{0.6}Fe_{2.4}O_y \) (M-Co, Cu, Mn) samples: EDX analysis, XRD, \( N_2 \) adsorption, Raman Spectroscopy, TPR/TPO used to study bulk properties of freshly prepared ferrospinels, which maintain their importance being the nature of surface sites determined by those properties.

### 5.1. Energy dispersive spectroscopy (EDX)

EDX is an addition characterization technique used for the elemental analysis or chemical characterization of the samples (the overall analytical accuracy is app. ± 2%). In the Table 5-1 are shown theoretical and measured ratios between \( Fe/M \) (M-foreign metal: Co, Cu, Mn). In all the cases the real ratio of \( Fe/M \) is slightly different from the expected one. This difference can first of all come from a weighing error and an incomplete pouring of the metal precursor solutions or to the slight hydration of the samples powders. Moreover, according to EDX analysis there is also a presence of Na < 1\% (as a residual which comes from the synthesis procedure).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Theoretical ratio, ( Fe/M )</th>
<th>Measured ratio, ( Fe/M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Co_{0.6}Fe_{2.4}O_y )</td>
<td>( Fe/Co - 4/1 )</td>
<td>( Fe/Co - 3.69/1 )</td>
</tr>
<tr>
<td>( Co_{0.54}Mn_{0.06}Fe_{2.4}O_y )</td>
<td>( Fe/Co - 4.4/1 )</td>
<td>( Fe/Co - 4.65/1 )</td>
</tr>
<tr>
<td></td>
<td>( Fe/Mn - 40/1 )</td>
<td>( Fe/Mn - 37.24/1 )</td>
</tr>
<tr>
<td>( Co_{0.3}Mn_{0.3}Fe_{2.4}O_y )</td>
<td>( Fe/Co - 8/1 )</td>
<td>( Fe/Co - 7.32/1 )</td>
</tr>
<tr>
<td></td>
<td>( Fe/Mn - 8/1 )</td>
<td>( Fe/Mn - 7.76/1 )</td>
</tr>
<tr>
<td>( Mn_{0.6}Fe_{2.4}O_y )</td>
<td>( Fe/Mn - 4/1 )</td>
<td>( Fe/Mn - 3.76/1 )</td>
</tr>
<tr>
<td>( Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y )</td>
<td>( Fe/Cu - 8/1 )</td>
<td>( Fe/Cu - 8.93/1 )</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M$_{0.6}$Fe$_{2.4}$O$_y$)

<table>
<thead>
<tr>
<th></th>
<th>Fe/Mn - 8/1</th>
<th>Fe/Mn - 7.62/1</th>
<th>Cu$<em>{0.6}$Fe$</em>{2.4}$O$_y$</th>
<th>Fe/Cu - 4/1</th>
<th>Fe/Cu - 4.47/1</th>
</tr>
</thead>
</table>

5.2. XRD and N$_2$ adsorption

XRD patterns of the fresh materials calcined at 450°C (for 8 h) are shown in Figure 5-1. Based on the obtained results a following conclusion can be stated: all M$_{0.6}$Fe$_{2.4}$O$_y$ ferrites display a spinel-like phase of magnetite (Fe$_3$O$_4$) with its characteristic diffraction peaks (the main peak – hkl (311) with 100% intensity at app. 35.5° 2theta). However, a significant broadening of the diffraction patterns observed for Mn-modified samples (Figure 5-1, see Mn$_{0.0}$Fe$_{2.4}$O$_y$, Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$, Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ and Co$_{0.54}$Mn$_{0.06}$Fe$_{2.4}$O$_y$) which first of all can be attributed to a decrease in a particle size/-crystallite size or as a fact of a lower crystallinity. Crystallite size of the following samples was calculated using Scherrer equation, results are listed in the Table 5-2 (values are obtained for (440) plane at app.62.5° 2theta).
Further characterization such as N\textsubscript{2} adsorption (BET) has shown that all the Mn-ferrospinel ferrites possess apparent differences in specific surface area (SSA). The highest SSA is shown by Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}, and this value declines with an increase of Co- and Cu-content. This indicates the presence of smaller particles, which is also in a good agreement with previously discussed XRD results. A further confirmation was obtained from the average particle size (Table 5-2), which can be calculated from the SSA results making some assumption about the particle shape (the particles are spherical and non-porous)\textsuperscript{130}.

### 5.3. Raman Spectroscopy

The crystallographic structure of spinel oxides group is formed by a nearly closed-packed face centered cubic (fcc) of anions with two unequivalent sites for cations, which differ in oxygen coordination\textsuperscript{89}. In the normal spinel, the A cations (divalent) occupy all the tetrahedral sites, and the B cations (trivalent) fill the octahedral sites. In inverse spinel, the B cations occupy the tetrahedral sites, and the octahedral sites contains a mixture of B and A cations\textsuperscript{89,91}. The preference of the individual ions for the two types of lattice sites is determined by: the ionic radii of the specific ions; the size of the interstices; temperature; the orbital preference for specific coordination.
Many of the ferrites exhibit inversion of the cations between the tetrahedral and octahedral sites. Normally, Fe₃O₄ and CoFe₂O₄ are completely inverse spinels. Raman spectra of these inverse spinels is more complicated and show additional Raman-active modes over the five predicted by group theory. Unlike the other ferrites MnFe₂O₄ is a normal spinel. However, nanostructured powders of various synthesis and treatment methods have exhibited differing degrees of inversion. Thus, the nature of the substituted ions, charges and their distribution among the O₈ and T₄ sites of the ferrospinels affect their catalytic properties. Substitution of ‘Fe’ centers with other transition/non-transition/inner-transition metals leads to the formation of an inverse/normal, either mixed spinels with different degree of inversion. In spite of this, such an introduction may strongly modify the redox properties of the resultant ferrites.

Raman features of ferrites are samples specific, depending on non-stoichiometry, cation distribution, defects, and also on the experimental conditions. According to the literature, there are five predicted Raman active modes: A₁g, Eₘ, and three T₂g modes (Eₘ, Eₘ, 3T₂g). Additional modes may appear in vibrational spectra due to local distortions of the crystal.
lattice. These defects do not affect the long-range ordering of the system, and are often cannot be detected by x-ray diffraction\textsuperscript{108,131}.

Figure 5-2 shows the Raman spectra obtained over TYPE II ferrites with a nominal composition of $M_1^{0.6-x}M_2^xFe_{2.4}O_y$ (where $M_1^1 = Co/Cu$ and $M_2^2 = Mn$). The spectrum $A - Co_{0.6}Fe_{2.4}O_y$ reveals 6 vibration modes: 5 predicted by the literature and an additional one caused by the local distortions in the lattice. With increasing the Mn-contain the shape of the most intensive band $A_{1g}$ at 688 cm$^{-1}$ which corresponds to the Fe-O symmetric stretching in tetrahedron become more broad for $Co_{0.54}Mn_{0.06}Fe_{2.4}O_y$ and each peak can be presented like a doublet. A higher intensity mode $A_{1g}$ (\textasciicircum 688 cm$^{-1}$) for mixed Mn-Co- and only Co- iron-rich ferrites has a shoulder at lower frequency (\textasciicircum 613 cm$^{-1}$), which is caused by disorder effects of $M_2^{2+}$ and $Fe^{3+}$ over the Td and Oh sites\textsuperscript{109}. However, the spectra of $Mn_{0.6}Fe_{2.4}O_y$ and $Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y$ possess completely different vibration modes, a broad band at \textasciicircum 663 cm$^{-1}$ which can be an overlap of $Fe^{3+}/Mn^{2+}$ in the tetrahedral sites have hardly visible doublet structure and no lower frequency shoulder can be seen. As a result, according to the following substitution mechanism, where Mn$^{2+}$ ions partly replace Fe$^{3+}$ ions in the Td sites thus changing the degree of inversion towards the formation of the normal spinel\textsuperscript{110}. The resulting spectrum of $Mn_{0.6}Fe_{2.4}O_y$ is in agreement with previous reports.\textsuperscript{111} The low intensity of the peaks and partial energy shifts can be related also to a high defectivity\textsuperscript{107} and a low crystallinity as confirmed by XRD. It should be emphasized that Co$^{2+}$ was previously found to increase the hyperfine field of the B sublattice over a similar composition range. Thus, the presence of an inversion center in the centrosymmetrical space group Fd3m implies mutual exclusion of Raman and IR activities for the same vibrational mode. Furthermore, the bands in IR and Raman spectroscopy are sensitive to coordination geometry and oxidation states.
5.4. Temperature programmed reduction (TPR)

RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M$_{0.6}$Fe$_{2.4}$O$_{4}$)
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M_{0.6}\text{Fe}_{2.4}\text{O}_4)

C_{0.51}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4

C_{0.51}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4 + 0.18\text{H}_2 \rightarrow 0.955\text{Co}_{0.51}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4 + 0.18\text{H}_2\text{O}\ (\alpha \sim 5\%)

0.955\text{Co}_{0.51}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4 + 0.2\text{H}_2 \rightarrow 0.33\text{Co}_2\text{O}_3 + 0.29\text{Mn}_2\text{O}_3 + 0.75\text{Fe}_2\text{O}_3 + 0.2\text{H}_2\text{O}\ (\alpha \sim 10\%)

0.75\text{Fe}_2\text{O}_3 + 0.75\text{H}_2 \rightarrow 2.26\text{FeO} + 0.75\text{H}_2\text{O}\ (\alpha \sim 28\%)

0.31\text{Co}_2\text{O}_3 + 0.31\text{H}_2 \rightarrow 0.31\text{Co}_3 + 0.31\text{H}_2\text{O}\ (\alpha \sim 36\%)

0.76\text{FeO} + 0.76\text{H}_2 \rightarrow 0.76\text{Fe} + 0.76\text{H}_2\text{O}\ (\alpha \sim 55\%)

At the end of TPR1: incomplete reduction of FeO and MnO phases: MnO_{FeO} \rightarrow \text{Mn}_2\text{O}_3_{Fe}_2\text{O}_3

C_{0.75}\text{Fe}_{2.4}\text{O}_4

C_{0.75}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4 + 0.65\text{H}_2 \rightarrow 0.26\text{Cu} + 0.3\text{Mn}_2\text{O}_3 + 0.75\text{Fe}_2\text{O}_3 + 0.65\text{H}_2\text{O}\ (\alpha \sim 14\%)

0.76\text{Fe}_2\text{O}_3 + 0.76\text{H}_2 \rightarrow 2.29\text{FeO} + 0.76\text{H}_2\text{O}\ (\alpha \sim 35\%)

0.44\text{FeO} + 0.44\text{H}_2 \rightarrow 0.44\text{Fe} + 0.44\text{H}_2\text{O}\ (\alpha \sim 46\%)

At the end of TPR2: incomplete reduction of FeO and MnO phases: MnO_{FeO} \rightarrow \text{Mn}_2\text{O}_3_{Fe}_2\text{O}_3

Cu_{0.5}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4

Cu_{0.5}\text{Mn}_{0.5}\text{Fe}_{2.4}\text{O}_4 + 0.65\text{H}_2 \rightarrow 0.26\text{Cu} + 0.3\text{Mn}_2\text{O}_3 + 0.75\text{Fe}_2\text{O}_3 + 0.65\text{H}_2\text{O}\ (\alpha \sim 14\%)

0.76\text{Fe}_2\text{O}_3 + 0.76\text{H}_2 \rightarrow 2.29\text{FeO} + 0.76\text{H}_2\text{O}\ (\alpha \sim 35\%)

0.44\text{FeO} + 0.44\text{H}_2 \rightarrow 0.44\text{Fe} + 0.44\text{H}_2\text{O}\ (\alpha \sim 46\%)

At the end of TPR2: incomplete reduction of FeO and MnO phases: MnO_{FeO} \rightarrow \text{Mn}_2\text{O}_3_{Fe}_2\text{O}_3
RESULTS AND DISCUSSION, PART II: TYPE I SPINELS (M_{0.6}Fe_{2.4}O_y)

Figure 5-3. TPR profiles of M_{0.6}Fe_{2.4}O_y ferrospinel including the box with reduction passages.

*Data on the reduction passages were made based on the following: initial composition, reduction potentials of corresponding redox couples and amount of consumed H_2.
Temperature-programmed reduction (TPR) measurements were performed to investigate the role of different metals on the reducibility of M-modified ferrites, denoted as TYPE II ferrospinels with a generic formula of $\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y$. As discussed previously, the acquired data were elaborated based on the amount of consumed hydrogen considering the nature of the incorporated metals. Being guided by the results obtained over TYPE I ferrospinels ($\text{MFe}_2\text{O}_4$), the TPR profiles of TYPE II samples ($\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y$) follow the same reduction scheme (as depicted in Figure 4-3) and can be conditionally divided into two parts: the reduction of iron oxide to metallic iron and the reduction of incorporated foreign metal oxide to its metallic component. As it was seen previously, the reduction temperature of ‘$\text{Fe}_3\text{O}_4$→FeO→Fe’ passage and completeness of the process itself strongly depends on the nature of a present foreign metal M (M=Co, Cu, Mn) that also follows from observed differences in the initiation of the reduction process and the total amount of consumed hydrogen (Figure 5-3 and Figure 5-5). The low-T reduction shoulder at $\sim 200^\circ\text{C}$, which accounts for $\sim5\%$ of the total reduction, was experimentally observed for the Co, Co/Mn and Mn-incorporated sample and attributed to the reduction of $\text{M}_{0.57}\text{Fe}_{2.28}\text{O}_4$ to $\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_4$ due to the presence of cation vacancies in the highly defective materials (note: presence of only Fe$^{3+}$ cations in the fresh samples was confirmed by Mössbauer experiments). The values of IS ($\delta$) lie in a typical range for Fe$^{3+}$ species: 0.31-0.35 mm/s. Further reduction of $\text{Co}_{0.6}\text{Fe}_{2.4}\text{O}_y^{(A)}$, $\text{Co}_{0.54}\text{Mn}_{0.06}\text{Fe}_{2.4}\text{O}_y^{(B)}$, $\text{Co}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}\text{O}_y^{(C)}$ and $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y^{(D)}$ samples follows the same stages as for Co-, Co/Mn- and Mn-incorporated TYPE I ferrospinels (see the pass II, illustrated in Figure 4-3); where the first small peak at $\sim 400^\circ\text{C}$ was attributed to the primary spinel reduction with a stepwise formation of CoO and Fe$_3$O$_4$ (or CoO, MnO and Fe$_3$O$_4$) phases (which corresponds to $\alpha \sim 8\%$), whereas in only Mn-incorporated ferrite, $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y$, this step starts at lower temperature of $\sim 380^\circ\text{C}$ (note: $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_4 + 0.2 \text{H}_2 \rightarrow 0.6 \text{MnO} + 0.8 \text{Fe}_3\text{O}_4 + 0.2 \text{H}_2\text{O}$). However, the Co-containing samples reached significantly higher reduction extents ($\alpha \sim 80^{(A)}$, 75$^{(B)}$ and 55$^{(C)}$%) in comparison to the Mn-containing sample ($\alpha \sim 58^{(D)}$%); and it was again attributed to the formation of the scarcely reducible phase of MnO (or in the form of wustite-like Mn$_x$Fe$_y$O oxide). Looking at the TPR profiles of $\text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_y^{(E)}$and $\text{Cu}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}\text{O}_y^{(F)}$ ferrites, the first peak at $\sim 350^\circ\text{C}$ was attributed to the primary stepwise spinel reduction with the final formation of Cu$^{0(E)}$/Cu$^{0}$$+\text{MnO}^{(F)}$ and Fe$_3$O$_4$ phases (which accounts for $\alpha \sim 23^{(E)}/16^{(F)}$%) following the pass I$^{(E)}/\text{III}^{(F)}$ (Figure 4-3); the further reduction of Fe$_3$O$_4$→FeO and FeO→
Fe\textsuperscript{0}\textsubscript{incom} appears at higher temperatures with the total reduction extent of \( \sim 52^{(E)}/46^{(F)} \)%.

As explained previously for the Co/Mn- and Mn-incorporated ferrospinel, the reduction of 
\( \text{MnO} \rightarrow \text{Mn}\textsuperscript{0} (-1.18 \text{ eV}) \)\textsuperscript{106} can occur only at very extreme temperatures (see \( \Delta G\textsubscript{react}^{0} \), Table 4-3) which, in turn, leads to the formation of the scarcely reducible phase of MnO/Mn\textsubscript{x}Fe\textsubscript{y}O.

Summarizing the TPR results over TYPE I/II ferrospinel, a general reduction path for the 
\( \text{M}_{0.6}\text{Fe}_{2.4}\text{O}_{y} \) samples was illustrated as follows:

\[ \begin{align*}
\text{I. } & \text{M}_{0.6}\text{Fe}_{2.4}\text{O}_{y} \rightarrow 0.6 \text{M}^{2+} + 0.8 \text{Fe}_{3}\text{O}_{4} \\
\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_{y} \rightarrow 0.6 \text{M}^{2+} + 0.8 \text{Fe}_{3}\text{O}_{4} \\
\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_{y} \rightarrow 0.6 \text{M}^{3+} + 0.8 \text{Fe}_{3}\text{O}_{4} \\
\text{II. } & \text{Fe}_{3}\text{O}_{4} \rightarrow \text{FeO} \\
\text{III. } & \text{M}^{2+} \rightarrow \text{M}^{3+} \\
\text{IV. } & \text{FeO} \rightarrow \text{Fe} \\
\text{V. } & \text{M}^{3+} \rightarrow \text{Mn} \\
\end{align*} \]

where \( \text{M}^{1} = \text{Co}, \text{M}^{2} = \text{Cu} \) and \( \text{M}^{3} = \text{Mn} \)

Figure 5-4. General scheme for \( \text{M}_{0.6}\text{Fe}_{2.4}\text{O}_{y} \) reduction
5.5. **Ferrospinel TYPE II: study of Co$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ system**

This section is focused on the study of Co$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ mixed ferrites as potentially new oxygen carrier materials for chemical-loop reforming process. The new materials were tested in terms of both redox properties (Paragraph 5.4) and catalytic activity to generate hydrogen by oxidation with steam, after a reductive step carried out with ethanol. In addition, the section includes in-situ DRIFTS and in-situ XPS studies that allowed to extract information at molecular level and to follow surface changes within the reduction/re-oxidation processes during ethanol chemical-loop reforming.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M_{0.6}Fe_{2.4}O_{y})

5.6. Surface characterization: in-situ DRIFTS experiments

The adsorption of alcohols over metal oxides can lead to different kinds of adsorbed species depending on the surface properties of the material under study. According to the literature, ethanol adsorbs on the surface mainly as an ethoxide, formed from the scission of the O-H bond. However, the species formed with increasing temperatures are more related to the surface chemistry of each compound. Figure 5-6 shows spectra of adsorbed...
ethanol at RT over the four samples. Ethoxy bands (dissociative adsorption) can be observed at 1057 and 1103 cm$^{-1}$ for the C-O/C-C stretching modes together with the bands of the undissociated ethanol (at 1383 cm$^{-1}$ and 1274 cm$^{-1}$ for CH$_3$δ and OHδ, respectively). The complex absorption in the 2800-2400 cm$^{-1}$ region is probably due to a Fermi resonance of the overtone of the OHδ vibration mode with the CH- stretching modes at 2971, 2929, and 2863 cm$^{-1}$ (CH$_3$(as), CH$_2$(as) and CH$_3$(s) modes of the ethoxide species). Figure 5-6(A-C) show a strong band at 3252 cm$^{-1}$ that may be assigned to the OH stretching of ethanol H-bonded to the surface, which also was observed over the stoichiometric CoFe$_2$O$_4$ ferrospinel in our previous paper. The sharp band at 3681 cm$^{-1}$ together with a shoulder at 3635 cm$^{-1}$ is assigned to the –OH stretching vibration of chemisorbed undissociated ethanol over surface Lewis acid sites (M$^{n+}$). The shoulder at lower frequency may indicate the presence of different active sites on the materials. However, with increasing the Mn-contain the shoulder decreases in intensity and only for Mn$_{0.6}$Fe$_{2.4}$O$_y$ it completely disappears. This effect was already seen by Raman spectroscopic measurements, described above (Paragraph 5.6).
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M$_{0.6}$Fe$_{2.4}$O$_{4}$)
Some remarkable differences between the DRIFTS spectra of samples are observed when the temperature is increased (Figure 5-7); acetate bands appear (at 1334, 1439, 1590 cm\(^{-1}\)) for the CH\(_3\)  \(\delta\), (OCO\(\nu\)(s)), and OCO\(\nu\)(as) vibrations, respectively. The increasing in intensity and broadening of the band at 1590 cm\(^{-1}\) (at 250\(^\circ\)C) also indicates the formation of carbonate species.\(^{136}\) These species could further produce CO\(_2\), which is detected as the doublet at the 2358-2338 cm\(^{-1}\) region and corresponds to adsorbed and/or gaseous CO\(_2\) rotation vibration P and R bands.\(^{137}\) The DRIFT spectra obtained on Mn\(_{0.6}\)Fe\(_{2.4}\)O\(_4\) (Figure 5-7-D), also exhibit the bands for acetate species, formed by the reaction of ethoxy species with surface oxygen (1598, 1555, 1433 and 1334 cm\(^{-1}\)).\(^{98,138}\) When the temperature is increased (up to 400\(^\circ\)C) the intensity of the bands corresponding to ethoxy species is reduced, whereas the bands associated with acetate species (strongly bounded to the surface) remain almost unchanged. However, the main difference between the spectra of Mn\(_{0.6}\)Fe\(_{2.4}\)O\(_4\) and of other Co- and Co-Mn ferrospinel spectra lies in the absence of the bands associated with carbonate species; the band of the adsorbed CO\(_2\) was not observed as well. Thus, the results may indicate that Co and Co-Mn-modified systems were more reactive than the Mn ferrospinel. This is also followed by the presence of a broad absorbed
feature in the 3000-1800 cm$^{-1}$ region, which is attributed to the electronic absorption of the partially reduced sample.$^{94,139}$

In summary, the redox properties of M-modified ferrospinels and hence their catalytic activity in the chemical-loop reforming of ethanol are strongly influenced by the nature of M and by the M$^{n+}$ distribution among the Oh and Td sites in the crystal lattice. The main differences between the four spinels studied are the following: the incorporation of only Co leads to the formation mainly of an inverse spinel, however the addition of Mn resulted in the substitution of Td coordinated Fe$^{3+}$ ions with Mn$^{2+}$ and, as a consequence, the formation of new type of active sites. The reduction of M-modified ferrospinels appears to be a complex process due to the presence of various reduced forms of Fe oxides together with oxides of substituted metal ions (Co$_x$O$_y$ and Mn$_x$O$_y$). Besides, it was observed that incorporation of Co-Mn metal cations into magnetite structure affects its reducibility, which directly depends on the nature of the incorporated metal cation. In particular, the Co-Mn system presents a cooperative influence on each other’s reduction profiles. Moreover, during the ethanol anaerobic decomposition/oxidation step over Co and mixed Co-Mn ferrospinels, acetates and carbonates appeared to be important surface intermediates and in the case of the only Mn containing catalyst, there was no evidence for the carbonates formation.
In order to study the kinetics of the reduction and re-oxidation processes that take place on the catalytic surface, *in-situ* XPS measurements were performed. In particular, by monitoring the changes occurred in the photoemission spectra of Fe2p, Co2p and Mn2p, during ethanol ($5\times10^{-6}$ mbar at 450°C) and water ($2\times10^{-4}$ mbar at 450°C) exposure, it was possible to determine the role played by each component of the Co/Mn-modified ferrospinels on the surface chemistry.

Let us first concentrate on the changes in the XPS data after the sample annealing at 450°C in UHV. As an example, in Figure 5-9 we compare the spectra of Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_{y}$ as...
received and after annealing: a significant decrease of the FWHM in the O 1s spectrum and a small shift of Fe2p and Mn2p peaks lower binding energy (BE) values are clearly observed, which indicate a surface modification occurred after elimination of the adsorbed hydroxyl (OH-) groups or/and water molecules, and the reduction of highly oxidized metal species (e.g. Fe2O3 to Fe3O4 formation). In any case, the spectra obtained after this UHV annealing are taken as a reference for the subsequent chemical changes induced by the chemical treatments.

The chemical composition determined by photoemission and the spectral fingerprints observed confirm the presence of M-modified ferrospinel whose stoichiometric ratio is in agreement with the nominal ratio of the synthesis protocol.

The samples were exposed to an increasing amount of ethanol and the evolution of the main core level spectra (see Figure 5-10 - Figure 5-13), was measured observing clear differences in the surface composition as a function of the presence of different M.

Starting from the very beginning of ethanol feeding, the reduction of iron from Fe3+ to Fe2+ was observed for all tested samples, which is evidenced by the decrease of the intensity of the Fe 2p peak in conjunction with the energy shift of Fe 2p3/2 satellite from 8 eV (typical for Fe3+) to 5 eV, which can be ascribed to oxides with a lower valence.\cite{140,141}

In the case of prolonged ethanol exposure, the appearance of a further component at 707.0 eV indicates the formation of a metal component. Such a phenomenon is strongly dependent on the actual composition of the corresponding sample, and especially on the Co/Mn ratio. As shown in Figure 5-8, it was found that Co(II)-incorporation effectively improves the reducibility of the catalyst, whereas addition of Mn has an opposite effect. This effect is once again confirmed by the previously described TPR and DRIFTS results (Paragraphs 5.4 and 5.6 respectively). Moreover, Co0.54Mn0.06Fe2.4Oy showed a stronger reduction in comparison to the sample without Mn (Co0.6Fe2.4Oy - Figure 5-8). This behavior can be explained by the size effect induced by the presence of Mn (with increasing of Mn-content the specific surface area also increased (Paragraph 5.2). In the Co0.3Mn0.3Fe2.4Oy ferrospinel within 80 min of reduction by ethanol, a peak corresponding to the formation of an iron metal phase was not detected and it was seen only after 120 min of ethanol feeding (see Figure 5-11). This resilience towards the reduction was observed also for Mn0.6Fe2.4Oy, whose reduction behavior is very similar (see Figure 5-10).
Moreover, we could observe changes in the line shape of Mn 2p only after the annealing in UHV at 450°C (due to desorption of surface OH- groups and/or water molecules), whereas afterwards spectra remained unchanged, despite the iron and cobalt underwent substantial reduction.

It has been already mentioned that Co boosts the reduction of ferrospinels; however it is interesting to compare the tendency toward the reduction of Co vs Fe. The photoemission peak of Co 2p overlaps with Fe Auger peak, which complicates its analysis, nevertheless some qualitative information can be obtained. Cobalt is present as Co$^{2+}$ and therefore no more reduced species can be formed, but the metal. As a matter of fact in the Co 2p photoemission line it can be observed a progressive disappearance of the Co$^{2+}$ 2p$_{1/2}$ peaks (795.5 eV) and its satellite in favour of the formation of a metal component (793.3 eV). Metal components of Fe and Co were observed almost at the same time, however it can be noted that cobalt was fully reduced to metal in the case Co$_{0.6}$Fe$_{2.4}$O$_{y}$ and Co$_{0.54}$Mn$_{0.06}$Fe$_{2.4}$O$_{y}$ whereas the reduction of iron species to metallic iron was only partial (Figure 5-8).

In the case of relatively large Mn-content (Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_{y}$), Co cations are not reduced immediately, but a relevant oxidized component can be observed in standard conditions (80 min of ethanol feeding), whereas only after 120 min is fully reduced. It is also interesting to note that such reaction seems to be autocatalytic; actually in the stage from 80 to 120 min there is a fast increase in the reduced components with the formation of metallic phases. These experiments suggest that when Mn is present in large amount there is a substantial depression of reduction. This indicates that the synthesized ferrospinel are homogeneous and not a physical mixture of Co$_{0.6}$Fe$_{2.4}$O$_{y}$ and Mn$_{0.6}$Fe$_{2.4}$O$_{y}$. Moreover, the chemical activity of the M-modified ferrospinels is ruled in a complex way by the sum of the effects due to the two incorporated metals.

To summarize the picture emerging from the XPS investigation we can propose that the reduction process involves the fast formation of a reduced oxide with a satellite at 5 eV and afterwards the nucleation of iron metal. This shift of the satellite can be qualitatively associated with the reduction of Fe$^{3+}$ to Fe$^{2+}$ which from the structural point of view corresponds to the reduction to wustite, and only afterwards this latter is progressively reduced to metal iron.
The formation of the metal phase seems to be a rather slow process and requires a significant induction period whereas the first reduction from Fe$^{3+}$ to Fe$^{2+}$ is quite fast in the used conditions.

Figure 5-9. (a) Fe 2p, (b) Mn 2p, (c) Co 2p, (d) O1s photoemission spectra of Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ before (solid line) and after (dot line) annealing at 450°C for 30 minutes.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)

Figure 5-10. (a) Mn 2p (b) Fe 2p (c) O 1s photoemission peak of $Mn_{0.6}Fe_{2.4}O_y$ (i) after annealing at 450°C in UHV for 20 min, and after (II) 20 min, (III) 50, min (IV), 80 min ethanol exposure at 450°C. ($P_{Ethanol}: 5 \times 10^{-6}$ mbar). In (b) the dotted line shows the change in the position of the satellite of the Fe 2p$_{3/2}$ line whereas the solid vertical line indicates the BE position of iron metal.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)

Figure 5-11. (a) Fe 2p (b) Co 2p (c) O 1s (d) Mn 2p photoemission peaks of Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ (I) after annealing at 450°C in UHV for 20 min, and after (II) 20 min, (III) 50 min, (IV) 80 min, (V) 120 min ethanol exposure at 450°C ($P_{\text{ethanol}}$: 5x10$^{-6}$ mbar), and after (VI) 30 min and (VII) 60 min water exposure at 450°C ($P_{\text{water}}$: 2x10$^{-4}$ mbar). In (a) the dotted vertical line indicates the BE position of iron metal, in (b) the BE position of metal component is shown by solid vertical lines, whereas the position of the Co(II) 2P$_{3/2}$ peak maximum position and its satellite are indicated by dotted lines.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}$Fe$_{2.4}$O$_y$)

Figure 5-12. (a) Fe 2p (b) Co 2p (c) O 1s (d) Mn 2p photoemission peaks of $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (I) after annealing at 450°C in UHV for 20 min, and after (II) 20 min, (III) 50 min (IV), 80 min ethanol exposure at 450°C ($P_{ethanol}$: $5x10^{-5}$ mbar). In (a) the dotted vertical line indicates the BE position of iron metal and whereas the dotted line the shift of Fe 2p$_{3/2}$ satellite peak, in (b) the BE position of metal component is shown by solid vertical lines, whereas the position of the Co(II) 2p$_{1/2}$ peak maximum position and its satellite are indicated by dotted lines.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}$Fe$_{2.4}$O$_y$)

Figure 5-13. (a) Co 2p (b) Fe 2p (c) O 1s photoemission peaks of $Co_{0.6}Fe_{2.4}O_y$ (i) after annealing at 450°C in UHV for 20 min, and after (ii) 20 min, (iii) 50, min (IV), 80 min ethanol exposure at 450°C ($P_{Ethanol}$: 5x10$^{-6}$ mbar) and after (VI) 30 min water exposure at 450°C ($P_{water}$: 2x10$^{-4}$ mbar). In (b) the dotted vertical line indicates the BE position of iron metal and whereas the dotted line the shift of Fe 2p$_{3/2}$ satellite peak.

Conclusions on the in-situ XPS study

Globally from photoemission we can outline a scenario where the reactivity of the ferrospinels is strongly dependent on the type of M introduced in the lattice, which however determines a quite complex reactivity scheme based on a synergetic effect. Manganese in large amount has the effect of slowing down the reduction reaction and in any case it can never be reduced. The high thermodynamic stability of Mn$^{2+}$ is the probable origin of its scarce attitude toward reduction. Cobalt on the contrary can be reduced to the metallic state very quickly, even faster and in a larger extent than iron.

In order to get information on the second step of the chemical loop we have investigated the exposure of ethanol reduced $Co_{0.6}Fe_{2.4}O_y$ and$Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ to water at 450°C. In both cases Fe 2p spectra indicate a fast oxidation process that leads to an almost complete suppression of the metal component. However, it must be noted that the final Fe 2p spectrum is rather broad with a smeared fine structure, which can be due to the co-presence of many different phases: not only ferrospinels but also iron suboxides and hydroxides. The presence of these latter is supported by the larger FWHM and increased intensity on the high BE side of the O 1s peak after water dosing. Similarly in the Co 2p
spectra, the quick formation of oxidized species i.e. Co$^{2+}$ can be observed immediately after water exposure. However, whereas in the pure cobalt ferrospinel the oxidation of cobalt is almost quantitative, in the case of the Co/Mn sample such process is partial and a large metal cobalt component is visible even after extended water dosing (60 min). Such difference can be probably traced back to the presence of manganese, which somehow hinders the reaction with water.

5.8. Reactivity tests: Co$_{0.6-x}$Mn$_x$Fe$_2.4$O$_y$ system

This section includes discussion of the results obtained over Co$_{0.6-x}$Mn$_x$Fe$_2.4$O$_y$ ferrospinels tested on the laboratory-scale plant. The cycling time was chosen according to the initial results achieved over pristine Fe$_3$O$_4$ and M-ferrospinels - CoFe$_2$O$_4$, NiFe$_2$O$_4$, reported by Trevisanut and et al.$^{129,126}$ It was found that in approximately 20 min of ethanol feeding, the material was constantly reduced until it reached its `steady state` with the stable composition under these reaction conditions. Therefore, we were able to avoid a further coke deposition that occurred over the strongly reduced spinel.

1st step: 20 min reduction with ethanol

Figure 5-14 shows conversion and yield for the main products (yield >5%), obtained during the first step of the chemical loop, where the material is being reduced by ethanol at 450$^\circ$C for 20 min. The conversion of ethanol over Co$_{0.6}$Fe$_{2.4}$O$_y$ (Figure 5-14, A) reached 100% starting from the first minutes of the reaction, and it was stable during 20 min of ethanol feeding. One of the main products of ethanol conversion was hydrogen, with an initial yield of about 50%, which increased up to 82% while the extent of spinel reduction increased. Also, CO and CO$_2$ have similar increasing trends as for H$_2$, thus suggesting that the main reactions during spinel reduction involved the partial oxidation of ethanol:

1. $C_2H_5OH + MeO_x \rightarrow 2 CO + 3 H_2 + MeO(x-1)$
2. $C_2H_5OH + 3 MeO_x \rightarrow 2 CO_2 + 3 H_2 + 3 MeO(x-1)$

The formation of acetone, which declined with time, can be a result of an aldol condensation of the intermediately formed acetaldehyde, with further isomerization of aldol into hydroxyketone followed by a reverse reaction to form acetone and formaldehyde (converted into CO and H$_2$). Either, as recently proposed by Rodrigues et al., by ketonization
of carboxylates (acetates) which are obtained by dehydrogenation of this alcohol followed by oxidation\textsuperscript{127}. In fact, the formation of acetates over Co\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} samples was confirmed by DRIFTS study. The formation of water (with yield \textasciitilde11\%) involves several possible reactions:

3. C\textsubscript{2}H\textsubscript{5}OH + 6 MeO\textsubscript{x} \rightarrow 2 CO\textsubscript{2} + 3 H\textsubscript{2}O + 6 MeO\textsubscript{(x-1)}

4. H\textsubscript{2} + MeO \rightarrow H\textsubscript{2}O + Me

5. C\textsubscript{2}H\textsubscript{5}OH \rightarrow 2 C + 2 H\textsubscript{2} + H\textsubscript{2}O
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M$_{0.6}$Fe$_{2.4}$O$_y$)
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)

Coke and heavy compounds (mainly aromatics) also formed starting from the very beginning of the reaction time (~20%), with a progressive increase in yield. Under these reaction conditions it was impossible to avoid the formation of carbonaceous species. The generation of coke was likely due to dehydrogenation and total deoxygenation of ethanol:

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C} + \text{CO} + 3 \text{H}_2 \]  

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{C} + \text{H}_2\text{O} + 2 \text{H}_2 \]

Moreover, disproportionation of CO (Boudouard reaction) can result in coke deposition:

\[ 2 \text{CO} \rightarrow \text{CO}_2 + \text{C} \]

Figure 5-14. Conversion and yields for the main products during 20 min reduction with ethanol at 450°C over: (A) $\text{Co}_{0.6}\text{Fe}_{2.4}O_y$; (B) $\text{Co}_{0.54}\text{Mn}_{0.06}\text{Fe}_{2.4}O_y$; (C) $\text{Co}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}O_y$; (D) $\text{Mn}_{0.6}\text{Fe}_{2.4}O_y$

Figure 5-15. Integrated Yields for the coke and heavy compounds during 20 min reduction with ethanol at 450°C
Results obtained with the other samples (Figure 5-14, B,C,D) demonstrate similar trends in the products distribution. However, some significant differences can be seen: with increasing Mn-content the conversion of ethanol was slightly decreasing. The Mn$_{0.6}$Fe$_{2.4}$O$_y$ sample (Figure 5-14, D) at first showed 100% of conversion followed by its decrease down to 80%. The main reason for such behavior can be an accumulation of MnO phase in the catalyst, which has a high thermodynamic stability and as a consequence its scarce attitude towards the reduction to metallic component. This result also has been confirmed by TPR, DRIFTS and in-situ XPS measurements.

As discussed above, we could not completely avoid coke formation, but despite this, we were able to significantly reduce its amount by changing the composition of the catalyst, as shown in Figure 5-15, plotting the overall yield to C residues integrated over the 20 min reduction time. Indeed, the presence of Mn had the beneficial effect of decreasing the coke deposition, which is an important issue in order to produce C-free hydrogen. The integrated yields for other products formed during 20 min of reduction with ethanol are plotted in Figure 5-16. In particular, Co-containing ferrospinels (Co$_{0.6}$Fe$_{2.4}$O$_y$ and Co$_{0.54}$Mn$_{0.06}$Fe$_{2.4}$O$_y$) have shown high yields to CO$_2$, CO and H$_2$O and enhanced reactivity in the anaerobic decomposition/oxidation of ethanol. On the other hand, Mn$_{0.6}$Fe$_{2.4}$O$_y$ appeared to be more active in the formation of acetone, which is the result of the reverse aldol condensation reaction.

![Figure 5-16. Integrated Yields for other compounds during 20 min reduction with ethanol at 450°C](image-url)
Figure 5-17 shows the degree of reduction for the four catalysts with different ratio Co/Mn as a function of reaction time (20 min), as calculated from the oxygen balance. Even though the highest surface area was shown by Mn<sub>0.6</sub>Fe<sub>2.4</sub>O<sub>y</sub> catalyst, and it declined with an increase of Co-content, the samples with high content of Co (Co<sub>0.6</sub>Fe<sub>2.4</sub>O<sub>y</sub> and Co<sub>0.54</sub>Mn<sub>0.06</sub>Fe<sub>2.4</sub>O<sub>y</sub>) were strongly reduced (almost 100 %) in comparison to only Mn-modified ferrospinel with just app. 20% of reduction extent. This suggests that the difference in the reducibility of the four M-modified ferrospinels is related to the nature of the incorporated M cation and its intrinsic reactivity, which is also confirmed by in-situ XPS results.

![Graph showing the degree of reduction for different catalysts](image)

Figure 5-17. Reduction extent of Co<sub>0.6-x</sub>Mn<sub>x</sub>Fe<sub>2.4</sub>O<sub>y</sub> samples after 20 min of ethanol exposure (at T=450°C)
2\textsuperscript{nd} step: 20 min re-oxidation with water
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)

Figure 5-18. Yields for the H2, CO2 and CO during 20 min re-oxidation with water at 450°C over: (A) $Co_{0.6}Fe_{2.4}O_y$; (B) $Co_{0.54}Mn_{0.06}Fe_{2.4}O_y$; (C) $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$; (D) $Mn_{0.6}Fe_{2.4}O_y$

After the reduction with ethanol, the materials were re-oxidized with steam at 450°C, which corresponds to the second step of the chemical loop. Figure 5-18 (A-D) reports the yield of H2, CO2 and CO versus time (yields have been calculated based on the H or O content in products, with respect to the water fed – described in Paragraph 2.11), whereas Figure 5-19 reports the overall yields to H2, CO and CO2, integrated over the 20 min oxidation time. High hydrogen yields were obtained over $Co_{0.6}Fe_{2.4}O_y$, $Co_{0.54}Mn_{0.06}Fe_{2.4}O_y$ and $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$. The common problem of all samples was the formation of CO and CO2 during the re-oxidation step (Figure 5-18 and Figure 5-19), because of the gasification of carbonaceous
residues, previously formed during the reduction step. The main reactions occur during re-oxidation process are defined as following:

(9) Me + H₂O → MeO + H₂

(10) 3 MeO + H₂O → Me₃O₄ + H₂

(11) C + H₂O → CO + H₂

(12) C + 2 H₂O → CO₂ + 2 H₂

The main difference was in the amount of produced COₓ. According to the obtained results, Mn-containing catalysts were more selective to hydrogen formation, as shown in Table 5-3, reporting the ratio between the overall yield to H₂ and the overall yield to CO+CO₂.

Figure 5-19. Integrated values of yields to H₂, CO₂ and CO during the re-oxidation with H₂O

Table 5-3. Ratio H₂/(CO+CO₂) obtained during the re-oxidation step with water

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂/CO+CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₀.₆Fe₂.₄Oₓ</td>
<td>28.0</td>
</tr>
<tr>
<td>Mn₀.₃Co₀.₃Fe₂.₄Oₓ</td>
<td>12.2</td>
</tr>
<tr>
<td>Mn₀.₀₆Co₀.₅₄Fe₂.₄Oₓ</td>
<td>5.2</td>
</tr>
<tr>
<td>Co₀.₆Fe₂.₄Oₓ</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Determination of carbon content (CHNS analysis)

In order to quantify the real amount of coke formed on the tested materials an elemental analysis (CHNS) was carried out. Table 5-4 shows the obtained results: Mn-containing materials (Mn$_{0.6}$Fe$_{2.4}$O$_y$ and Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$) showed the lowest amount of C residues accumulated during the first reduction step. However, with all materials a part of the coke still remained on the surface after one complete cycle, being not completely re-oxidized with water at that temperature (450°C). As a consequence, these materials underwent some morphological changes significantly affected by accumulation of coke, sintering (particle size increased to ~90-100 nm) and segregation (Figure 5-20, B,C; these images are of samples which underwent several redox cycles).

![Figure 5-20. TEM images of Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$: (A) fresh material calcined at 450°C; (B) after 4 cycles·20 min+ 1red·20 min; (C) after 20 min·5 cycles](image)

However, the behavior shown by Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ can be considered the most promising one, since it forms less coke during the 1$^{st}$ step of ethanol reduction and less CO$_x$ during the 2$^{nd}$ step of re-oxidation with steam, nevertheless it can provide high hydrogen yield. On the other hand, Mn$_{0.6}$Fe$_{2.4}$O$_y$ and Mn$_{0.3}$Co$_{0.3}$Fe$_{2.4}$O$_y$ were less efficient in the removal of C residues during the re-oxidation with steam; this means that the low amount of CO and CO$_2$ formed during the 2$^{nd}$ step are also due to the fact that coke is only in minimal part re-oxidized by steam. This may be due to the lower degree of reduction achieved during the 1$^{st}$ step, since the reduced metal may catalyze the gasification of coke by reaction with steam.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>C content(%) after 20 min of reduction (ethanol)</th>
<th>C content(%) after 20 min reduction (ethanol) + 20 min re-oxidation ($H_2O$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Mn_{0.6}Fe_{2.4}O_y$</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>$Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$</td>
<td>7.9</td>
<td>6.5</td>
</tr>
<tr>
<td>$Co_{0.5}Mn_{0.06}Fe_{2.4}O_y$</td>
<td>11.0</td>
<td>6.1</td>
</tr>
<tr>
<td>$Co_{0.6}Fe_{2.4}O_y$</td>
<td>9.7</td>
<td>6.2</td>
</tr>
</tbody>
</table>

5.9. Conclusions on the study of $Co_{0.6-x}Mn_xFe_{2.4}O_y$ ferrospinels

The chemical-loop reforming of ethanol for $H_2$ production was studied by using $M$-modified ferrospinels of general composition $Co_{0.6-x}Mn_xFe_{2.4}O_y$ ionic oxygen carrier materials. The redox properties of ferrospinels were found to depend strongly on the nature of incorporated cation in addition to its distribution inside the crystal lattice. The four catalysts with different ratio between two supplemented metals ($Co/Mn$) were investigated. Substitution of $Fe^{2+}$ with $Co^{2+}$ ions led to the formation mainly of an inverse spinel, however the addition of $Mn$ resulted in the substitution of Td coordinated $Fe^{3+}$ ions with $Mn^{2+}$ and as a consequence the formation of new type of active sites. The reduction of $M$-modified ferrospinels appeared to be a complex process due to the presence of various reduced forms of $Fe$ oxides together with $Co$ and $Mn$ oxides. Besides, it was observed that incorporation of $Mn-Co$ metal cations into magnetite ($Fe_3O_4$) crystal structure affects its reducibility, depending on the nature of the incorporated metal cation. In particular, $Co/Mn$ systems showed a cooperative influence on each other’s reduction profiles. Moreover, in-situ DRIFTS study was performed in order to follow the stepwise reduction of the catalyst surface, which allowed us to detect different adsorbed species and their transformation into the products. Acetates and carbonates appeared to be important surface intermediates over $Co$- and mixed $Co-Mn$- ferrospinels and in the case of the only $Mn$-containing catalyst, there was no evidence of the carbonates formation. Furthermore, according to the results
obtained by means of catalytic tests and CHNS elemental analysis, the addition of Mn hindered carbon deposition, which also caused a decrease of the amount of CO\textsubscript{x} generated by oxidation with water steam, which is an important issue to produce clean H\textsubscript{2}. However, the Mn containing ferrospinels showed a lower efficiency in the removal of the C residues accumulated during the first step. This may lead to the need of a third step of coke removal by air oxidation, if a clean material is needed to perform a following cycle. In an alternative approach, as already pointed out in the literature, the unreactive coke may be maintained as an inert material, provided (that) during successive cycles the further accumulation of coke occurs at a limited extent only\textsuperscript{22,142}.

Co-Mn mixed ferrospinels, with high levels of Co, enhanced reactivity in the anaerobic decomposition/oxidation of ethanol. Thus, the behavior shown by Co\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} can be considered to be the most promising one, as this type of M-modified ferrospinel formed less coke during the reduction step (as a result less CO\textsubscript{x} generated during the re-oxidation step with water), and still high hydrogen yield could be obtained.

Therefore, one of the key points to improve the proposed process and make it industrially attractive is reducing the amount of carbonaceous species which in principle can be done by changing the catalyst composition and thus tuning its redox properties in order to optimize the ratio between the degree of reduction and the amount of coke deposition.

Hence, the use of bulk M-modified spinel oxides as oxygen carrier materials for the chemical-loop reforming of ethanol has its positive aspects which allow to achieve a good recyclability of the starting material due to the formation of thermodynamically stable spinel oxide phase during cycling using the “same mild temperatures” for both reduction and re-oxidation steps. In comparison to other approaches reported in literature, such as the use of high temperatures\textsuperscript{143,144} to limit a coke formation and structured materials with morphologies aimed to confine the negative effects of sintering\textsuperscript{145–147}.

\section*{5.10. Ferrospinels \textbf{TYPE II}: study of Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system}

The study of Co\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrospinels (see previous Paragraph 5.5) have shown that Mn(II) incorporation into the system helps to significantly reduce the amount of coke and hence to avoid a fast deactivation of the material. Therefore, the present section onward explores physicochemical and catalytic properties of the M\textsubscript{1.0.6-x}M\textsuperscript{2}Fe\textsubscript{2.4}O\textsubscript{y} spinel type.
systems and the particular interest represents the effect of Mn-incorporation on the morphology, magnetic, redox and catalytic properties of the resulted Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrospinels.

*Characterization of fresh Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrites*

The section includes a discussion of the results obtained from several characterization techniques: Mössbauer Spectroscopy, Magnetic measurements and TPR over fresh Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrospinels.

5.1.1. Mössbauer spectroscopy
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}\text{Fe}_{2.4}O_y$)

Figure 5-21. Room temperature $^{57}$Fe Mössbauer spectra of samples $\text{Cu}_{0.6}\text{Fe}_{2.4}O_y$, $\text{Cu}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}O_y$ and $\text{Mn}_{0.6}\text{Fe}_{2.4}O_y$
Table 5-5. Room temperature $^{57}$Fe Mössbauer parameters

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\delta^*$ (mm/s)</th>
<th>$\Delta_{EQ}$ (mm/s)</th>
<th>$B_{HF}$ (T)</th>
<th>$\Gamma$ (mm/s)</th>
<th>Relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{0.6}$Fe$</em>{2.4}$O$_y$</td>
<td>0.35</td>
<td>0.04</td>
<td>Distribution</td>
<td>0.65</td>
<td>100</td>
</tr>
<tr>
<td>Cu$<em>{0.3}$Mn$</em>{0.3}$Fe$_{2.4}$O$_y$</td>
<td>0.34</td>
<td>1.02</td>
<td>-</td>
<td>0.47</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>0.32</td>
<td>0.58</td>
<td></td>
<td>0.45</td>
<td>55</td>
</tr>
<tr>
<td>Mn$<em>{0.6}$Fe$</em>{2.4}$O$_y$</td>
<td>0.32</td>
<td>1.11</td>
<td>-</td>
<td>0.56</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>0.31</td>
<td>0.61</td>
<td></td>
<td>0.56</td>
<td>66</td>
</tr>
</tbody>
</table>

* Isomer shift referred to $\alpha$-Fe metal.

Figure 5-22. Internal magnetic field distribution obtained from the best fit of the room temperature $^{57}$Fe Mössbauer spectrum of sample Cu$_{0.6}$Fe$_{2.4}$O$_y$.

The room-temperature Mössbauer spectra of the Mn-Cu-ferrites are shown in Figure 5-21. The three spectra were quite different, because of the magnetic characteristics of the Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrites, which are strongly dependent upon the size of the particles. The Mn-rich ferrite system (sample Mn$_{0.6}$Fe$_{2.4}$O$_y$) is characterized by a simple quadrupole split spectrum, which indicates the pure paramagnetic nature of the iron species in the solid. This
observation can be attributed to the presence of superparamagnetic ferrite nanoparticles with sizes below \( \sim 5 \) nm. Such superparamagnetic behavior at room temperature is rather common for nanosized iron oxides, and has already been reported for MnFe\(_2\)O\(_4\) nanoparticles by C. R. Alves et al\(^\text{148}\), among others. Due to relatively large experimental linewidth, the spectrum was fitted by two quadrupole doublets representing either tetrahedrally (A sites) or octahedrally (B sites) coordinated trivalent iron centres. No divalent iron seems to be present in the sample.

The sample with an equal amount of Mn and Cu atoms (Cu\(_{0.3}\)Mn\(_{0.3}\)Fe\(_{2.4}\)O\(_y\)) also shows a similar quadrupole split spectrum typical of trivalent iron undergoing superparamagnetic relaxation, in agreement with the results of magnetic studies.

The spectrum of the copper rich sample (Cu\(_{0.6}\)Fe\(_{2.4}\)O\(_y\)), on the other hand, is more complicated and shows the presence of two components in the fitting curve (a doublet and a sextet); it has the typical shape of iron oxides with a relatively large size (or magnetic domains size) distribution undergoing magnetic relaxation. The doublet component is derived from the superparamagnetic contribution of the sample; magnetization randomly changed under the effect of the temperature and only the effect of the electric field gradient at the nucleus is observed which gives rise to a doublet in the total spectra. Besides a doublet, a distribution of sextets is needed to fit the total spectra that derive from the larger ferromagnetic particles that are amorphous. In this case, the fit was performed using a distribution of Internal Magnetic Fields (Figure 5-22).

In summary, the \( \delta \) values(Table 5-5) for all three M-modified ferrites are in the range from 0.31 to 0.35 mm/s which indicates that all iron is in Fe\(^{3+}\) state. The small decrease in the isomer shift with an increase of Mn-content (from 0.35 to 0.31 mm/s) can be explained by the very slight decrease of the s-electron density at the \(^{57}\)Fe nuclei due to the decrease of Fe–O covalency\(^\text{149}\).
5.12. Magnetic measurements

RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M_{0.6}Fe_{2.4}O_y)

Zero-field-cooled (ZFC) magnetizations were measured by cooling the Cu_{0.6}Fe_{2.4}O_y, Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y, and Mn_{0.6}Fe_{2.4}O_y samples in a zero magnetic field and then increasing the temperature in a static field, while field-cooled (FC) curves were obtained by cooling the samples in the same static field. Figure 5-23 shows the temperature dependence of ZFC and FC magnetizations, measured with applied field of 50 Oe. The magnetic properties of the Mn_{0.6}Fe_{2.4}O_y and Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y samples are in a good agreement with previously discussed Mössbauer measurements and characteristic for superparamagnetic particles with blocking temperatures below room temperature. The blocking temperature (T_B), which can be estimated as the position of ZFC maximum, is a threshold temperature between the blocked and the superparamagnetic state whose characterization is closely dependent on the time scale of the measurement method used^{150}. In fact, for a particle system with a certain size, T_B is the temperature at which the relaxation time (t) equals the attempt time (t_m). The ZFC magnetization shows its maximum at ~82 K for Mn_{0.6}Fe_{2.4}O_y sample and at ~92 K for the Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y sample. However, for the copper rich ferrite (Cu_{0.6}Fe_{2.4}O_y) we have not yet reached the blocking temperature which is related to a larger particle size of the sample. This is in a good correlation with the XRD results discussed above (Paragraph 5.2).
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}\text{Fe}_{2.4}\text{O}_y$)

![Graph](image_url)

- $M_{0.6}\text{Fe}_{2.4}\text{O}_y$
- $M_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}\text{O}_y$
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y})

The magnetic properties of Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} spinel ferrites have been examined by isothermal magnetization hysteresis curve measurements at 300 K (Figure 5-24). The hysteresis curves of the Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} and Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} samples do not reach complete saturation even at 60 kOe. This is often observed in nanosized materials and can be a result of the spin disordered surface layer which requires a larger field to be saturated together with the concurrent effect of the small mean size of nanoparticles with not too high anisotropy which are still fast relaxing even at 60 kOe\textsuperscript{151}. On the contrary, for the Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} sample all particles are already blocked and almost completely oriented with a field of \(~50\) kOe. Table 5-6 gives the magnetic susceptibility values estimated for three ferrospinels (Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y}) using the Langevin function. For Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} and Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} samples CHI equals to 5.0\cdot10^{-4} and 2.5\cdot10^{-4} m\textsuperscript{3}kg\textsuperscript{-1} respectively. These values are about four orders of magnitude higher than those typically observed for paramagnetic materials (because magnetic moments of the grains are much larger than magnetic moments of the individual atoms), indicating that Mn-containing materials are in a superparamagnetic state compared to only Cu-ferrospinel. Such difference can be explained by partial substitution of Fe\textsuperscript{3+} cations with Mn\textsuperscript{2+}\textsuperscript{106} caused a disorder in the cation distribution between octahedral and...
tetrahedral sites which influence such fundamental magnetic properties as saturation magnetization, exchange couplings, and ferromagnetic ordering temperatures\textsuperscript{152}.

Table 5-6. Magnetic measurements results obtained on Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrites

<table>
<thead>
<tr>
<th>Sample</th>
<th>A Langevin</th>
<th>B Langevin</th>
<th>Temperature</th>
<th>Mu</th>
<th>n</th>
<th>CHI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>emu/g</td>
<td>A m\textsuperscript{2}kg\textsuperscript{-1}</td>
<td>A m\textsuperscript{3}kg\textsuperscript{-1}</td>
<td>K</td>
<td>A m\textsuperscript{2}kg\textsuperscript{-1}</td>
<td>m\textsuperscript{3}kg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>25.56</td>
<td>25.56</td>
<td>1.79E-03</td>
<td>300</td>
<td>5.90E+28</td>
<td>1.53E-02</td>
</tr>
<tr>
<td>Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>13.6</td>
<td>13.6</td>
<td>1.11E-04</td>
<td>300</td>
<td>3.66E+27</td>
<td>3.71E-04</td>
</tr>
<tr>
<td>Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}</td>
<td>9.952</td>
<td>9.952</td>
<td>7.45E-05</td>
<td>300</td>
<td>2.45E+27</td>
<td>2.47E-04</td>
</tr>
</tbody>
</table>

5.13. Temperature programmed reduction (TPR) study

![Figure 5-25. Degree of reduction (\(\alpha\)) vs temperature (T) for Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrites](image)
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M_{0.6}Fe_{2.4}O_y)

Figure 5-26. Degree of reduction (α) vs time (t) for Cu_{0.6-x}Mn_xFe_{2.4}O_y ferrites

Figure 5-25 shows α-versus-T reduction curves of Cu_{0.6-x}Mn_xFe_{2.4}O_y samples. The shape of this curve can reveal information on the reduction model of the solid, as discussed in details in PART I of the discussion (Paragraph 4.4). Increasing the temperature of the reduction markedly increased the reduction rate of all oxides regardless of the nature of incorporated metal M and this in turn can be justified by Arrhenius equation (exponential relation between K and T). However, looking at the plotted results for Cu-incorporated ferrites (Cu_{0.6}Fe_{2.4}O_y-red and Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y-blue) this produces an S-shaped (sigmoidal) curve which primarily was assigned as a “nucleation and autocatalytic reduction” model, when reduced metal formed in the early stages of reduction (Cu^{2+}→Cu^0) catalyzes the reduction by H_2 activation (H_2→H+H) which in turn facilitates the reduction of the whole system (details are in the Paragraph 4.4). In contrast to this, the plotted curve for Mn_{0.6}Fe_{2.4}O_y ferrite (Figure 5-25-green) is elongated and resembles more to an “egg-shell” reduction model, which is characterized by a total coverage of the solid oxide particle with a thin layer of newly formed product. Indeed, it appears that Mn_{0.6}Fe_{2.4}O_y sample reduces by a spontaneous nucleation over the entire surface immediately on contact with hydrogen that leads to the formation of the hardly reducible layer of Mn_{x}Fe_{y}O oxide (like an egg-shell). This elucidates the elongated shape of the reduction curve, since the initially formed compact
Mn₅Fe₃O layer may aggravate H₂ diffusion into the bulk (Figure 5-26) leading to starvation and decrease its reduction rate.

To summarize, TPR results indicate the reduction path of the Cu₀.₆Fe₂.₄O₉ and Cu₀.₃Mn₀.₃Fe₂.₄O₉ materials (Figure 5-25) goes through the formation of metallic copper (Cu⁰) which generates a high concentration of active hydrogen on the surface and promotes the reduction. In the case of Mn₀.₆Fe₂.₄O₉ nucleation occurs over entire surface immediately on the contact with hydrogen causing the formation of hardly reducible layer (in form of MnₓFeₙO) and at this point the reduction is controlled by the H₂-diffusion into the bulk.

Table 5-7 shows the integrated values of consumed H₂ and O₂ during TPR₁/TPO/TPR₂ experiments at 450°C. Since spinel ferrites may be used as a material for ‘pure hydrogen’ production, the combination of two techniques can provide useful information in the study of reactivity, redox behavior and cycling stability of the resulted ferrospinels. The important conclusion can be drawn: Cu₀.₆-xMₙFe₂.₄O₉ ferrospinels can be reduced (TPR₁), re-oxidized (TPO) and then re-reduced for the second time (TPR₂) with no significant loss in the activity (table, TPR₁/TPR₂~1). However, Cu-containing samples have shown a higher reduction extent in comparison to Mn₀.₆Fe₂.₄O₉ (Figure 5-26). The main reason for such behavior can be an accumulation of MnₓFeₙO phase in the catalyst, which has a high thermodynamic stability and as a consequence its scarce attitude towards the reduction to its metallic component. This result also has been confirmed by in-situ DRIFTS, ex-situ XRD studies and reactivity experiments with ethanol (discussed below).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Temperature, °C</th>
<th>TPR₁, cm³/g</th>
<th>TPO, cm³/g</th>
<th>TPR₂, cm³/g</th>
<th>TPR₁/TPR₂</th>
<th>Surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₀.₆Fe₂.₄O₉</td>
<td>450</td>
<td>115</td>
<td>56</td>
<td>108</td>
<td>1.06</td>
<td>72</td>
</tr>
<tr>
<td>Cu₀.₃Mn₀.₃Fe₂.₄O₉</td>
<td>450</td>
<td>98</td>
<td>40</td>
<td>91</td>
<td>1.07</td>
<td>131</td>
</tr>
<tr>
<td>Mn₀.₆Fe₂.₄O₉</td>
<td>450</td>
<td>66</td>
<td>31</td>
<td>58</td>
<td>1.14</td>
<td>157</td>
</tr>
</tbody>
</table>
5.14. Surface characterization: in-situ DRIFTS experiments

Figure 5-27 shows DRIFT spectra of Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrites. The spectrum on the bottom corresponds to the adsorption of ethanol at 30°C. According to the literature, ethanol adsorbs on the surface mainly as an ethoxide, formed from the scission of the O-H bond$^{95-99}$. Ethoxy bands (dissociative adsorption) over Cu$_{0.6}$Fe$_{2.4}$O$_y$ sample can be observed at 1062 and 1105 cm$^{-1}$ for the C-O/C-C stretching modes together with the bands of the undissociated ethanol (at 1383 cm$^{-1}$ and 1279 cm$^{-1}$ for CH$_3$δ and OHδ, respectively).$^{94,132}$ The complex absorption in the 2800-2400 cm$^{-1}$ region is due a Fermi resonance of the overtone of the OHδ vibration mode with the CH- stretching modes at 2970, 2926, and 2859 cm$^{-1}$ (CH$_3$(as), CH$_2$(as) and CH$_3$(s) modes of the ethoxide species).$^{97,94}$ The sharp band at 3683 cm$^{-1}$ together with a shoulder at 3636 cm$^{-1}$ is assigned to the –OH stretching vibration of chemisorbed undissociated ethanol over surface Lewis acid sites (M$^{n+}$).$^{133-135}$

Looking at the adsorption of ethanol at 30°C for Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ (B) and Mn$_{0.6}$Fe$_{2.4}$O$_y$ (C) ferrites, similar species are formed, with a slightly shifted position. Accordingly, the ethoxy bands observed at 1064/1107(B) and 1064/1104(C) cm$^{-1}$ for the C-O/C-C stretching modes together with the bands of the undissociated ethanol (at 1381(B) and 1384/1272(C) cm$^{-1}$ for CH$_3$δ/OHδ).$^{94,132}$ The CH- stretching modes detected at 2972/2927/2864(B) and 2973/2930/2871(C) cm$^{-1}$, were assigned as CH$_3$(as), CH$_2$(as) and CH$_3$(s) modes of the ethoxide species.$^{97,94}$ The sharp band centered at 3685(B) and 3681(C) cm$^{-1}$ is assigned to the –OH stretching of chemisorbed undissociated ethanol, however in contrast to the Cu$_{0.6}$Fe$_{2.4}$O$_y$ sample, the shoulder at lower frequency is not well resolved (for Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$) due to the broadening of the main peak with a complete disappearance for Mn$_{0.6}$Fe$_{2.4}$O$_y$ ferrite (the effect of Mn-incorporation)$^{106}$. 

---

RESULTS AND DISCUSSION, PART II: **TYPE II SPINELS (M$_{0.6}$Fe$_{2.4}$O$_y$)** 173
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_4$)
Some remarkable differences between the DRIFTS spectra of Cu-, Cu-Mn- and Mn-modified ferrites are observed with increasing the temperature from 30-400°C, which is related to the surface chemistry of each compound. Acetate bands (T-200°C) over Cu$_{0.6}$Fe$_{2.4}$O$_y$ (A) and Cu$_{0.6}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ (B) (Figure 5-27 - A, B) samples appear at 1333/1440/1577 cm$^{-1}$ (for the CH$_3$δ, OCOν(s), and OCOν(as) vibrations, respectively). The broadening of the band at 1577/1582 cm$^{-1}$ and the apparent complexity of both main components suggest that carbonate species, responsible for bands in the same region, should also form. These species could further produce CO$_2$, which is detected as the doublet at the 2363-2333 cm$^{-1}$ region and corresponds to adsorbed and/or gaseous CO$_2$ rotation vibration P and R bands. Moreover, a new band at 1262(A) and 1249(B) cm$^{-1}$ is observed (for Cu-containing samples only) at higher temperature (T-400°C) and has been attributed to aldehyde adsorbed in η$^2$ configuration. The DRIFT spectra obtained over the Mn$_{0.6}$Fe$_{2.4}$O$_y$ sample (Figure 5-27, C), also exhibited the bands for acetate species, formed by the reaction of ethoxy species with surface oxygen (1598, 1555, 1433 and 1334 cm$^{-1}$). When the temperature was increased (up to 400°C) the intensity of the bands corresponding to ethoxy species was reduced, whereas the bands associated with acetate species were strongly bounded to the surface and remained practically unchanged.
However, the main difference between the spectra of $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y$ and other Cu- and Cu-Mn-modified ferrites spectra lies in the absence of the bands associated with carbonate species, as well as the band of the adsorbed linear $\text{CO}_2$ was not observed. Thus, the results may indicate that Cu- and Cu-Mn-modified ferrite systems were more “reactive” than the Mn-modified ferrite sample. This is also followed by the presence of a broad absorbed feature in the 3000-1800 cm$^{-1}$ region, which is attributed to the electronic absorption of the partially reduced sample $^{94,139}$.

### 5.15. Ex-situ XRD study of the reduced samples

![Figure 5-28. Stepwise reduction of $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y$ ferrite with ethanol](image)

**Table 5-8. Rietveld refinement of $\text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y$ ferrite after stepwise reduction with ethanol**

<table>
<thead>
<tr>
<th>Reduction time, min</th>
<th>Phase composition</th>
<th>Degree of reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Spinel 95.38%</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>$\text{Mn}_x\text{Fe}_y\text{O}$ 7.55%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Spinel 87.47%</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>$\text{Mn}_x\text{Fe}_y\text{O}$ 12.53%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Spinel 80.53%</td>
<td>5</td>
</tr>
</tbody>
</table>
The evolution of a phase composition of the Mn$_{0.6}$Fe$_{2.4}$O$_y$ sample was studied by means of XRD using ex-situ approach, which is the most suitable one for a deep understanding of the results obtained on the laboratory-scale plant. Figure 5-28 shows XRD patterns obtained after 1, 3, 5 and 20 min of ethanol exposure over Mn$_{0.6}$Fe$_{2.4}$O$_y$ ferrospinel. Table 5-8 summarizes obtained results using Rietveld refinement. The data clearly indicate that after feeding ethanol for 1 min the formation of a new Mn$_x$Fe$_y$O phase (app. 7%$_w$) was observed. With increasing the reduction time from 1 to 20 min the spinel relative ratio continued decreasing whereas that of the Mn$_x$Fe$_y$O increased without the appearance of other phases. This apparently shows that the reduction of the Mn$_{0.6}$Fe$_{2.4}$O$_y$ goes through the formation of Mn$_x$Fe$_y$O phase, which is an important proof of the previously discussed TPR results where we proposed the reduction mechanism which goes through the formation of hardly reducible layer of Mn$_x$Fe$_y$O oxide.

A further investigation of the Cu- and Cu/Mn-incorporated ferrites are reported in Table 5-9. Rietveld refinement of the XRD patterns has been done for the samples Cu$_{0.6}$Fe$_{2.4}$O$_y$, Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ and Mn$_{0.6}$Fe$_{2.4}$O$_y$. It worth noting, that an addition of Cu$^{2+}$ ions strongly affects its redox properties (detailed discussion in Paragraph 5.4) which in turn determines the reduction mechanism and, as a consequence, the phases which are formed during the reduction step. According to the previously discussed TPR results and ex-situ XRD studies of the TYPE I ferrospinels, the reduction of Cu-containing samples goes through the formation of metallic Cu$_0$ with further autocatalytic reduction evolution of newly reformed Fe-enriched spinel (with generic formula - Mn$_{0.6-x}$Fe$_{2.4+x}$O$_y$). From the obtained results, it is clear that the reduction of Cu$_{0.6}$Fe$_{2.4}$O$_y$ and Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ samples does not go through the formation of Mn$_x$Fe$_y$O oxide, which acts as a shielding layer and prevents a deep reduction of the following ferrite to its metallic component. Phases detected after 20 min of ethanol exposure over Cu$_{0.6}$Fe$_{2.4}$O$_y$ and Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ were identified as follows: spinel- 4.84 %$_w$,
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y})

Cu\textsuperscript{0} -14.7 \%\textsubscript{w}, Fe -0.7 \%\textsubscript{w}, Fe\textsubscript{3}C-52.0 \%\textsubscript{w} and Fe\textsubscript{5}C\textsubscript{2}-27.76 \%\textsubscript{w} and spinel-48.40 \%\textsubscript{w}, Fe\textsubscript{5}C\textsubscript{2}-44.59 \%\textsubscript{w}, Fe\textsubscript{3}C-7.01\%\textsubscript{w}, respectively. The absence of Mn\textsubscript{x}Fe\textsubscript{y}O in these two samples makes it possible to clarify the main difference in the reduction paths of Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrites. Since metallic Cu\textsuperscript{0} was one of the formed phases in Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}, we can suggest that its reduction goes through the formation of metallic copper (Cu\textsuperscript{0}) which generates a high concentration of active sites on the surface and promotes a further deep reduction to iron carbides: Fe\textsubscript{3}C and Fe\textsubscript{5}C\textsubscript{2}. Moreover, despite that we could not quantify Cu\textsuperscript{0} phase in the case of Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} (it should be recall that X-ray diffraction is not extremely sensitive and app. 5% of a new phase could easily not be detected, since Cu content is twice lower), the presence of iron carbides enables us to assume that this sample follows the same reduction path as only Cu-containing one or has a mixed character, since a small amount of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} (as a component of the Mn\textsubscript{x}(Fe\textsuperscript{2+},Fe\textsuperscript{3+})\textsubscript{y}O\textsubscript{x+y} phase) nevertheless is present in the sample and was detected with a help of Mössbauer spectroscopy (see Paragraph 5.16). However, in the case of Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} the nucleation occurs over entire surface immediately on the contact with ethanol causing the formation of hardly reducible layer (in form of Mn\textsubscript{x}Fe\textsubscript{y}O) and at this point the reduction is controlled by the ethanol-diffusion into the bulk, since Mn\textsubscript{x}Fe\textsubscript{y}O acts as a core-catalyst of the newly reformed material.

Moreover, in Table 5-9 are listed values of the reduction degree (after 20 min of reduction time) for the Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrites calculated on the basis of Rietveld refinement data. Even though the highest surface area was shown by Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} catalyst (SSA values of the fresh samples reported in Paragraph 5.2), and it declined with an increase of Cu-content, the samples which contain copper cations (Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} and Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y}) reached higher reduction extent (about 98 and 59%, respectively) in comparison to only Mn-modified ferrospinel (with just 16%). The similar trends were obtained from elaborated TPR results. This suggests that the difference in the reducibility of the resulted M-modified ferrospinels is related to the nature of the incorporated M cation and its intrinsic reactivity.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M_{0.6}Fe_{2.4}O_{4})
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS ($M_{0.6}Fe_{2.4}O_y$)

**Figure 5-29.** Rietveld refinement of XRD patterns taken after 20 min of reduction with ethanol over $Cu_{0.6}Fe_{2.4}O_y$, $Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y$, and $Mn_{0.6}Fe_{2.4}O_y$ ferrites.

**Table 5-9.** Rietveld refinement data of $Cu_{0.6-x}Mn_xFe_{2.4}O_y$ ferrites after 20 min reduction with ethanol.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Degree of reduction, %</th>
<th>Formed phases during ethanol reduction for 20 min, %&lt;sub&gt;wt&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Mn_{0.6}Fe_{2.4}O_y$</td>
<td>16</td>
<td>SPINEL – 35.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Mn_xFe_yO$ – 64.5</td>
</tr>
<tr>
<td>$Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y$</td>
<td>59</td>
<td>SPINEL – 48.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Fe_5C_2$ – 44.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Fe_3C$ – 7.0</td>
</tr>
<tr>
<td>$Cu_{0.6}Fe_{2.4}O_y$</td>
<td>98</td>
<td>SPINEL – 4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Cu$ – 14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Fe$ – 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Fe_3C$ – 52.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Fe_5C_2$ – 27.8</td>
</tr>
</tbody>
</table>
5.16. Mössbauer study of the reduced samples

\[ \text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_y, 20 \text{ min ethOH} \]

\[ \text{Cu}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}\text{O}_y, 20 \text{ min ethOH} \]
RESULTS AND DISCUSSION, PART II:

Figure 5-30. Mössbauer spectra of Cu$_{0.6}$Mn$_x$Fe$_{2.4}$O$_y$ ferrites taken after 20 min of ethanol reduction

Mössbauer spectra of the Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrites after reduction with ethanol at 450°C (20 min) were taken in order to proof the differences in the phase composition discussed previously (Paragraph 5.15). Experimental data and Lorentzian functions, used for the fitting of the spectra for three examined samples, are reported in the following pages.

Figure 5-30 shows Mössbauer spectra of Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ samples. In the Table 5-10 are listed hyperfine parameters derived from the fitting of the corresponding experimental results. The spectrum of Cu$_{0.6}$Fe$_{2.4}$O$_y$ ferrite was fitted with 4 sextets. The first sextet is characterized by an $\delta$ equal to 0.3 mm/s and an Internal magnetic field (H) of 48.7 T with a contribution of only 3%$_{at}$ to the total spectral area; and it was assigned to $T_d$ coordinated Fe$^{3+}$ in the remained re-formed spinel (with generic formula of Cu$_{0.6}$Fe$_{2.4+x}$O$_y$). The other 3 sextets correspond to the two iron carbides (Fe$_5$C-cementite and Fe$_5$C$_2$-Hagg carbide), formed during the reduction process. The best fit of the experimental spectrum was obtained with two sextets for Fe$_5$C$_2$, one sextet for Fe$_5$C and the one shared sextet for (Fe$_5$C$_2$+Fe$_5$C). The obtained parameters of the corresponding sextets are in a good agreement with reported literature$^{122-124}$. The large contribution of the iron carbides phase
(Fe\textsubscript{3}C+Fe\textsubscript{5}C\textsubscript{2} \sim 97%), as was previously detected by XRD, once again reaffirms that a deep reduction of the M-ferrites (Co, Cu, Ni and Fe\textsuperscript{126,101,129} leads to the formation of Fe\textsubscript{6}C\textsubscript{γ} phase.

The experimental spectrum of Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} with its best fits is shown in Figure 5-30. Two doublets and eight sextets are used to fit the room temperature Mössbauer spectra of the sample. Spinel component (55\%\textsubscript{at}) with generic formula: Cu\textsubscript{0.3-x}Mn\textsubscript{0.3-z}Fe\textsubscript{2.4+x+z}O\textsubscript{y} composed of 5 sextets; and each one of these sextets correspond to a given environment for the ferric cations in the ferrite compound referred to a different Fe\textsuperscript{3+} in the structure, in accordance with Sawatzky et al\textsuperscript{153,154}. Another 3 sextets are similar to those discussed above and were attributed to the existence of a relatively high amount of Fe\textsubscript{6}C\textsubscript{γ} phase (Fe\textsubscript{3}C+Fe\textsubscript{5}C\textsubscript{2} \sim 35\%\textsubscript{at}). Remaining two doublets (10\%\textsubscript{at}) which represent ferric (Fe\textsuperscript{3+}) and ferrous (Fe\textsuperscript{2+}) iron oxides characterized by an \(\delta\): Fe\textsuperscript{2+} - 0.85 mm/s; Fe\textsuperscript{3+} - 0.26 mm/s and a \(\Delta\): Fe\textsuperscript{2+} - 1.13 mm/s; Fe\textsuperscript{3+} - 0.92 mm/s and were attributed to the presence of the Mn\textsubscript{x}Fe\textsubscript{γ}O solid solution (a small amount of Fe\textsuperscript{3+} in FeO was also seen by Johnson\textsuperscript{125}). Eventually, obtained results are indicating an incomplete reduction of the Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} ferrite which assumed to be a direct result of Mn-incorporation (leading to the formation scarcely reducible phase - Mn\textsubscript{x}Fe\textsubscript{γ}O).

The last spectrum corresponds to the Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} sample; it reveals information on the reduction path and contribution of Mn-cations to the whole reduction process. The spectrum was fitted with 2 sextets and 2 doublets. The two doublets (60\%\textsubscript{at}) attributed to the same ferric (Fe\textsuperscript{3+}) and ferrous (Fe\textsuperscript{2+}) iron oxides as detected in Cu\textsubscript{0.3}Mn\textsubscript{0.3}Fe\textsubscript{2.4}O\textsubscript{y} sample (\(\delta\): Fe\textsuperscript{2+} - 1.02 mm/s; Fe\textsuperscript{3+} - 0.27 mm/s and a \(\Delta\): Fe\textsuperscript{2+} - 0.75 mm/s; Fe\textsuperscript{3+} - 0.79 mm/s. Remaining two sextets are used to fit Fe\textsuperscript{3+} ions in T\textsubscript{d} (\(\delta\)-0.27 mm/s and H-48.5 T) and O\textsubscript{h} (\(\delta\)-0.54 mm/s and H-45.0 T) sites of the reformed spinel phase. From the obtained results, it is clear that the reduction of Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} samples follows a different reduction path which goes through the formation of only two thermodynamically stable phases: Mn\textsubscript{0.6-x}Fe\textsubscript{2.4+x}O\textsubscript{4} and Mn\textsubscript{x}Fe\textsubscript{γ}O. This results support the information obtained from TPR, in-situ DRIFT and ex-situ XRD studies (discussed above).
Table 5-10. Hyperfine parameters derived from the fitting of the Mössbauer spectra

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>δ</th>
<th>Δ</th>
<th>H</th>
<th>Rel. Int.</th>
<th>Phase name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mm/s)</td>
<td>(mm/s)</td>
<td>(T)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₀.₆Fe₂.₄O₂⁺ after 20 min reduction</td>
<td>0.30</td>
<td>0.00</td>
<td>48.7₉(Td)³</td>
<td>spinel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.00</td>
<td>11.2₉(I)⁹</td>
<td>Fe₃C₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.00</td>
<td>18.8₉(II)¹²</td>
<td>Fe₅C₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.0020.₆₉(III+I)⁷⁶</td>
<td>Fe₃C₂ + Fe₅C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₀.₃Mn₀.₃Fe₂.₄O₂⁺ after 20 min reduction</td>
<td>0.34</td>
<td>49.2</td>
<td>12</td>
<td>spinel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>48.0</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>46.0</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>43.6</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>39.8</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>20.₅₉(III+I)²⁷</td>
<td>Fe₃C + Fe₅C₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>18.₆₉(I)³</td>
<td>Fe₅C₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>11.₀₉(II)⁵</td>
<td>Fe₅C₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>1.₁₃</td>
<td>-</td>
<td>Fe²⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>0.₉₂</td>
<td>-</td>
<td>Fe³⁺</td>
<td></td>
</tr>
<tr>
<td>Mn₀.₆Fe₂.₄O₂⁺ after 20 min reduction</td>
<td>0.₅₄</td>
<td>4₅.₀₉(Oh)²₄</td>
<td>spinel</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.₂₇</td>
<td>4₈.₅₉(Td)¹₆</td>
<td>Fe²⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.₀₂</td>
<td>0.₇₅</td>
<td>-</td>
<td>Fe³⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.₂₇</td>
<td>0.₇₉</td>
<td>-</td>
<td>Fe³⁺</td>
<td></td>
</tr>
</tbody>
</table>

To finalize the Mössbauer study, it is worth noting that: the reduction of the Cu₀.₆Fe₂.₄O₂⁺ and Cu₀.₃Mn₀.₃Fe₂.₄O₂⁺ ferrites have the same nature and goes through the formation of metallic copper (Cu⁰) which generates a high concentration of the active sites on the surface and promotes a very deep reduction of the corresponding ferrites. In turn, this results in the formation of the iron carbides (FeₓCᵧ) as the main phase of the reduction process. However, in the reduced Cu₀.₃Mn₀.₃Fe₂.₄O₂⁺ sample apart of the FeₓCᵧ phase, the ferric (Fe³⁺) and ferrous (Fe²⁺) iron oxides are also present in a small amount, which may indicate a mixed
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y})

The reduction character of the following ferrite, which is explained by the presence of Mn-ions (formation of wurstite-like Mn\textsubscript{x}Fe\textsubscript{y}O oxide solid solution). On the other hand, the reduction of Mn\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} occurs over entire surface immediately on the contact with ethanol causing the formation of a hardly reducible layer and at this point the reduction is controlled by the ethanol-diffusion into the bulk, since Mn\textsubscript{x}Fe\textsubscript{y}O may act as a shell-catalyst resulting in a decrease of total reduction of the remained Fe-rich spinel.

5.17. Reactivity tests: Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} system

This section includes discussion of the results obtained over Cu\textsubscript{0.6-x}Mn\textsubscript{x}Fe\textsubscript{2.4}O\textsubscript{y} ferrospinels tested on the laboratory-scale plant. The scale is limited to 1 cycle of 20 min (20 min reduction followed by 20 min re-oxidation). The cycling time was chosen according to the results reported by Trevisanut and et al.\textsuperscript{129,126}.

1\textsuperscript{st} step: 20 min reduction with ethanol

![Figure 5-31. Conversion and yields for the main products during 20 min reduction with ethanol at 450°C over Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y}](image)

Figure 5-31 to Figure 5-33 show conversion and yields for the main products (yield >5%), obtained during the ethanol reduction at 450°C for 20 min. Cu\textsubscript{0.6}Fe\textsubscript{2.4}O\textsubscript{y} ferrite (Figure 5-31) starting from the first minutes of the reaction showed 97% of conversion followed by its decrease down to 95%, while the extent of spinel reduction increased (from 0 to 95%,
One of the main products of ethanol conversion was hydrogen, with an initial yield of about 61%, which increased up to 83%. In addition, CO shows the same increasing trend as for H₂, starting from 14 till 24%. Looking at CO₂ and H₂O profiles, one may notice a similar decreasing trend (starting yields: CO₂-27% and H₂O-10%, final yields: CO₂-22% and H₂O-1%) with its max yields (34 and 13%, respectively) at about 6 min of reduction time. According to the obtained results we suggest that the main reactions during spinel reduction involved the partial and total oxidation of ethanol:

1. \[ C_2H_5OH + MeO_x \rightarrow 2 \text{CO} + 3 \text{H}_2 + \text{MeO}_{(x-1)} \]
2. \[ C_2H_5OH + 3 \text{MeO}_x \rightarrow 2 \text{CO}_2 + 3 \text{H}_2 + 3 \text{MeO}_{(x-1)} \]
3. \[ C_2H_5OH + 6 \text{MeO}_x \rightarrow 2 \text{CO}_2 + 3 \text{H}_2 \text{O} + 6 \text{MeO}_{(x-1)} \]

In addition, the formation of water involves several possible reactions:

4. \[ \text{H}_2 + \text{MeO} \rightarrow \text{H}_2\text{O} + \text{Me} \]
5. \[ C_2H_5OH \rightarrow 2 \text{C} + 2 \text{H}_2 + \text{H}_2\text{O} \]

Acetone formation, which declined with time (from 32 to 4%), can be a result of an aldol condensation of the intermediately formed acetaldehyde, with further isomerization of aldol into hydroxyketone followed by a reverse reaction to form acetone and formaldehyde (converted into CO and H₂). Either, as recently proposed by Rodrigues et al., by ketonization of carboxylates (acetates) which are obtained by dehydrogenation of this alcohol followed by oxidation. In fact, the formation of acetates over all M₀.₆Fe₂.₄O₇ samples was confirmed by DRIFTS study (discussed in the Paragraphs 5.6 and 5.14).

Increasing yields for acetaldehyde (from 1 to 6%) together with hydrogen (from 61 to 83%) on the instantaneously reducing Cu₀.₆Fe₂.₄O₇ sample, indicates that dehydrogenation/deoxyhydrogenation of ethanol also occurred:

6. \[ C_2H_5OH \rightarrow C_2H_4O + \text{H}_2 \]
7. \[ C_2H_5OH + \text{MeO}_x \rightarrow C_2H_4O + \text{H}_2\text{O} + \text{Me} \]

Coke and heavy compounds (mainly aromatics) are formed at the very beginning of the reaction time (~18%), with a progressive increase in yield (to 34%). The generation of coke was likely due to dehydrogenation and total deoxygenation of ethanol:
RESULTS AND DISCUSSION, PART II: TYPE I SPINELS (M$_{0.6}$Fe$_{2.4}$O$_y$)

(8) $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C} + \text{CO} + 3 \text{H}_2$

(9) $\text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{C} + \text{H}_2\text{O} + 2 \text{H}_2$

Moreover, a disproportionation of CO (Boudouard reaction) can also lead to a coke deposition:

(10) $2 \text{CO} \rightarrow \text{CO}_2 + \text{C}$

Looking at the conversion and yields evolution over Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ ferrite (Figure 5-32), the results demonstrate similar trends in the products distribution and, as a consequence, a similar reduction path which involves the same set of reactions (eq. 1 to 10). The reduction of Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ sample started with 89% of ethanol conversion which approached to 95% after 20 min of reduction time. As for the previously discussed ferrite, hydrogen was one of the main products of ethanol conversion, with the following increasing trend: from 49 to 62%. Also, CO and CO$_2$ have similar increasing trends as for H$_2$, thus suggesting that the main reactions during spinel reduction involved the partial/total oxidation of ethanol (eq.1-3).

![Figure 5-32. Conversion and yields for the main products during 20 min reduction with ethanol at 450°C over Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$.](image)

**Figure 5-32.** Conversion and yields for the main products during 20 min reduction with ethanol at 450°C over Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$. 

---

187
The presence of \( \text{H}_2\text{O} \) at the very beginning of the reduction time (from 1 to 5\%) results from the reactions (eq. 3-5, 8). Acetaldehyde was observed in a small amount (app. 3\%). However, yields for the acetone were much higher (increasing in a range: from 46 to 29\%) in comparison to \( \text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_y \) ferrite. The overall reaction for the formation of acetone from acetaldehyde may be expressed as follows:

\[
(11) \quad 2 \text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2 + 2 \text{H}_2\text{O}
\]

Coke and heavy compounds (mainly aromatics) are also formed, however in a reasonably small amount (compare to only Cu-incorporated ferrite the values are twice smaller: from 10 to 18\%).

![Graph showing conversion and yields for main products during 20 min reduction with ethanol at 450°C over \( \text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y \)]

Results obtained with the \( \text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y \) sample (Figure 5-33) demonstrate different trends in the products distribution, with the instantaneously decreasing conversion and decreasing yields of the formed products. According to the XRD and Mössbauer results (discussed previously), the reduction of this sample goes through the formation of two phases: re-formed spinel (\( \text{Mn}_{0.6-x}\text{Fe}_{2.4+x}\text{O}_4 \)) and Mn/Fe solid solution (\( \text{Mn}_x\text{Fe}_y\text{O} \)). Thus, we should take into account this information. A significant decrease of the conversion (from 100 to 83\%)
over Mn$_{0.6}$Fe$_{2.4}$O$_y$ sample is attributed to an accumulation of Mn$_x$Fe$_y$O phase in the catalyst, which has a high thermodynamic stability and, as a consequence, its scarce attitude towards the reduction to the metallic component. Moreover, it also explains the decrease in yields (since conversion $\downarrow$) for the main products: H$_2$ (from 59 to 42%), CO$_2$ (24-13%), CO (6 to 5%), H$_2$O (0 to 4%), acetaldehyde (from 0 to 5%) and acetone (49-31%). However, the formation of acetone directly from ethanol is not excluded, especially in the case of Mn$_{0.6}$Fe$_{2.4}$O$_y$ (formed Mn$_x$Fe$_y$O acts as a catalyst; it worth noting that MnO may catalyze the direct transformation: ethanol $\rightarrow$ acetone, as was reported by Dolgychand et al$^{155}$). Coke and heavy compounds were formed in a small amount (9 to 11%).

![Coke and heavy compounds](image)

**Figure 5-34. Integrated selectivity to coke**

As discussed above, we could not completely avoid the coke formation (in Figure 5-34 are plotted integrated selectivity for Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ ferrites), but despite this, we were able to significantly reduce its amount by changing the composition of the catalyst (see CHNS results below). Indeed, the presence of Mn had a beneficial effect of decreasing the coke deposition, which is an important issue in order to produce C-free hydrogen. The integrated yields for the other products formed in minor quantities during 20 min of reduction with ethanol are plotted in Figure 5-35.
RESULTS AND DISCUSSION, PART II: TYPE II SPINELS (M₀.₆Fe₂.₄O₄)

In the Figure 5-36 are shown values of the reduction extent for the Cu₀.₆ₓMnₓFe₂.₄O₄ ferrites, as calculated on the basis of Rietveld refinement results. Even though the highest surface area was shown by Mn₀.₆Fe₂.₄O₄ catalyst, and it declined with an increase of Cu-content, the samples which contain copper cations (Cu₀.₆Fe₂.₄O₄ and Cu₀.₃Mn₀.₃Fe₂.₄O₄) reached higher reduction extent (about 98 and 59%, respectively) in comparison to only Mn-modified ferrospinel (with just 16%). The similar trends were obtained from elaborated TPR results. This suggests that the difference in the reducibility of the resulted M-modified ferrospinels is related to the nature of the incorporated M cation and its intrinsic reactivity.
2\textsuperscript{nd} step: 20 min re-oxidation with water

After the reduction with ethanol, the materials were re-oxidized with steam at 450°C, which corresponds to the second step of the chemical loop. Tests were carried out on the same apparatus used for the reduction step, feeding water by means of a syringe pump at 450°C, for 20min, after the reduction step. The gas mixture out flowing from the reactor was first passed through a water trap, in order to avoid a higher water concentration which could be harmful for the micro-GC columns. The analytical method used allowed us to carry out an analysis every few minutes. Reaction conditions are detailed in Paragraph 2.11.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>H₂</th>
<th>CO₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₀.₆MnFe₂₀₂₄O₄</td>
<td>51</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>Cu₀.₆Mn₃Fe₂₀₂₄O₄</td>
<td>19</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>Mn₀.₆Fe₂₀₂₄O₄</td>
<td>7</td>
<td>0.8</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Figure 5-37. Integrated yields for H₂, CO₂ and CO produced during the 2\textsuperscript{nd} re-oxidation step with steam at 450°C over Cu₀.₆₄Mn₃Fe₂₀₂₄O₄ ferrites
Figure 5-38 reports the yield of H₂, CO₂ and CO versus time (yields have been calculated based on the H or O content in products, with respect to the water fed – described in Paragraph 2.11), whereas Figure 5-37 reports the overall yields to H₂, CO and CO₂, integrated over the 20 min oxidation time. It is important to notice, that the increasing trends (within 0-5 min) shown in Figure 5-38 for Cu₀.₆Fe₂.₄O₄ and Cu₀.₂Mn₀.₄Fe₂.₄O₄ samples, most probably arise from the following fact: the stream, containing unconverted steam and products, needs a few minutes to reach the catalyst and then the on-line GC apparatus after
the start-up of the reaction. A common behavior for all three samples was a complete re-oxidation of the material in the chosen timeframe - app. in 20 min.

High hydrogen yield (51%) was detected for Cu$_{0.6}$Fe$_{2.4}$O$_y$ sample; whereas a lower amount of hydrogen produced during the re-oxidation process was obtained over Mn-incorporated samples: Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ (19%) and Mn$_{0.6}$Fe$_{2.4}$O$_y$ (7%) ferrites. This can be explained, taking into account the values of the reduction extent, calculated on the basis of Rietveld refinement: Cu$_{0.6}$Fe$_{2.4}$O$_y$ and Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ reached a higher reduction extent (about 98 and 59%, respectively) in comparison to only Mn-modified ferrospinel (with just 16%). Apart of produced hydrogen, the common feature for all the samples was the formation of CO and CO$_2$ during the re-oxidation step (Figure 5-37 and Figure 5-38), because of the gasification of carbonaceous residues, previously formed during the reduction step. The main reactions occur during re-oxidation process are defined as following:

\[(12) \text{Me} + \text{H}_2\text{O} \rightarrow \text{MeO} + \text{H}_2\]

\[(13) 3 \text{MeO} + \text{H}_2\text{O} \rightarrow \text{Me}_3\text{O}_4 + \text{H}_2\]

\[(14) \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\]

\[(15) \text{C} + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}_2\]

The main difference was in the amount of produced CO$_x$. According to the obtained results, Mn-containing catalysts produced less CO$_x$ which resulted from a lower amount of deposited carbon during the reduction step (results on the carbon content are summarized in Table 5-11, see CHNS analysis).

**Determination of carbon content (CHNS analysis)**

In order to evaluate the amount of coke formed during the reduction step with ethanol (within 20 min), an elemental analysis (CHNS) on the different materials was carried out. Table 5-11 summarizes the results of CHNS analysis over Cu$_{0.6}$Fe$_{2.4}$O$_y$ ferrospinel. According to the obtained results, the highest amount of coke accumulated during the ethanol reduction was detected over Cu$_{0.6}$Fe$_{2.4}$O$_y$ sample and it declines with Mn-incorporation (Cu$_{0.6}$Fe$_{2.4}$O$_y$>Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$>Mn$_{0.6}$Fe$_{2.4}$O$_y$). Such trend: ↑coke with ↑Cu-incorporation, confirms previously discussed values of coke accumulation, calculated on the basis of GC analysis (integrated yields: Cu$_{0.6}$Fe$_{2.4}$O$_y$- 32%>Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$- 15%>Mn$_{0.6}$Fe$_{2.4}$O$_y$ - 13%).
Table 5-11. CHNS results over Cu<sub>0.6-x</sub>Mn<sub>x</sub>Fe<sub>2.4</sub>O<sub>y</sub> ferrites after 20 min reduction

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>C content(%) after 20 min of reduction (ethanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn&lt;sub&gt;0.6&lt;/sub&gt;Fe&lt;sub&gt;2.4&lt;/sub&gt;O&lt;sub&gt;y&lt;/sub&gt;</td>
<td>2.2</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.3&lt;/sub&gt;Mn&lt;sub&gt;0.3&lt;/sub&gt;Fe&lt;sub&gt;2.4&lt;/sub&gt;O&lt;sub&gt;y&lt;/sub&gt;</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.6&lt;/sub&gt;Fe&lt;sub&gt;2.4&lt;/sub&gt;O&lt;sub&gt;y&lt;/sub&gt;</td>
<td>9.8</td>
</tr>
</tbody>
</table>

5.18. Conclusions on the study of Cu<sub>0.6-x</sub>Mn<sub>x</sub>Fe<sub>2.4</sub>O<sub>y</sub> system

The chemical-loop reforming of ethanol for H<sub>2</sub> production was studied by using Cu<sub>0.6-x</sub>Mn<sub>x</sub>Fe<sub>2.4</sub>O<sub>y</sub> ferrospinel as ionic oxygen carrier materials. The magnetic properties of Cu/Mn-modified ferrites, prepared via co-precipitation method, were examined by mean of Magnetic Study and Mössbauer Spectroscopy. According to the Mössbauer results, Cu<sub>0.3</sub>Mn<sub>0.3</sub>Fe<sub>2.4</sub>O<sub>y</sub> and Mn<sub>0.6</sub>Fe<sub>2.4</sub>O<sub>y</sub> samples are characterized by doublet-like spectra which arises due to the effect of the electric field gradient at the nucleus. This observation was explained by the presence of superparamagnetic ferrite nanoparticles with sizes below ~5 nm. A characteristic feature of superparamagnetic nanoparticles was confirmed by Magnetic Measurements: the CHI values estimated for three ferrospinel (Cu<sub>0.6-x</sub>Mn<sub>x</sub>Fe<sub>2.4</sub>O<sub>y</sub>) have shown that Cu<sub>0.3</sub>Mn<sub>0.3</sub>Fe<sub>2.4</sub>O<sub>y</sub> and Mn<sub>0.6</sub>Fe<sub>2.4</sub>O<sub>y</sub> materials are in the superparamagnetic state compared to only Cu-ferrospinel. This effect was correlated with the increase of Mn-incorporation and attributed to a disorder in the cation distribution between O<sub>h</sub> and T<sub>d</sub> sites, caused by a partial substitution of Fe<sup>3+</sup> cations with Mn<sup>2+</sup>ions.

The redox properties of ferrospinel were found to depend strongly on the nature of incorporated cation in addition to its distribution inside the crystal lattice. On this basis, the reduction of Cu<sub>0.6-x</sub>Mn<sub>x</sub>Fe<sub>2.4</sub>O<sub>y</sub> ferrites is further complicated and proceeds through the concurrent reactions of instantaneously formed new reduced phases until the system reaches its ‘steady state’ at these reaction conditions. Study of the H<sub>2</sub>-reduction curves (α- versus-T) brought us to an important conclusion on the reduction paths of the samples: the Cu<sub>0.6</sub>Fe<sub>2.4</sub>O<sub>y</sub> and Cu<sub>0.3</sub>Mn<sub>0.3</sub>Fe<sub>2.4</sub>O<sub>y</sub> materials reduces through the formation of metallic copper (Cu<sup>0</sup>) which generates a high concentration of active hydrogen on the surface and
promotes the reduction, so called “autocatalytic” model. In the case of Mn$_{0.6}$Fe$_{2.4}$O$_y$ nucleation occurs over entire surface immediately on the contact with hydrogen causing the formation of hardly reducible layer (in the form of Mn$_x$Fe$_y$O) and at this point the reduction is controlled by the H$_2$-diffusion into the bulk, as in the “egg-shell” model.

Apart of H$_2$-reduction, the particular interest represented also the reduction behavior of Cu$_{0.6-x}$Mn$_x$Fe$_{2.4}$O$_y$ samples using ethanol as a probe molecule (as a 1st step of the chemical-loop process). In-situ DRIFTS study was performed in order to follow the stepwise reduction of the catalyst surface, which allowed us to detect different adsorbed species and their transformation into the products. Acetates and carbonates appeared to be important surface intermediates over Cu- and mixed Cu-Mn- ferrospinel and in the case of the only Mn-containing catalyst, there was no evidence of the carbonates formation.

The evolution of a phase composition of the Mn$_{0.6}$Fe$_{2.4}$O$_y$ sample was studied by mean of XRD using ex-situ approach. The data clearly indicated that after feeding ethanol for 1 min the formation of a new Mn$_x$Fe$_y$O phase (app. 7%) was observed. With increasing the reduction time from 1 to 20 min the spinel relative ratio continued decreasing whereas that of the Mn$_x$Fe$_y$O increased without the appearance of other phases. This apparently showed that the reduction of the Mn$_{0.6}$Fe$_{2.4}$O$_y$ went through the formation of Mn$_x$Fe$_y$O phase, which is an important proof of the TPR results with an “egg-shell” reduction model. Furthermore, the Mössbauer study of the C$_2$H$_5$OH-reduced materials indicated a similar phase distributions. The only difference between H$_2$ and C$_2$H$_5$OH reduction paths was observed for Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ ferrite, where the ferric (Fe$^{3+}$) and ferrous (Fe$^{2+}$) iron oxides were also present in a small amount, which may indicate a “mixed reduction character” with a partial contribution from both “autocatalytic” (shown by Cu$_{0.6}$Fe$_{2.4}$O$_y$) and “egg-shell” (shown by Mn$_{0.6}$Fe$_{2.4}$O$_y$) mechanisms.

Moreover, the chemical-loop reforming was performed using Cu$_{0.6}$Fe$_{2.4}$O$_y$ ferrites as looping materials. The obtained results have shown that samples which contain copper cations (Cu$_{0.6}$Fe$_{2.4}$O$_y$ and Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$) reached higher reduction extent (about 98 and 59%, respectively) in comparison to only Mn-modified ferrospinel (with just 16%). In addition, conducted CHNS elemental analysis has shown the relationship between a ferrite composition and a carbon deposition: “↑%Cu” → “↑%C”. Thus, the addition of Mn hindered carbon deposition, which also caused a decrease of the amount of CO$_x$ generated by
oxidation with water steam, which is an important issue to produce clean H\textsubscript{2}. However, Mn-incorporation led to a lower efficiency of the 1\textsuperscript{st} step due to the formation of thermodynamically stable Mn\textsubscript{x}Fe\textsubscript{y}O which prevents a further deep reduction. This in turn reduces the yields for H\textsubscript{2} produced on the 2\textsuperscript{nd} re-oxidation step. Cu-incorporation has shown an opposite effect, leading to a higher reduction extent and as a consequence higher yields for H\textsubscript{2} produced during the steam re-oxidation stage.
6. CHEMICAL-LOOP REFORMING: REACTIVITY TESTS $\rightarrow$ $M_{0.6}Fe_{2.4}O_y$

The previous two chapters have included some results on the reactivity of $Co_{0.6-x}Mn_xFe_{2.4}O_y$ and $Cu_{0.6-x}Mn_xFe_{2.4}O_y$ ferrospinel: 1 complete cycle of 20 min (1st step – ethanol reduction – 20 min/ 2nd step – water re-oxidation – 20 min). This chapter contains a further discussion on the reactivity of $M_{0.6}Fe_{2.4}O_y$ materials, using a different cycling time and a sample composition as an important tool to improve the overall effectiveness of the chemical-loop reforming (CLR) process.

The choice of reaction conditions and cycling time was adopted according to the study of Cocchi (reducing agent: methanol, $T_{\text{red}}$ – 300 and 420°C/$T_{\text{re-ox}}$ – 420°C, looping materials: $Fe_3O_4$, $CoFe_2O_4$ and $NiFe_2O_4$) and Trevisanut (reducing agent: ethanol, $T_{\text{screen red}}$ – 400 and 450°C/$T_{\text{re-ox}}$ – 450°C, looping materials: $Fe_3O_4$, $CoFe_2O_4$ and $NiFe_2O_4$). Important to note, that the essential aim of the reduction step was to maximize the reduction extent with a minimum deactivation (an effect of coke accumulation) of the looping material along with an improving of its cycling stability. Hence, previously obtained results suggested the best reaction conditions to be as follows: 1st step – ethanol reduction at $T_{\text{red}}$-450°C and 2nd step – water re-oxidation at $T_{\text{re-ox}}$-450°C. Cycling time was chosen on the same basis and can be subdivided into: long cycles (duration time of one complete cycle: 1 h red/1 h re-ox) and short cycles (duration time of one complete cycle: 20 min red/20 min re-ox, 6 min red/6 min re-ox). The optimum time for both steps was set up as 20 min per each cycle (however, a comparison of the integrated mol of produced $H_2$ during the 2nd step for the same total $tos$ has been made, for example 1h (total→60 min) = 3 cyc·20 min (total→60 min) = 10 cyc·6 min (total→60 min).

The composition of $M_{0.6}Fe_{2.4}O_y$ ferrospinel was also varied in between transition metals: Co, Mn, Cu and alkaline earth metals: Ca, Mg. The aim of the following modifications was to pursue a higher selectivity to some valuable chemicals produced on the 1st reduction step along with a high purity $H_2$ produced during the 2nd re-oxidation step (Figure 1-10).
6.1. 1st step: reduction with ethanol at T-450°C

Figure 6-1. Conversion and Selectivity to the main products obtained for Fe₂O₃ during the 20 min cycling at T-450°C

Figure 6-2 shows the results obtained over M₀.₆Fe₂.₄O₄ samples (where M-Cu, Co, Mn, Ca and Mg) during 5 complete cycles of 20 min (plotted selectivity and conversion represent an integrated value and this has been done per each cycle). For comparison of any important differences with changing the composition of the ferrospinel, Fe₂O₄ was taken as a reference (studied in details by Trevisanut¹⁰¹). In Figure 6-1 plotted results obtained with bare magnetite over 5 complete cycles. As was seen by Trevisanut and others, the main drawback of the pure-Fe₂O₄ is a low cycling stability which derives from deep modifications of the looping material occurred during the redox cycles, such as: sintering, segregation, coke deposition (partly remains after each cycle due to an incomplete gasification with a steam) and incomplete re-oxidation, etc. As a consequence of the lost in the activity, the amount of produced H₂ on the 2nd step (see the next paragraph) over magnetite decreased with every repeated cycle, leading to a lower efficiency of the CLR process. As discussed previously in the Chapters 4 and 5, a slight change in the composition may strongly affect the final redox properties and catalytic behavior of the resulted sample. Thus, looking at the
plotted results in Figure 6-2, an average conversion of ethanol over Mn-/Mg-/Ca-modified samples showed the lowest values compared to Cu-/Cu-Mn-/Co-Mn- materials with a decreasing trend for almost all the samples. This can be explained by sintering (↑ of particle size ↓ of SSA, see TEM images for some cycled samples in the Chapter 5), segregation (mainly in the form of metal (M) and metal oxide (MO), as detected by XRD, see the next Paragraphs 6.2 and 6.4) and coke deposition (part of which remains after each cycle, see Raman spectroscopic study in the next Paragraph 6.5).

Looking at the selectivity to the different products (Figure 6-2), \( \text{H}_2 \) appears to be the main product of the reduction process over all M-modified ferrospinel. However, its selectivity affected by the nature of a foreign metal and in addition by the phase composition of a newly reformed material (the composition is changing continuously until the reduction extent reaches its plateau (its max at chosen reaction conditions). Incorporation of Mn and alkaline metals (like, Ca and Mg) gives a lower selectivity to \( \text{H}_2 \): \( \text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (with a decreasing trend from 49 to 34%), \( \text{Ca}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (with a decreasing trend from 54 to 41%) and \( \text{Mg}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (with a decreasing trend from 52 to 32%). On the contrary, a highest selectivity to hydrogen was obtained with incorporation of transition metals, such as Cu and Cu/Mn, Co/Mn: \( \text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (with ↓ trend from 80 to 60%), \( \text{Cu}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}\text{O}_y \) (from 62 to 60%, with a max at 69% for a 2\textsuperscript{nd} cycle) and \( \text{Co}_{0.3}\text{Mn}_{0.3}\text{Fe}_{2.4}\text{O}_y \) (with ↑ trend from 66 to 78%).

Moreover, other products formed during the ethanol reduction also have shown some differences in the selectivity distributions which vary according to the nature of the incorporated cations. High selectivity to acetone have shown the following ferrospinel: \( \text{Mn}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (from 38 to 31%), \( \text{Mg}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (from 35 to 22%) and \( \text{Ca}_{0.6}\text{Fe}_{2.4}\text{O}_y \) (from 38 to 21%). In addition, \( \text{CO}_x \) (see Chapter 5, eq. 1-3, 7, 9-10) and \( \text{H}_2\text{O} \) (see Chapter 5, eq. 3-5, 8, 10) formed over all tested materials, however the higher selectivity observed with Cu-, Cu/Mn- and Co/Mn-incorporated samples, which appear to achieve a higher reduction extents. The formation of coke (+heavy compounds) was also one of the products formed with all looping materials. The lowest selectivity to coke production have shown by Mn-, Ca- and Mg-incorporated samples. Hence, according to the present study, incorporation of Cu-, Cu/Mn- and Co/Mn- catalyze the reactions of total and partial oxidation of ethanol giving rise to higher selectivity to \( \text{CO}_x \) (or based on the calculation from H balance: to \( \text{H}_2 \) and \( \text{H}_2\text{O} \)). From the other hand, Mn-, Ca- and Mg-modification predominantly catalyze
dehydrogenation and condensation reactions leading to the formation of higher amount of acetaldehyde, acetone and pentanone.
Figure 6-2. Conversion and Selectivity to the main products obtained for TYPE II ferrospinel (M_{0.6}Fe_{2.4}O_{y}) during the 20 min cycling at T-450°C.
Characterization of the cycled materials by means of XRD is an important tool to elucidate several aspects on the stability of the spinel phase and its re-formation after each redox cycle. Moreover, identification of the phases during the reduction process can help to understand the results obtained from the catalytic tests.

Figure 6-3 shows XRD patterns for $M_{0.6}Fe_{2.4}O_y$ ferrospinsels which are taken after 4 complete cycles (20 min each step) + 1 ethanol reduction (20 min). At the first sight, a presence of the spinel phase (as a reformed phase: $M_{0.6-x}Fe_{2.4+x}O_4$) indicates an incomplete reduction which appears after cycling (possibly as a result of the sintering ($\uparrow$ particle size and $\downarrow$ SSA) and the partly remaining coke (the spinel phase is encapsulated inside). Moreover, the ethanol reduction of already cycled material led to the formation of the other phases, like metal (M) and metal oxide (MO). Reduction with ethanol led to the formation of: $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (reformed spinel ($Co_{0.3-x}Mn_{0.3+y}Fe_{2.4+x+y}O_4$) and metal oxides solid solution ($Mn_xFe_yO$); $Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (reformed spinel ($Cu_{0.3-x}Mn_{0.3+y}Fe_{2.4+x+y}O_4$), metal oxides solid solution ($Mn_xFe_yO$) and metal ($Cu^0$)), $Cu_{0.6}Fe_{2.4}O_y$ (reformed spinel ($Cu_{0.6-x}Fe_{2.4+x}O_4$), iron carbides ($Fe_3C$ and $Fe_5C_2$) and metal ($Cu^0$)), $Mg_{0.6}Fe_{2.4}O_y$ (reformed spinel ($Mg_{0.6-x}Fe_{2.4+x}O_4$) and metal oxides solid solution ($Mg_xFe_yO$)) and $Mn_{0.6}Fe_{2.4}O_y$ (reformed spinel ($Mn_{0.6-x}Fe_{2.4+x}O_4$) and metal oxides solid solution ($Mn_xFe_yO$)). As explained in the previous Chapter 5, the formation and further accumulation of a hardly reducible and thermodynamically stable $M_xFe_yO$ oxide (mainly, as $Mn_xFe_yO$ and $Mg_xFe_yO$) elucidates a decrease in the conversion for $Mg_{0.6}Fe_{2.4}O_y$ and $Mn_{0.6}Fe_{2.4}O_y$ samples (see Paragraph 6.1). Moreover, the formation of much higher amount of acetone (stable within 20 min) over these two samples could be also correlated to the presence of the thermodynamically stable $M_xFe_yO$ phase, which may catalyze the following reaction of the condensation of acetaldehyde with its further transformation to acetone (Chapter 5, eq. 11).
CHEMICAL-LOOP REFORMING: REACTIVITY TESTS $\rightarrow M_{0.6}Fe_{2.4}O_y$
CHEMICAL-LOOP REFORMING: REACTIVITY TESTS → $M_{0.6}Fe_{2.4}O_y$
6.3. 2\textsuperscript{nd} step: re-oxidation with water at T-450°C

After the reduction with ethanol, the materials were re-oxidized with water steam at 450°C, which corresponds to the second step of the chemical loop. Tests were carried out with the same $\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y$ materials using different cycling conditions (with duration of 1h, 20 min and 6 min). Important to note, that the Paragraph 6.1 includes the discussion on the 20 min reduction steps (as an optimum cycling time), however this part will touch on the results obtained from 1 h and 6 min cycles, in order to compare the integrated mol of produced $\text{H}_2$ during the 2\textsuperscript{nd} step for the same total $\text{tos}$: 1h (total→60 min) = 3 cyc·20 min (total→60 min) = 10 cyc·6 min (total→60 min).

Figure 6-4 shows integrated values for the produced $\text{H}_2$ and $\text{CO}_x$ obtained during the 3 complete cycles of 20 min (equal to the total $\text{tos}$ of 60 min), where bare-$\text{Fe}_3\text{O}_4$ was taken as a reference. The obtained results confirm a previously made statement that the nature of the M-incorporated metal affects the redox properties, stability, catalytic activity and overall effectiveness in CLR process of the resulting looping material. Thus, a higher amount of $\text{H}_2$ was obtained over Co-, Cu-, Cu/Mn- and Co/Mn-modified ferrites in comparison to a much lower amount produced over Mn-, Mg- and Ca-modified and non-modified $\text{Fe}_3\text{O}_4$ samples. These results lie in parallel with the results obtained during the reduction step.
carried out with ethanol; the materials containing in its composition as a foreign metal Co-, Cu-, Cu/Mn- and Co/Mn-cations reached a deeper reduction extent in comparison to Mn-, Ca- and Mg-cations, which in turn leads to a higher amount of H₂ produced on the re-oxidation step with water steam. However, the reduction by ethanol led to a coke deposition and a metal carbides formation. This turned into the generation of CO and CO₂ during the re-oxidation step (Figure 6-4), because of the gasification of carbonaceous residues. Partly, the problem of coke deposition can be overcome by tuning the M-ferrite composition (this effect has been for Co₀.₆₋ₓMnₓFe₂.₄O₇ and Cu₀.₆₋ₓMnₓFe₂.₄O₇ systems, see CHNS results discussed in the Chapter 5) or by shortening the cycling time of each step to avoid a strong reduction to FeₓCᵧ carbides (up to 6 min per 1 cycle). The latter in turn decreases the total amount of produced H₂ due to the incomplete reduction (the effectiveness of CLR process ↓), Figure 6-5. The experiments performed at longer cycling time (much longer than approximately 20 min→ like 1 h cycles) did not show a positive impact on the H₂ production (Figure 6-5), producing much less hydrogen (compare to 20 min cycles) and accumulating more coke (↑ amount of COₓ on the 2nd step and ↑ deactivation due to the incomplete gasification).

Figure 6-4. Integrated mol of produced H₂ and COₓ during 3 cyc-20 min over M₀.₆Fe₂.₄O₇ ferrites
Figure 6-5. Comparison of the $\text{H}_2$-integrated mol produced over $\text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y$ ferrites during the same total tos of 60 min with a different duration time per each cycle (6, 20 and 60 min).

6.4. Ex-situ XRD study over cycled materials after 5 cyc·20 min

![XRD spectrum](image-url)
$\text{Mn}_x\text{Fe}_y\text{O}_z$

(5 cys of 20 min)

$\Delta \text{Mn}_x\text{Fe}_y\text{O}_z$

$\text{Mg}_z\text{Fe}_4\text{O}_y$

(5 cys of 20 min)
One of the key points to obtain an efficient CLR process lies in the use of potentially stable (with ability to reform a spinel phase after each complete cycle) and highly active (with no significant loss in the redox performance with cycling) materials. By mean of the ex-situ XRD study, performed on the used $M_{0.6}Fe_{2.4}O_y$ materials, identification of the reformed phases after several complete cycles gave important information on the stability of the spinel phase. Figure 6-6 shows the XRD results taken on the cycled samples after 5 complete cycles. It can be seen that all tested materials underwent some morphological changes and were significantly affected by sintered temperature (narrowing of the patterns), segregation (presence of M and MO phases in addition the spinel one) and coke deposition (for some samples a broad reflection at $\sim$26° (2θ)).

Re-oxidation with water steam at 450°C led to the formation of the following phases: $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (reformed spinel, CoFe alloy and Mn$_x$Fe$_y$O), $Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y$ (reformed spinel, $Cu^0$ and Mn$_x$Fe$_y$O), $Cu_{0.6}Fe_{2.4}O_y$ (reformed spinel and $Cu^0$), $Mn_{0.6}Fe_{2.4}O_y$ (reformed spinel and Mn$_x$Fe$_y$O), $Mg_{0.6}Fe_{2.4}O_y$ (reformed spinel) and $Ca_{0.6}Fe_{2.4}O_y$ (reformed spinel and calcite – $Ca(CO_3)$). Nevertheless, all $M_{0.6}Fe_{2.4}O_y$ ferrites have shown that the reformed spinel ($M_{0.6-x}Fe_{2.4+x}O_4$) with a main 100% reflection of (311) plane at 35.5° (2θ) prevails to the other M and MO expelled phases. That is an important prove of the thermodynamic stability of a spinel oxide which allow us to re-obtain the initial spinel phase upon the cycling and in turn
increase the stability of looping material (as seen for Cu$_{0.6}$Fe$_{2.4}$O$_y$, Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$ and Co$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$, in the Paragraph 6.1). Moreover, the evidence of the lower amount of coke deposition over Mn-, Mg- and Ca-containing materials can be seen from the less intensive reflection of carbonaceous species at ~26° (2θ), supported by CHNS analysis (see Chapters 5). The presence of coke indicates that carbon was accumulating during cycling and cannot be simply eliminated by sending a water steam at 450°C. One of the possible solutions to overcome this problem is to add the 3rd step (O$_2$-feeding to clean the looping material after each complete cycle) (see PART I).

### 6.5. Raman spectroscopy over cycled materials

Raman spectroscopy was used to identify different kind of carbonaceous species (such as diamond, graphite, and etc.) formed on the surface of the reduced M$_{0.6}$Fe$_{2.4}$O$_y$ materials (Figure 6-7 and Figure 6-8). Ordered and disordered carbon may be identified in Raman spectra by its characteristic bands. The spectroscopic study of the cycled materials showed the formation of two types of carbonaceous species, which partly remained intact after the re-oxidation step:

- **G band** at 1580 cm$^{-1}$: crystalline graphite ($E_{2g2}$). This band is due to the stretching of C sp$^2$ atoms, which are present as an aromatic layer.

- **D1 band** at 1350 cm$^{-1}$: diamond-like ($A_{1g}$). This band is due to C sp$^3$ atoms present in the diamond structure, but also in defects present in C sp$^2$ structures$^{156}$. 

---

CHEMICAL-LOOP REFORMING: REACTIVITY TESTS $\rightarrow$ M$_{0.6}$Fe$_{2.4}$O$_y$ 212
Figure 6-7. Raman spectra of exhausted materials after 6 min·10 cycles over: (A) Co$_{0.6}$Fe$_{2.4}$O$_y$; (B) Mn$_{0.3}$Co$_{0.3}$Fe$_{2.4}$O$_y$; (C) Mn$_{0.6}$Fe$_{2.4}$O$_y$; (D) Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$; (E) Cu$_{0.6}$Fe$_{2.4}$O$_y$

Figure 6-8. Raman spectra of exhausted materials after 20 min·5 cycles over: (A) Mn$_{0.3}$Co$_{0.3}$Fe$_{2.4}$O$_y$; (B) Mn$_{0.6}$Fe$_{2.4}$O$_y$; (C) Cu$_{0.3}$Mn$_{0.3}$Fe$_{2.4}$O$_y$; (D) Cu$_{0.6}$Fe$_{2.4}$O$_y$
6.6. Conclusions on the study of $M_{0.6-x}Fe_{2.4}O_y$ ferrospinel

The catalytic activity in the ethanol chemical-loop reforming was studied by using TYPE II ferrospinel ($M_{0.6}Fe_{2.4}O_y$) as oxygen carrier looping materials. The composition of $M_{0.6}Fe_{2.4}O_y$ ferrospinel was varied in between the transition metals: Co, Mn, Cu and the alkaline earth metals: Ca and Mg, in order to pursue a higher selectivity to some valuable chemicals produced on the 1st reduction step along with a high purity $H_2$ produced during the 2nd re-oxidation step. The redox properties of ferrospinel were found to depend strongly on the nature of incorporated cation, which has its affect on the productivity of the 2nd step.

The reduction of $M$-modified ferrospinel appeared to be a complex process due to the presence of various metal - $M$ (where $M$ is Cu$^0$, CoFe alloy) and metal oxide-$MO$ (where $MO$ is $Mn_xFe_yO$ and $Mg_xFe_yO$) reduced forms. Besides, it was observed that the incorporation of Cu-, Mn/Co- or Mn/Cu- cations into a magnetite ($Fe_3O_4$) crystal structure have a beneficial effect on its stability. An important prove of the thermodynamic stability of spinel oxide was confirmed by XRD study which allow us to re-obtain the initial spinel phase upon the cycling and in turn increase the stability of looping material (as seen for $Cu_{0.6}Fe_{2.4}O_y$, $Cu_{0.3}Mn_{0.3}Fe_{2.4}O_y$ and $Co_{0.3}Mn_{0.3}Fe_{2.4}O_y$).

Moreover, the addition of Mn hindered carbon deposition, which also caused a decrease of the amount of $CO_x$ generated by oxidation with water steam, which is an important issue to produce clean $H_2$. However, the Mn containing ferrospinels showed a lower efficiency in the removal of the C residues accumulated during the first step. This may lead to the need of a third step of coke removal by air oxidation, if a clean material is needed to perform a following cycle. In an alternative approach, as already pointed out in the literature, the unreactive coke may be maintained as an inert material, provided (that) during successive cycles the further accumulation of coke occurs at a limited extentonly$^{22,53}$. 
The previous Chapters included the results on reactivity tests and material characterizations of TYPE I (Chapter 4) and TYPE II (Chapters 5 and 6) ferrospinels. Consequently, it was necessary to make a general comparison between the various materials in order to make an overall conclusion.

Figure 7-1 summarizes the integrated values for \( H_2 \) produced during the 2\(^{nd} \) re-oxidation step (referred to 1 complete cycle of 20 min) carried out with the water steam over MFe\(_2\)O\(_4\) and M\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) ferrospinels. For understanding the results from different prospective, some important properties are provided in Table 7-1. The are several aspects that have to be underlined, taking into account the primary proposed looping material - Fe\(_3\)O\(_4\):

- Mn-incorporation into the MFe\(_2\)O\(_4\)/M\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) ferrites showed its positive aspect on the lowering the amount of produced coke which tends to accumulate during the 1\(^{st} \) reduction step carried out with ethanol stream, see C\(%_w\) (CHNS) in Table 7-1;

- Mn-incorporation increased the \( H_2/CO_x \) ratio, which follows from the previously made statement (to note: the higher is the \( H_2/CO_x \) ratio the more ‘pure’ \( H_2 \) is generated during the 2\(^{nd} \) re-oxidation step); for comparison Fe\(_3\)O\(_4\) itself accounts for \( H_2/CO_x=3.5 \), whereas TYPE I: MnFe\(_2\)O\(_4\) \( (H_2/CO_x=15) \), Co\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\) \( (H_2/CO_x=15) \) and TYPE II: Mn\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) \( (H_2/CO_x=14) \), Co\(_{0.3}\)Mn\(_{0.3}\)Fe\(_{2.4}\)O\(_y\) \( (H_2/CO_x=7) \), all the other \( H_2/CO_x \) values are listed in Table 7-1;

- Incorporation of the transition metals, as Cu/Co/Mn (Fe:Cu or (-Co,-Mn) is equal to 2 or 4), has its beneficial effect on the total amount of produced \( H_2 \) derived from \( H_2O \) in comparison to a non-modified Fe\(_3\)O\(_4\) spinel. Hence, the best performance was shown by the following binary/ternary M-modified ferrospinels: TYPE I - CuFe\(_2\)O\(_4\) (Y-52%), Cu\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\) (Y-46%), Cu\(_{0.5}\)Mn\(_{0.5}\)Fe\(_2\)O\(_4\) (Y-37%) and TYPE II – Cu\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) (Y-50%), Co\(_{0.6}\)Fe\(_{2.4}\)O\(_y\);

- Cu/Co- incorporation leads to the increase of \( n_{H2}/n_{Eth} \) ratio, as for TYPE I: CuFe\(_2\)O\(_4\) \( (n_{H2}/n_{Eth}=1.2) \), Cu\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\) \( (n_{H2}/n_{Eth}=1.0) \) and TYPE II: Cu\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) \( (n_{H2}/n_{Eth}=1.1) \), Co\(_{0.6}\)Fe\(_{2.4}\)O\(_y\) \( (n_{H2}/n_{Eth}=1.0) \); which roughly could be correlated to the feasibility of producing \( H_2 \) starting from bio-ethanol being based on the \( H_2 \) vs. Ethanol heating values (referred to LHV (Lower Heating Value), MJ/kg): \( 119.96 \) and \( 28.86 \),
respectively (note: in the case of using bio-ethanol as a potential fuel). In another words, the higher is $n_{H_2}/n_{Eth}$ the higher is the potential efficiency of CLR (ethanol) process. Of course, there many more aspects that have to be undertaken in order to calculate the actual cost of the CLR process and to estimate a final price of H$_2$ produced via CLR technology and compare it to the existing ones (not encompassed in this study).

Figure 7-1. Integrated Yields for H$_2$ produced during 2$^{nd}$ re-oxidation step carried out with steam at 450°C over MFe$_2$O$_4$ and M$_{0.6}$Fe$_{2.4}$O$_4$ ferrospinels (note: listed data correspond to the values obtained after 1 complete cycle of 20 min).

Table 7-1. Parameters calculated for MFe$_2$O$_4$ and M$_{0.6}$Fe$_{2.4}$O$_4$ ferrites (note: listed data correspond to the values obtained after 1 complete cycle of 20 min).

<table>
<thead>
<tr>
<th>TYPE I: MFe$_2$O$_4$</th>
<th>C %$_w$ after 20 min red with ethanol</th>
<th>H$_2$/CO$_x$</th>
<th>Moles of H$<em>2$/Moles of Ethanol ($n</em>{H_2}/n_{Eth}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>11.6</td>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>16.3</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>6.9</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>6.1</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>1.5</td>
<td>15</td>
<td>0.1</td>
</tr>
<tr>
<td>MnFe₂O₄</td>
<td>1.7</td>
<td>15</td>
<td>0.09</td>
</tr>
<tr>
<td>--------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>REFERENCE MATERIAL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>5.3</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>TYPE II: M₀.₆Fe₂.₄Oₙ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₀.₆Fe₂.₄Oₙ</td>
<td>9.7</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>Co₀.₃Mn₀.₃Fe₂.₄Oₙ</td>
<td>7.9</td>
<td>7</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu₀.₆Fe₂.₄Oₙ</td>
<td>9.8</td>
<td>3</td>
<td>1.1</td>
</tr>
<tr>
<td>Cu₀.₃Mn₀.₃Fe₂.₄Oₙ</td>
<td>5.0</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>Mn₀.₆Fe₂.₄Oₙ</td>
<td>2.2</td>
<td>14</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca₀.₆Fe₂.₄Oₙ</td>
<td>-</td>
<td>3</td>
<td>0.3</td>
</tr>
<tr>
<td>Mg₀.₆Fe₂.₄Oₙ</td>
<td>-</td>
<td>7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Being guided by the data presented above, Figure 7-2 and Table 7-2 resume a further comparison between TYPE I and TYPE II ferrospinels, in particularly focusing on the H₂ produced during several consecutive cycles (referred to 3 complete cycles of 20 min). From this point, the samples been narrowed to the ones which gave the max yields to hydrogen (see Figure 7-1). Hence, the following statements can be made:

- Consecutive utilization of TYPE I: CoFe₂O₄, CuFe₂O₄, Cu₀.₃Co₀.₃Fe₂O₄ and TYPE II: Co₀.₆Fe₂.₄Oₙ, Co₀.₃Mn₀.₃Fe₂.₄Oₙ, Cu₀.₆Fe₂.₄Oₙ, Cu₀.₃Mn₀.₃Fe₂.₄Oₙ, Co₀.₃Mn₀.₃Fe₂.₄Oₙ ferrospinels as looping materials resulted in higher amounts of produced hydrogen (given in moles) which surpass the value obtained over the reference material – Fe₃O₄, see Figure 7-2;

- Increasing the total tos from 20 to 60 min (accounts the total time for the reduction/re-oxidation step) leads to the decreasing of H₂/COₓ ratio, which in its turn affects the final purity of the target gas – H₂ (note: this problem can be overcome by implementation of 3 steps CLR process with the 3rd step being carried out with air, as discussed in Chapter 4);

- CuFe₂O₄ (as representative of TYPE I ferrospinel group of materials) and Co₀.₆Fe₂.₄Oₙ (as representative of TYPE II ferrospinel group of materials) showed the higher n₉/H₂/n₉th ratio of 1 (referred to the total value for 3 consecutive cycles) which is in fact twice as much as obtained with Fe₃O₄ (n₉/H₂/n₉th=0.5).
Figure 7-2. Integrated moles for \( \text{H}_2 \) and \( \text{CO}_x \) produced during 2\textsuperscript{nd} re-oxidation step carried out with steam at 450\(^\circ\)C over \( \text{MFe}_2\text{O}_4 \) and \( \text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y \) ferrospinels (note: listed data correspond to the values obtained after 3 complete cycle of 20 min)

Table 7-2. Parameters calculated for \( \text{MFe}_2\text{O}_4 \) and \( \text{M}_{0.6}\text{Fe}_{2.4}\text{O}_y \) ferrites (note: listed data correspond to the values obtained after 3 complete cycle of 20 min)

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}_2/\text{CO}_x )</th>
<th>Moles of ( \text{H}_2 )/Moles of Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TYPE I: ( \text{MFe}_2\text{O}_4 )</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CoFe}_2\text{O}_4 )</td>
<td>5</td>
<td>0.7</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.5}\text{Co}</em>{0.5}\text{Fe}_2\text{O}_4 )</td>
<td>3</td>
<td>0.9</td>
</tr>
<tr>
<td>( \text{CuFe}_2\text{O}_4 )</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>REFERENCE MATERIAL</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Fe}_3\text{O}_4 )</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>TYPE II: ( \text{M}<em>{0.6}\text{Fe}</em>{2.4}\text{O}_y )</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Co}<em>{0.6}\text{Fe}</em>{2.4}\text{O}_y )</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{Co}<em>{0.3}\text{Mn}</em>{0.3}\text{Fe}_{2.4}\text{O}_y )</td>
<td>3</td>
<td>0.9</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.6}\text{Fe}</em>{2.4}\text{O}_y )</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.3}\text{Mn}</em>{0.3}\text{Fe}_{2.4}\text{O}_y )</td>
<td>3</td>
<td>0.7</td>
</tr>
</tbody>
</table>
7.1. Conclusions: TYPE I vs. TYPE II ferrospinels

To finalize the comparison between TYPE I (MFe$_2$O$_4$, where Fe/M=2/1) vs. TYPE II (M$_{0.6}$Fe$_{2.4}$O$_y$, where Fe/M=4/1) ferrospinels and the reference material – Fe$_3$O$_4$:

- M-incorporation (such as Cu, Co, Mn or Cu/Co, Co/Mn, Cu/Mn) strongly affects the final redox properties of the resulted materials → MFe$_2$O$_4$ and M$_{0.6}$Fe$_{2.4}$O$_y$ ferrospinels. Besides, the presence of M in its smaller amount (as in the TYPE II - $M_{0.6}$Fe$_{2.4}$O$_y$ with Fe/M=4/1) was already sufficient to see positive results on the production of H$_2$ via 2 steps CLR of bio-ethanol compared to the non-modified Fe$_3$O$_4$. Further increase of the M amount didn’t contribute to any additional improvements of the materials performance (as in the TYPE I - MFe$_2$O$_4$ with Fe/M=2/1), but, even on the contrary, had shown an opposite effect (as in the case of CoFe$_2$O$_4$ and Co$_{0.6}$Fe$_{2.4}$O$_y$ ferrites and explained by scarce attitude of the Co$^0$ to be re-oxidized by means of water as the only oxidant). That is to say, the utilization of TYPE II - $M_{0.6}$Fe$_{2.4}$O$_y$ ferrospinels, as oxygen and electrons carrier materials, appears to be more appealing for the 2 steps CLR of bio-ethanol, since the 2$^{nd}$ step carried out with water steam leads to incomplete re-oxidation of the previously reduced M$^{2+}$ to its metallic component (Co$^0$ and Cu$^0$), which in its turn results in the conclusion that as much of Co and Cu are present in the final M-modified ferrite as less material in its re-oxidized form is available for further reduction in the consecutive cycles.

In conclusion despite that several improved looping materials have been identified, complete appraisals of their performance and further optimization studies are required in order to give information on the overall conversion efficiencies, process design and economics.
LITERATURE


26 M. A. Pefia, 1996, 144, 7–57.
31 D. Yamaguchi, L. Tang and N. Burke, .


88 1–29.


90 B. D. Hosterman, 2011.


130 I. Chemicals, 2013.


Personally, I think that 3 years of my research work was driven by 3 forces: perception, curiosity and uncertainty. That is why I would like to refer to the statements of two great men:

"Science is perhaps the only human activity in which errors are systematically criticized and, in time, corrected."
-- Karl Popper (philosopher)

"As far as the laws of mathematics refer to reality, they are not certain, and as far as they are certain, they do not refer to reality."
-- Albert Einstein (theoretical physicist)

And, being inspired by the people who have contributed to the great discoveries, enabled me to "reach the end" of the endless.

Of course, a research project like this is never the work of anyone alone. The contributions of many different people, in their different ways, have made this possible. I would like to extend my appreciations especially to the following:

Prof. Fabrizio Cavani not only for his supervision in carrying out the research project but also for his relevant and extremely useful suggestions/comments, responsibility for the ongoing work that created an excellent atmosphere for doing a research and, in addition, for his kindness and geniality.

Prof. Francesco Di Renzo for being a great supervisor and especially for his "questioning part" that at the end was important and pertinent for understanding the things from different perspectives.

Prof. Stefania Albonetti for her extreme support and understanding that encouraged me to move on.

Dr. Jean-Marc Millet as one of the co-supervisors of the research project that passed his knowledge in the field of materials characterization. Moreover, for his inspirational phrase referring to Aristotel: "le doute est le commencement de la sagesse".

Since this research project was performed in between three institutions, I would like to thank to all young researches that certainly became my friends:

**Bologna:** Juliana, Francesco (Ciccio), Erica, Cristian, Elena, Lorenzo, Dodo, Claudia, Stefania, Alice, Tommaso, Andrea, Mugno, Max, Mattia, Sara, Nico, Chiara, Erika, Danilo, Giada.

**Montpellier:** Laura, Bilel, Chems, Elodie, Roberta, Youss, Gwendoline, Caroline, Arnaud, Enrico, Thomas, Lorenzo, Moulay.

**Lyon:** Florina, Aziz, Matteo, Nelly, Max, Zoe, Elodie.

**SINCHEM friends:** Maria, Emilia, Giuliana, Atif, Yu, Aisha, Valeria, Tapish, Andreas, Alba, Iqra.

To my family:

**Viktor and Irina (my parents)** for giving their support and encouragement to pursue my research and study, for giving love and time for me. Mom and Dad, a million thanks to you. I will be grateful forever for your love and support.

**Ekaterina (my sister),** despite the fact that she is so far away, for her love, support, trust, and patience.

And of course to my best young family members **Ulyana (niece)** and **Viktor (nephew)**...