Alma Mater Studiorum - Università di Bologna

Facoltà di Chimica Industriale
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Catalytic liquid- and gas-phase oxidations for the synthesis of intermediates and specialty chemicals: some examples of industrial relevance

Tesi di Dottorato di Ricerca

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INDEX

EXECUTIVE SUMMARY

Nowadays, it is clear that the target of creating a sustainable future for the next generations requires to re-think the industrial application of chemistry. It is also evident that more sustainable chemical processes may be economically convenient, in comparison with the conventional ones, because fewer by-products means lower costs for raw materials, for separation and for disposal treatments; but also it implies an increase of productivity and, as a consequence, smaller reactors can be used. In addition, an indirect gain could derive from the better public image of the company, marketing sustainable products or processes.

In this context, oxidation reactions play a major role, being the tool for the production of huge quantities of chemical intermediates and specialties. Potentially, the impact of these productions on the environment could have been much worse than it is, if a continuous efforts hadn't been spent to improve the technologies employed. Substantial technological innovations have driven the development of new catalytic systems, the improvement of reactions and process technologies, contributing to move the chemical industry in the direction of a more sustainable and ecological approach. The roadmap for the application of these concepts includes new synthetic strategies, alternative reactants, catalysts heterogenisation and innovative reactor configurations and process design.

Actually, in order to implement all these ideas into real projects, the development of more efficient reactions is one primary target. Yield, selectivity and space-time yield are the right metrics for evaluating the reaction efficiency. In the case of catalytic selective oxidation, the control of selectivity has always been the principal issue, because the formation of total oxidation products (carbon oxides) is thermodynamically more favoured than the formation of the desired, partially oxidized compound. As a matter of fact, only in few oxidation reactions a total, or close to total, conversion is achieved, and usually the selectivity is limited by the formation of by-products or co-products, that often implies unfavourable process economics; moreover, sometimes the cost of the oxidant further penalizes the process.

During my PhD work, I have investigated four reactions that are emblematic of the new approaches used in the chemical industry.

In the Part A of my thesis, a new process aimed at a more sustainable production of menadione (vitamin K3) is described. The “greener” approach includes the use of hydrogen peroxide in place of chromate (from a stoichiometric oxidation to a catalytic oxidation), also avoiding the production of dangerous waste. Moreover, I have studied the possibility of using an heterogeneous catalytic system, able to efficiently activate hydrogen peroxide. Indeed, the overall process would be carried out in two different steps: the first is the methylation of 1-naphthol with methanol to yield 2-methyl-1-naphthol, the second one is the oxidation of the latter compound to menadione. The catalyst for this latter step, the reaction object of my investigation, consists of Nb_2O_5-SiO_2 prepared with the sol-gel technique. The catalytic tests were first carried out under conditions that simulate the in-situ generation of hydrogen peroxide, that means using a low concentration of the oxidant. Then, experiments were carried out using higher hydrogen peroxide concentration. The study of the reaction mechanism was fundamental to get indications about the best operative conditions, and improve the selectivity to menadione.

In the Part B, I explored the direct oxidation of benzene to phenol with hydrogen peroxide. The industrial process for phenol is the oxidation of cumene with oxygen, that also co-produces acetone. This can be considered a case of how economics could drive the sustainability issue; in fact, the new process allowing to obtain directly phenol, besides avoiding the co-production of acetone (a burden for phenol, because the market requirements for the two products are quite different), might be economically convenient with respect to the conventional process, if a high selectivity to phenol were obtained. Titanium silicalite-1 (TS-1) is the catalyst chosen for this reaction. Comparing the reactivity results obtained with some TS-1 samples having different chemical-physical properties, and analyzing in detail the effect of the more important reaction parameters, we could formulate some hypothesis concerning the reaction network and mechanism.

Part C of my thesis deals with the hydroxylation of phenol to hydroquinone and catechol. This reaction is already industrially applied but, for economical reason, an improvement of the selectivity to the para di-hydroxilated compound and a decrease of the selectivity to the ortho isomer would be desirable. Also in this case, the catalyst used was the TS-1. The aim of my research was to find out a method to control the selectivity ratio between the two isomers, and finally to make the industrial process more flexible, in order to adapt the process performance in function of fluctuations of the market requirements. The reaction was carried out in both a batch stirred reactor and in a re-circulating fixed-bed reactor. In the first system, the effect of various reaction parameters on catalytic behaviour was investigated: type of solvent or co-solvent, and particle size. With the second reactor type, I investigated the possibility to use a continuous system, and the catalyst shaped in extrudates (instead of powder), in order to avoid the catalyst filtration step.

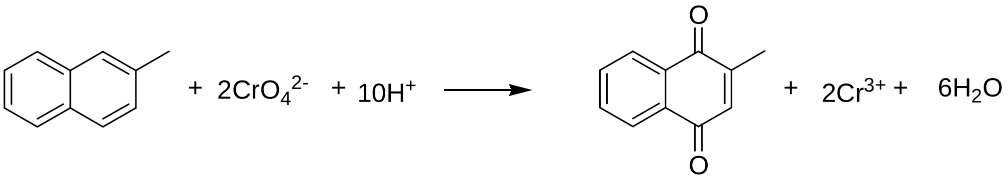
Finally, part D deals with the study of a new process for the valorisation of glycerol, by means of transformation into valuable chemicals. This molecule is nowadays produced in big amount, being a co-product in biodiesel synthesis; therefore, it is considered a raw material from renewable resources (a bio-platform molecule). Initially, we tested the oxidation of glycerol in the liquid-phase, with hydrogen peroxide and TS-1. However, results achieved were not satisfactory. Then we investigated the gas-phase transformation of glycerol into acrylic acid, with the intermediate formation of acrolein; the latter can be obtained by dehydration of glycerol, and then can be oxidized into acrylic acid. Actually, the oxidation step from acrolein to acrylic acid is already optimized at an industrial level; therefore, we decided to investigate in depth the first step of the process. I studied the reactivity of heterogeneous acid catalysts based on sulphated zirconia. Tests were carried out both in aerobic and anaerobic conditions, in order to investigate the effect of oxygen on the catalyst deactivation rate (one main problem usually met in glycerol dehydration). Finally, I studied the reactivity of bifunctional systems, made of Keggin-type polyoxometalates, either alone or supported over sulphated zirconia, in this way combining the acid functionality (necessary for the dehydrative step) with the redox one (necessary for the oxidative step).

In conclusion, during my PhD work I investigated reactions that apply the “green chemistry” rules and strategies; in particular, I studied new greener approaches for the synthesis of chemicals (Part A and Part B), the optimisation of reaction parameters to make the oxidation process more flexible (Part C), and the use of a bioplatform molecule for the synthesis of a chemical intermediate (Part D).

PART A: The oxidation of 2-methyl-1-naphthol to menadione

CHAPTER 1: INTRODUCTION

Vitamins are fine chemicals produced in amounts ranging between 1,000 and 10,000 tonnes per year[1]. Among these, menadione, that is the common chemical name for vitamin K3 (2-methyl-1,4-naphthoquinone) is an important synthetic product and is the key intermediate for the production of all the others vitamin belonging to the K family. Traditionally, menadione is produced on an industrial scale via stoichiometric oxidation of 2-methylnaphthalene with CrO_3 in sulfuric acid, but yield and selectivity are moderate (typically around 50%); the remaining being mainly the 6-methyl-1,4-naphthoquinone isomer along with phthalic acid, acetic acid and CO_2. However, the main problem of this process is that 18 Kg of toxic inorganic waste are also produced per each Kg of target product.



To avoid environmental and safety problems due to the formation of Cr^{3+}, and, also, to improve yield and selectivity to menadione, several alternative methods have been proposed in the literature.

To circumvent disposal problems alternative catalysts have been studied based on the catalytic oxidation of 2-methylnaphthalene: homogeneous catalysts like CH_3ReO_3[2], Pd(II)-modified polystyrene sulfonic acid resins[3], metalloporphyrin[4] or metallophthalocyanine[5] complexes. In all cases, however, yields and selectivities achieved are relatively low and processes are not economically competitive with respect to the chromium-based one. In addition to these

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[1] W. Bonrath, T. Netscher, *Appl.Catal A* 280 (2005) 55.

[2] W.A. Hermann, J.J. Haider, R.W. Fischer, *J. Mol. Catal. A* 138 (1999) 115.

[3] S.Yamaguchi, M. Inone, S. Enomoto, *Chem Lett.* (1985) 827.

[4] R. Song, A. Sorokin, J. Bernadou, B. Meunier, *J. Org. Chem.* 62 (1997) 673.

[5] A.B. Sorokin, S. Mangematin, C. Pergrale, *J. Mol. Catal. A* 182-183 (2002) 267.

catalytic methods, oxidation with Ce methanesulfonate and subsequent electrolytic oxidation of reduced cerium is commercially practiced[6]. Heterogeneous catalysts for the oxidation of 2-methylnaphthalene with hydrogen peroxide or t-butylhydroperoxide, such as Fe-zeolite[7,8] have also been reported.

An alternative route for menadione synthesis has been proposed by Matveev et al.[9], consisting in a modification of the starting material: 2-methyl-1-naphthol (MN) instead of 2-methylnaphthalene. The oxidation of 2-methyl-1-naphthol (MN) with Keggin heteropolyacids of the type $H_5PMo_{10}V_2O_{40}$ in the presence of oxygen is the core of the Vikasib technology. This process includes two-steps, in which MN (2-methyl-1-naphthol) first reacts with an aqueous solution containing the oxidized heteropolycompound, and then the reduced compound is regenerated with molecular oxygen, to restore the original oxidation state. Yields and selectivities reported are high but the kinetics of heteropolycompound reoxidation (the second step) is slow as compared to the synthesis step. An improvement of the performance was recently proposed by the use of a modified cyclic redox approach[10].

The oxidation of 2-methyl-1-naphthol (MN) with Ti-MMM-2[11] or silica-supported iron phthalocyanine[12] have been reported and particularly with Ti-MMM-2, 78% selectivity to menadione at total substrate conversion was achieved. Carbon-supported gold catalyzes the oxidation of MN with oxygen[13].

Matveev's process is the most interesting and convenient with respect to the other ones described in the literature; however, some problems could become limitative for a future industrial application. First of all, the starting material, 2-methyl-1-naphthol (MN), is more expensive than 2-methylnaphthalene. Nowadays 2-methyl-1-naphthol (MN) is produced by Friedel-Crafts reaction, using $AlCl_3$ as a Lewis acidic catalyst from 1-naphthol and methyl chloride. Moreover, the

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[6] R.M. Spotnitz, R.P. Kreth, J.T. Lundquist, P.J. Press, *J. Appl, Electochem.* 20 (1990) 201.

[7] O.A. Anunziata, L.B. Pierella, A.R. Beltramone, *J. Mol. Catal. A* 149 (1999) 255.

[8] O.A. Anunziata, A.R. Beltramone, J. Cussa, *Appl. Catal. A* 270 (2004) 77.

[9] K.I. Matveev, V.F. Odyakov, E.G. Zhizhina, *J. Mol. Catal. A* 114 (1996) 151.

[10] F. Monteleone, F. Cavani, C. Felloni, R. Trabace, *EurPatent Appl* 014832 (2004).

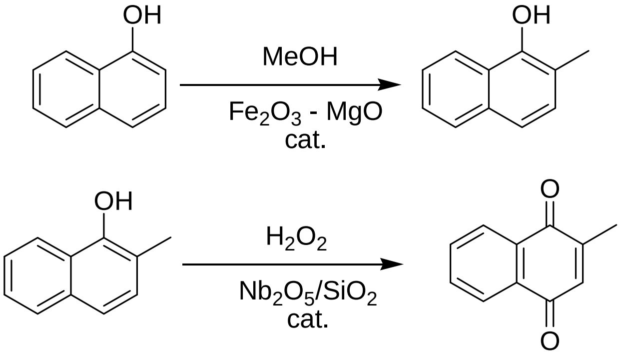
[11] O.A Kholdeeva, O.V. Zalomaeva, A.N. Shmakov, M.S. Melgunov, A.B. Sorokin, *J. Catal* 236 (2005) 62.

[12] O.A Kholdeeva, O.V. Zalomaeva, A.B. Sorokin, *C.R. Chemie* 10 (2007) 598.

[13] O.A Kholdeeva, O.V. Zalomaeva, A.B. Sorokin, I.D. Ivanchikova, C. Della Pina, M. Rossi *Catal Today* 121 (2007) 58.

cost of the oxidation catalyst, a polyoxometalate with the Keggin structure, is very high. To obtain a significant productivity a great amount of catalyst is needed. This is due to the low amount of oxygen per unit catalyst weight that is transferable from the polyoxometalate to the substrate; moreover, the reoxidation can become limiting for the overall process. Finally, also the recovery of the Keggin compound from reaction mixture could be quite difficult. So considering all these aspects, a new integrated process for the synthesis of menadione from 1-naphthol has been studied in the Part A of this thesis.

This new process consists in two separate steps: the first one is the selective methylation in the gas phase of 1-naphthol to 2-methyl-1-naphthol with methanol as the alkylating agent; the second step is the oxidation of 2-methyl-1-naphthol in the liquid phase, using hydrogen peroxide as the oxidant.



During my PhD, I have not investigated the methylation step; therefore, I will describe only the main features of this reaction. This step consists in a gas phase reaction between 1-naphthol and methanol, catalysed by basic systems, in particular by Mg-Fe mixed oxides. The introduction of host cations in the MgO lattice allows modulation of the H^+ abstracting properties; for example, the incorporation of Fe^{3+} in MgO lead to the formation of medium–strength basic sites. These latter sites are preferred for industrial applications because deactivate less than sites in stronger basic catalysts, like alkali and alkaline-earth metal oxides. The presence of Fe^{3+}, with a higher electronegativity, in place of Mg^{2+} decreases the charge density on the neighbouring O^{2-} and makes the latter less nucleophilic than O atoms in MgO. This class of catalysts is quite active, very chemo-selective and regio-selective even in the C-methylation of phenol in the gas phase; in fact, a high yield to o-cresol, the ortho-methylated product, is obtained[14].

The oxidation step is characterized by the use of H_2O_2 (HP) as the oxidant instead of oxygen. The cost of HP is higher than that of O_2, but the whole process might become convenient provided: (a) an heterogeneous catalyst, easy to filtrate and re-usable, may be used for the oxidative step; (b) the selectivity with respect to both HP and MN is high, and (c) eventually, HP is generated in-situ by means of reaction between hydrogen and oxygen. In the scientific literature there are several papers dealing with the generation of HP in diluted water solution, with supported Pd catalysts.[15]

In this work we describe our attempts to selectively oxidize MN to menadione using HP as the oxidant and mixed oxides as heterogeneous catalysts, namely Nb_2O_5-SiO_2 prepared by the sol-gel technique. The preparation of these materials was carried out by the team of Prof. Strukul, University of Venezia, and has been previously described.[16] These systems proved to be effective catalysts for the selective epoxidation of olefins and allylic alcohols with hydrogen peroxide as the oxidant.[17]

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[14] N.Ballarini, F.Cavani, L.Maselli, A.Montaletti, S.Passeri, D.Scagliarini, C.Flego, C.Perego *J.Catal.* 251 (2007) 423-436

[15] V.R. Choudhary, C. Samanta, T:V: Choudhary, *Appl.Catal. A.* 308 (2006) 128.

[16] F. Somma, P. Canton, G. Strukul, *J. Catal.* 229 (2005) 490.

[17] F. Somma, A. Puppinato, G. Strukul, *Appl. Catal. A* 309 (2006) 115.

CHAPTER 2: RESULTS AND DISCUSSION

2.1 LIQUID PHASE OXIDATION OF 2-METHYL-1-NAPHTHOL TO MENADIONE

2.1.1 Micro-plant description

The laboratory scale micro-plant used for the oxidation of 2-methyl-1-naphthol to menadione in liquid phase includes two main zones (fig 1):

1) Feeding Zone. A syringe pump was used to feed the liquid mixture of reactants. Either an aqueous solution of hydrogen peroxide or a solution of 2-methyl-1-naphthol in acetone were fed, depending on the method chosen for carrying out the reaction (the two different methods are described below).
2) Reaction Zone. The reaction was carried out in a semi-batch reactor continuously mixed, operating at atmospheric pressure. The reactor was a volumetric flask and an hot plate magnetic stirrer was used to heat the mixture and mix it. The temperature was controlled by means of a thermometer placed inside the liquid phase. The effluent gases exiting from the refrigerant pass through a solution containing $Ba(OH)_2$. In this way it was possible to detect the formation of CO_2, that caused the precipitation of $BaCO_3$, an insoluble white salt (Kps $\approx 10^{-9}$)

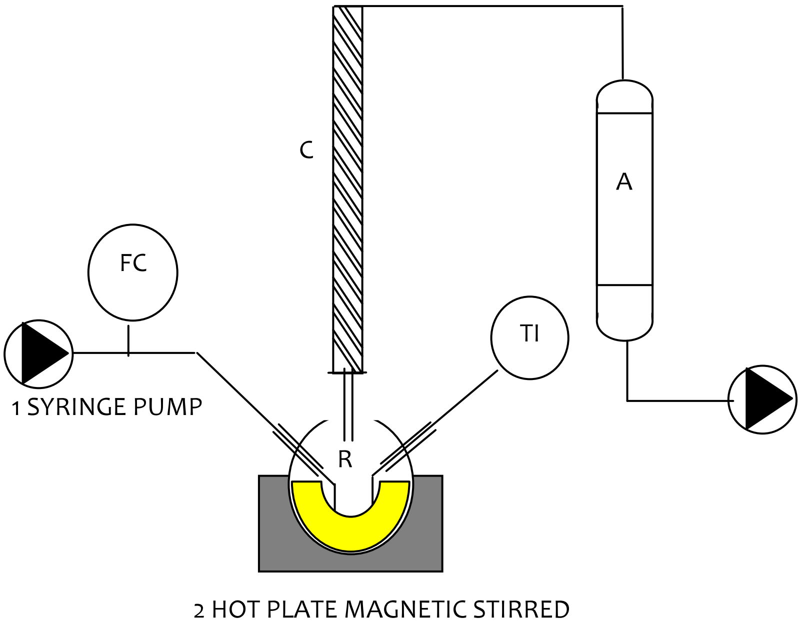

Fig 1: Laboratory micro-plant scheme. FC flow controller (syringe pump); R reactor: volumetric flask; TI temperature indicator thermometer ; C refrigerant; A adsorber.

Catalytic tests were carried out at 70°C, using acetone as the solvent. Two different solutions were prepared: (i) a HP/water solution with HP concentration of either 3.5 or 35 wt.%, and (ii) a 2-methyl-1-naphthol solution in acetone. The reaction was carried out in two different ways; the main difference consists in which solution is present in the heated flask, and which one is added slowly by means of the syringe pump. Mixing was anyway performed so to minimize the risk inherent in mixing acetone and HP. More in detail:

Method A: the 2-methyl-1-naphthol (MN)/acetone solution was continuously added to a large excess of HP containing the catalyst; or, viceversa, **method B:** the HP solution was continuously added to the MN/acetone solution containing the catalyst. In **method A** the amount of acetone is from small to moderate as the reaction proceeds, but a large excess of water is always present, while in **method B** the oxidant is consumed while adding; in this way its amount in acetone remains small. In both cases the chances of forming the potentially explosive acetone peroxide was minimized.

The temperature of the reaction was at the boiling point of the mixture, that was a function of the procedure adopted for the reaction: in the case of

method B, the boiling point of the mixture, and the operative temperature as well, was comprised between 55°C and 65°C. With **methods A**, where initially the water inside the reactor was in excess, the temperature decreased from the initial value of 80°C down to 65°C, during operation.

In both modes of operation, the feed was completed in 2 hours; then the mixture reacted for further 0.5 h. 1 mL of the reaction mixture was sampled at 0.5 h time intervals, and then analyzed with the following procedure. The sample was treated 3 times (5 mL each) with toluene, to extract the reactants and products; preliminary tests demonstrated that this procedure allowed the quantitative extraction of the compounds. Then the extracted fractions were mixed; 10 μL of internal standard (mesitylene) was added, and finally a small amount of Na_2SO_4 was also added to remove completely traces of water. Finally, the solution was analysed by gas-chromatography using a Thermo Focus GC instrument, equipped with a FID detector and a HP5 column; the oven temperature was programmed from 70°C to 300°C, with heating rate of 20°C/min. HP concentration was determined using the iodometric method.

2.1.2 Catalytic systems

Catalysts were prepared by the sol-gel method as described elsewhere[18,19]. The sol-gel technique allows obtaining samples with a high specific surface area and in which the active component is well dispersed inside the matrix. In this way it is possible to have ions of niobium (V) with a low aggregation degree, either in an isolated form or in the form of nano aggregates, but not in the form of bulk niobium oxide. A high dispersion is a prerequisite for systems used as catalysts for electrophilic oxidations.

Initially the sol contains niobium in a monomeric or oligomeric form (depending on the pH of the solution and the concentration of Nb), in the form of an alkoxide species $Nb(OPr)_5$, and the silicon source is $Si(OEt)_4$; the solvent is isopropanol. The gelification process forms a co-gel of silica-niobia with direct incorporation of Nb^{5+} in the silica matrix. Two different samples were synthesized both containing 0.5 wt% of Nb, but using a sol at different pH. The hydrolysis in basic conditions was faster than that one done at acidic conditions, and produced

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[18] F. Somma, P. Canton, G. Strukul, *J. Catal*. 229 (2005) 490.

[19] F. Somma, A. Puppinato, G. Strukul, *Appl. Catal. A* 309 (2006) 115.

an amorphous gel (**sample B**); in acidic medium the gelification was slow, and the sample (**sample A**) obtained had structural differences as compared to sample B (see Table 1 and Figure 2). In both cases the evaporation of the solvent was carried out in supercritical conditions, at high temperature, in an autoclave at 80 bar. Both materials were then calcined in air at 500°C for 2 hr. The hydrofobic aerogels obtained in this way were characterized by high specific surface area and by high porosity; this improved the dispersion of Nb, the active component. The traditional thermal treatment to evaporate the solvent would have caused a collapse of the porous structure due to surface tension phenomena, which were avoided in supercritical conditions.

Characterization of catalysts (Table 1 and Fig 2) was performed by N_2 adsorption isotherms and powder x-ray diffraction analysis, evidencing a high surface area and the presence of mesoporosity, a high dispersion of Nb, and the absence of niobium oxide segregation. Surface acidity was characterized by thermal programmed pyridine desorption (TPD). Typically, a sample of the calcined catalyst (5 mg) was activated in air flow (30 ml/min) at 500°C for 60 min, cooled down to RT and saturated for 5 min with a stream of pyridine coming from a saturator kept at RT. The sample was then purged with He (25 ml/min) at 100°C. The temperature was cooled down at 40°C and then the TPD was started (heating ramp 10°C/min, maximum temperature 400°C). The desorption of pyridine was monitored by an on-line connected FID.

Table 1: General properties of the Nb_2O_5-SiO_2 catalysts used in this study

Characterization of samples Nb_2O_5-SiO_2 by sol-gel		
	Sample A **Acidic conditions**	**Sample B** **Basic conditions**
Specific surface area (m^2/g)	940	916
Medium diameter of pores(nm)	35	19
Volume of pores (cm^3/g)	5	3,2
Presence of Nb_2O_5	No	No
Presence of acid site	Low and medium strength	Low and medium strength, in high concentration

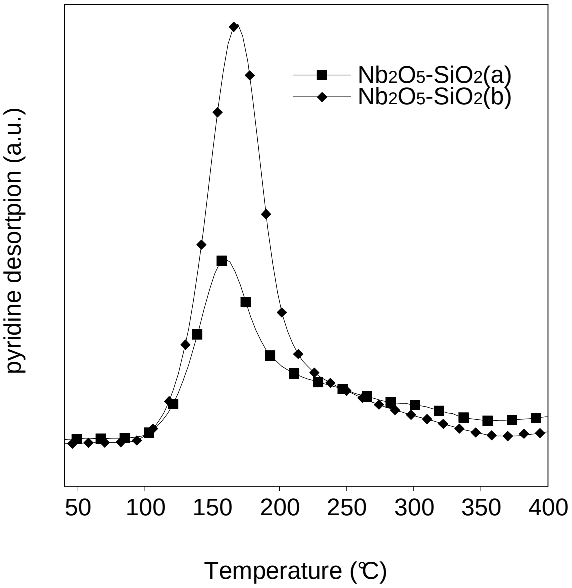


Fig. 2: Pyridine TPD profiles of the different Nb_2O_5-SiO_2 catalysts: Nb_2O_5-SiO_2 made under acidic conditions (sample A, a, ■) and Nb_2O_5-SiO_2 made under basic conditions (sample B, b, ◆).

2.1.3 Catalytic experiments

USE OF DILUTED HYDROGEN PEROXIDE

Initial tests were carried out with **method A** using 3.5% hydrogen peroxide, by slowly adding a solution of MN/acetone to a diluted aqueous solution of HP, the latter having been already pre-loaded in the reactor. This procedure simulates the reaction environment during the in-situ generation of HP by means of the catalytic oxidation of H_2 with O_2.

The conversion and yields in function of the reaction time are reported in Fig. 3, using **sample A**; the data obtained in the absence of catalyst are also reported, for reference purpose.

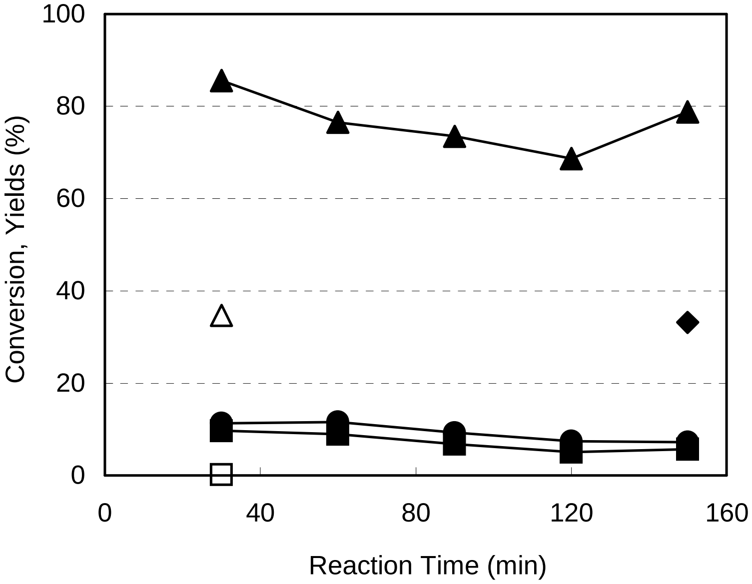
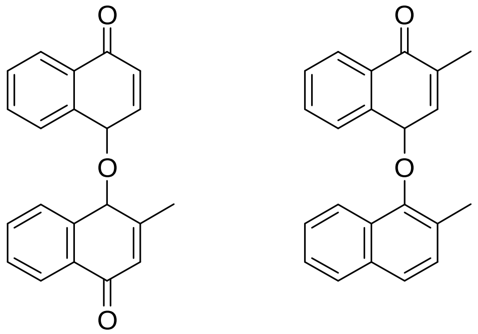


Fig 3: Oxidation of 2-methyl-1-naphthol with HP using CATALYST A and METHOD A. Catalyst (0.065 g), 3.5% HP (6 ml), 2-methyl-1-naphthol (0.37 mmol in 10 ml acetone) added dropwise. Conversion (▲), menadione yield (■), menadione selectivity (●), HP converted (◆). Without catalyst: conversion (△), menadione yield (□). HP/2-methyl-1-naphthol molar ratio = 19. Yield and conversion are calculated with respect to the amount fed up to a given time.

Initially the conversion of 2-methyl-1-naphthol (MN) was high, because the reactant was added dropwise to the oxidant solution, although it slowly decreased with time. There are two possible reasons to explain this trend: either a fast deactivation phenomena due to the deposition of heavy compounds, or a kinetic effect caused by progressive decrease of the HP/MN ratio. The selectivity to menadione also decreased during the increasing feed time; this is due to consecutive reactions of menadione degradation, due to the large excess of oxidant present in the system (also CO_2 was detected). This hypothesis is also supported by the analysis of reaction mixture by LC-MS that permitted to identify a large amount of "heavies", such as those shown below.



Scheme 1: Heavy by-products in 2-methyl-1-naphthol oxidation with HP

Interestingly, a blank reaction carried out in the absence of catalyst under the same conditions indicated that MN can indeed be converted, but without menadione formation. In the presence of the catalyst, menadione yield was relatively low (10-12%), because of the large amount of "heavies" formed by radical coupling followed by oxidation. At the end of the reaction HP conversion was 33%, largely exceeding the amount required by the reaction stoichiometry, as a consequence of overoxidation and/or radical-type decomposition of the oxidant.

Increasing the concentration of substrate (1.06 mmol in 10 ml), while keeping the other reaction conditions unchanged, resulted in an increase of the conversion (90-100%), a decrease in selectivity, but with the same menadione yield as in the previous experiment. This implies that the formation of "heavies" was even more favoured by the high concentration of substrate (MN) being formed by bi-molecular reactions.

Switching to **method B** led to the results shown in Fig. 4. In this case the HP was added dropwise to MN/acetone solution. As expected, the conversion increased with time (being the amount of oxidant added proportional to time). However menadione yield and selectivity were very low, and decreased with time, implying that the low HP/MN molar ratio favours radical-type side bimolecular reactions leading to the formation of "heavies" and HP decomposition. Here again, the uncatalyzed reaction showed a significant activity, but without formation of menadione. The use of catalyst **B** led essentially to the same results.

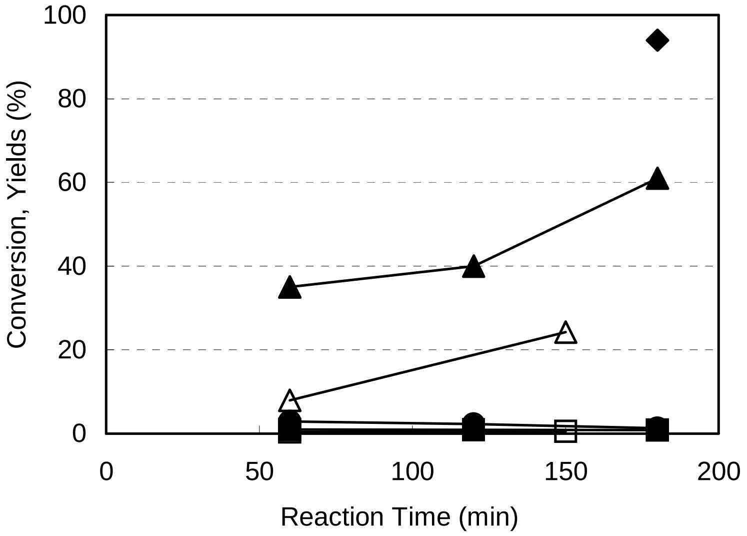


Fig 4: Oxidation of 2-methyl-1-naphthol with HP using CATALYST A and METHOD B. Catalyst (0.058 g), 3.5% HP (3 ml) added dropwise, 2-methyl-1-naphthol (1.14 mmol in 12 ml acetone). Conversion (▲), menadione yield (■), menadione selectivity (●), HP converted (◆). Without catalyst: conversion (△), menadione yield (□). HP/2-methyl-1-naphthol molar ratio = 3

The results reported in these experiments suggest that a good yield of menadione is obtained at high concentration of HP. On the contrary, a low oxidant concentration in the reactor favours mainly radicals formation arising from HP decomposition leading to substrate coupling reaction products rather than substrate oxidation. This is in good agreement with literature findings, showing that in the oxidation of MN catalysed by Ti-MMM-2, crucial factors affecting the menadione yield include MN concentration and HP/MN molar ratio[20].

The presence of the catalyst, probably involving the Nb^{5+}/Nb^{4+} redox pair, reinforced radical reactions without significantly affecting the desired reaction.

USE OF CONCENTRATED HYDROGEN PEROXIDE

Previous experiments have highlighted the importance of having a high concentration of HP, in order to improve the oxidation pathway leading to

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[20] O.A Kholdeeva, O.V. Zalomaeva, A.N. Shmakov, M.S. Melgunov, A.B. Sorokin, *J. Catal* 236 (2005) 62.

menadione; therefore, we used an aqueous solution of 35% HP. Results obtained using **sample A** and **method A**, are reported in Fig. 5.

The high HP concentration favoured menadione formation also in absence of catalyst. At the end of the reaction, both with and without catalyst, conversion and menadione selectivity were high and quite similar. The fact that in certain reaction conditions it is possible to form menadione from 2-methyl-1-naphthol with HP without any catalyst is mentioned also in literature[21]. The role of the catalyst is evident at the beginning of the reaction, where the carbon balance was quite good (menadione yields was similar to substrate conversion, implying an high selectivity). This data is also in good agreement with the hypothesis that the selective oxidation reaction needs an higher concentration of HP than coupling side-reactions.

The conversion behaviour suggests that after about 100 min the catalyst role was virtually finished, and that the deactivation phenomena prevailed. On the other hand, the continuous decrease in menadione yield, even after 100 min, is an indication that degradation phenomena were not due to the catalyst.

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[21] O.A Kholdeeva, O.V. Zalomaeva, A.B. Sorokin, I.D. Ivanchikova, C. Della Pina, M. Rossi *Catal Today* 121 (2007) 58.

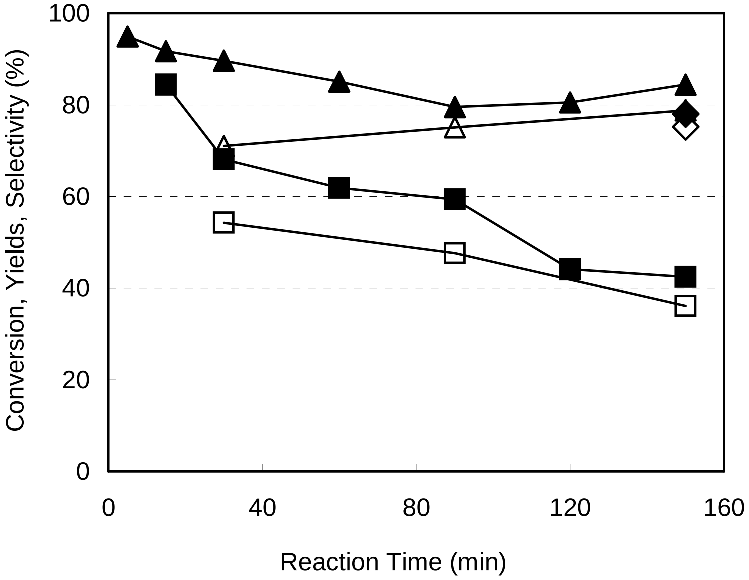


Fig 5: Oxidation of 2-methyl-1-naphthol with HP with CATALYST A using METHOD A. Catalyst (0.113 g), 35% HP (6 ml), 2-methyl-1-naphthol (0.67 mmol in 10 ml acetone) added dropwise. Conversion (▲), menadione yield (■), HP converted (◆). Without catalyst: conversion (△), menadione yield (□), HP converted (◇). HP/2-methyl-1-naphthol molar ratio = 105. Yield and conversion are calculated with respect to the amount fed up to a given time.

With the aim of investigating the role of the catalyst, we carried out a test with only 0.067 g of catalyst; in this case, after 50 min of reaction, the catalytic reaction had stopped, and only the homogeneous, uncatalyzed reaction was left. Under the latter conditions, filtering off the catalyst after 60 min and then continuing the reaction without catalyst, no further menadione formation was observed, while MN conversion remained high, indicating a sort of steady-state for menadione production. The side products formed from new menadione, stabilizing its concentration. In other words, there are significant consecutive reactions that consume menadione, and as a consequence of this, there is a critical value of menadione concentration in the reaction mixture that depends mainly on the reaction medium, rather than on the catalyst.

In order to understand the nature of these degradation processes, an experiment was carried out in the presence of a radical scavenger. 2,6-Di-*tert*-butyl-*p*-cresol (DBPC) was added to the system in equimolar amount with respect to MN. Results are shown in Fig. 6.

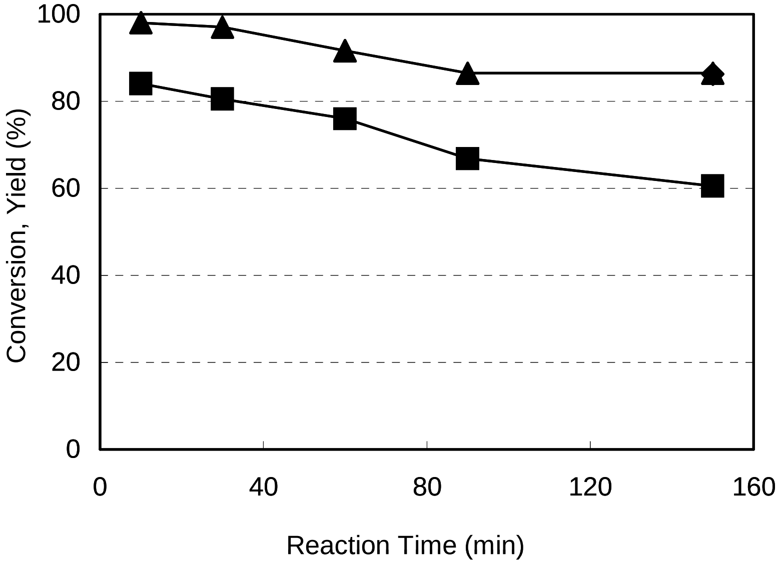


Fig 6: Oxidation of 2-methyl-1-naphthol with HP with CATALYST A using METHOD A. and with the addition of DBPC (0.67mmol) Catalyst (0.113 g), 35% HP (6 ml), 2-methyl-1-naphthol (0.67 mmol in 10 ml acetone) added dropwise. Conversion (▲), menadione yield (■). HP/2-methyl-1-naphthol molar ratio = 105. Yield and conversion are calculated with respect to the amount fed up to a given time.

The formation of overoxidized products derives from radical reactions; in fact, in the presence of the radical scavenger, the MN conversion was virtually unaffected, while menadione yield was significantly improved.

Also the effect of the reaction temperature was investigated; a decrease of temperature (50°C instead of 70°C) had only a moderate effect on the conversion, but menadione yield dropped dramatically down to less than 5%. Changing solvent into acetonitrile had a similar effect: conversion remained higher than 90%, while menadione yield dropped to 3-4%, in that case the main product being menadione epoxide (yield 12%).

Using **sample B,** the conversion jumped very close to 100%, and remained stable throughout all the experiment (Figure 7); however the efficiency of this catalyst was not so good: the results of experiments were very similar when obtained either with or without catalyst. Considering that the main difference between **sample A** and **sample B** is the number of acid sites (see Table 1), it is possible to say that an higher acidity favours the formation of side products, and also that this kind of catalyst has only a modest effect on menadione formation.

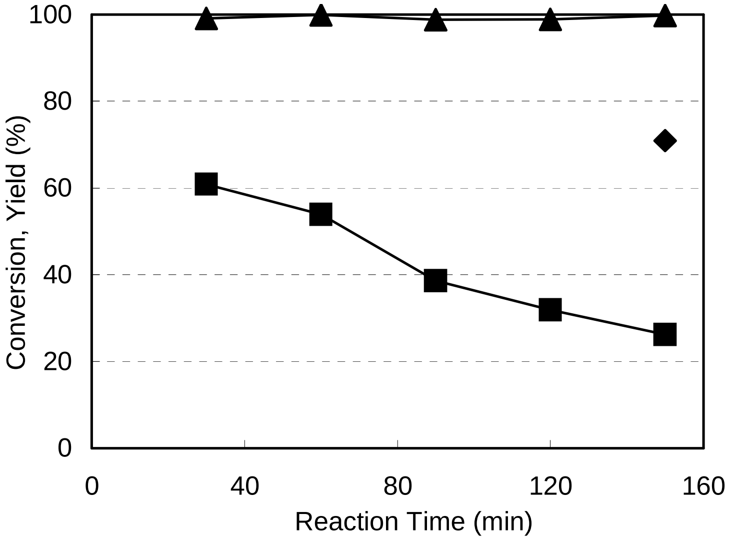


Fig 7: Oxidation of 2-methyl-1-naphthol with HP with CATALYST B using METHOD A. Catalyst (0.112 g), 35% HP (6 ml), 2-methyl-1-naphthol (1.20 mmol in 10 ml acetone) added dropwise. Conversion (▲), menadione yield (■), HP converted (◆). HP/2-methyl-1-naphthol molar ratio = 60. Yield and conversion are calculated with respect to the amount fed up to a given time.

Changing to **method B**, but using again **sample A**, we obtained the expected increase in substrate conversion and menadione yield (Figure 8). Product selectivity remained constant at about 20% indicating that, as expected, the lower HP concentration in the system did not give any benefit to the consecutive degradation reactions. Therefore, by feeding dropwise the oxidant, the by-products formed mainly from parallel reactions involving the starting MN (2-methyl-1-naphthol). The role of the catalyst was mainly that to favour the side reactions, and the results obtained in the absence of catalyst confirm again this hypothesis: the conversion of 2-methyl-1-naphthol was lower, but menadione yield was the same.

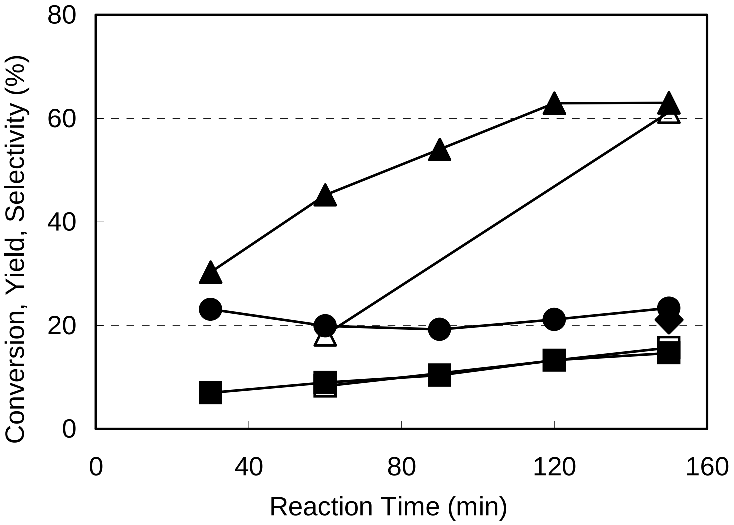


Fig 8: Oxidation of 2-methyl-1-naphthol with HP using CATALYST A and METHOD B. Catalyst (0.067 g), 35% HP (3 ml) added dropwise, 2-methyl-1-naphthol (1.40 mmol in 15 ml acetone). Conversion (▲), menadione yield (■), menadione selectivity (●), HP converted (◆). Without catalyst: conversion (△), menadione yield (□). HP/2-methyl-1-naphthol molar ratio = 24.

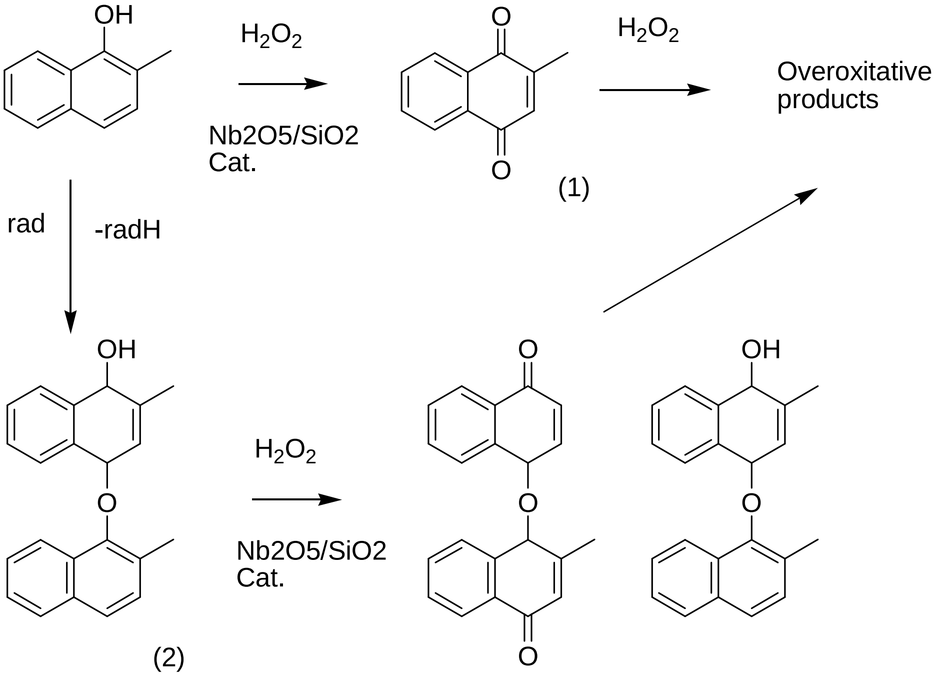
We tried to recover and recycle the catalyst. To this purpose, **sample B**, used for tests reported in Fig. 7, was filtered off, washed with acetone and dried; then, a new run under the same conditions was performed. The new profile obtained was practically identical to that observed during the first experiment. Furthermore, no Nb was detected by ICP-OES, analysing the filtrate solution; therefore, these catalysts are very stable under reaction conditions, they can be recycled, and the leaching of Nb was not observed after the first run.

OVERALL REACTION SCHEME

The outcome of these experiments is that the oxidation of MN is a complex process, and that the desired pathway is affected by both parallel and consecutive side reactions. The direct oxidation to give menadione **1** (Scheme 2) requires high concentration of HP, but can be accomplished even without the presence of a catalyst. Indeed results show that a significant catalyst effect is present only at the beginning of the reaction (carried out using method A) when HP concentration is high and free MN in the system is negligible. Under these conditions selectivity to menadione can be as high as 93%.

Changing the feeding mode or decreasing the HP concentration favours side reactions. The nature of by-products obtained suggests that intermediate phenoxy radical form by hydrogen abstraction; dimerisation leads to the intermediate compound **2**. Alternatively, Nb^{5+} itself may provide the necessary electrons. Actually, the formation of higher oligomers cannot be excluded (as shown in Scheme 2). Formation of radicals capable of triggering the reaction leading to **2** is relatively easy at 70°C or even at 50°C, where the oxidation reaction is virtually suppressed.

Both unidentified overoxidized products and CO_x could form either from menadione or from by-products, but in order to avoid these processes it is essential to use method B, where the concentration of HP is low, and a steady-selectivity to menadione in function of time is observed, indicating that consecutive reactions are virtually negligible.



Scheme 2: The reaction network in the oxidation of 2-methyl-1-naphthol with HP.

CHAPTER 3: CONCLUSIONS

It should be noted that when Nb_2O_5-SiO_2 made by sol-gel are used in the oxidation of allylic alcohols with HP under conditions similar to those adopted in this work, clean epoxidation occurs with only moderate waste of oxidant and moderate formation of by-products formed by acid catalysed epoxide ring opening. The oxidation of 2-methyl-1-naphthol seems to be dominated by radical pathways favoured by the nature of the substrate and the peculiar use of acetone as the solvent. In this medium, formation of small amounts of acetone peroxide, that could trigger relatively uncontrolled radical chain reactions, must be considered. This explains the generally large amount of undesired side products and the observation that the uncatalyzed reaction is always significantly present and, in some cases, prevalent. This point of view is in line with the behaviour in acetonitrile as the solvent that is not capable of forming peroxides under the reaction conditions employed and where it was demonstrated that epoxidation becomes the significant pathway. However, choosing appropriate conditions and taking care of the amount of the oxidant allow coupling a high conversion to high menadione selectivity with a significant influence of the catalyst on the overall process.

PART B: The oxidation of benzene with hydrogen peroxide and TS-1

CHAPTER 1: INTRODUCTION

Chemists are becoming increasingly concerned about the need for developing new environmentally safer chemical transformations by reducing or removing the toxic waste and the by-products obtained in chemical processes, and finally making them ecologically more sustainable. Therefore, it is necessary to develop eco-friendly methods for the production of bulk chemicals, intermediates and fine chemicals.

Phenol is one of the most important intermediates of the chemical industry with a global production estimated to be around 7.3 $x10^6$ t/y, and its principal uses are in plastic material, resins, detergents pharmaceutical industry, and in the preparation of colouring agents.

The industrial production of phenol is, in general, based on three multistep processes: (1) alkylation of benzene to cumene and its transformation to phenol and acetone; (2) a two-stage oxidation of toluene; (3) chlorination of benzene and hydrolysis of chlorobenzene to phenol.

All these processes have some environmental drawback. The first one, for instance, represents the most important route for acetone production, coproduced in 1:1 molar ratio with respect to phenol. Phenol market is growing faster than the acetone one; moreover, the value of acetone may be not high enough to economically sustain phenol production and, in some cases, it is treated as a waste, making the whole process unprofitable. Therefore, during last years much efforts have been devoted to the development of new processes for phenol synthesis, with no co-product formation and, eventually, by means of one-step synthetic methods.

The second process, toluene oxidation, consists of a two-step gas-phase catalytic process with molecular oxygen: the first step employs a V_2O_5/TiO_2 catalyst, with a series of additives, for the oxidation of toluene to benzoic acid; in the second step benzoic acid is converted to phenol using a NiO-Fe_2O_3 bulk oxide catalyst impregnated with small amounts of sodium and vanadium.

The third process co-produces one atom of Cl (in the form of NaCl) per each mole of phenol. Nowadays, however, the production of phenol is almost totally carried out using the cumene route.

An alternative method is the direct hydroxylation of benzene to phenol; looking at the literature, it can be noted that this process has become of the most important challenge for the modern chemical industry[22][23]. The development of a process based on the direct oxidation of benzene to phenol would be an important goal in industrial organic chemistry. However this reaction is usually affected by a poor selectivity due to the lack of kinetic (catalytic) control; indeed phenol is more easily oxidized that benzene itself, and substantial amount of over-oxygenated by-products (cathecol, hydroquinone, benzoquinone, and tars) are also formed. Anyway, there are three main pathways for benzene hydroxylation, that make use of different oxidants.

The first process is the BIC/SOLUTIA technology, that uses N_2O as the oxidant and is carried out in the gas phase over a zeolite catalyst doped with small amount of Fe: Fe-ZSM-5, Fe-TS-1, Fe/MFI. The selectivity is up to 90%, with benzene conversion up to 20% [24,25]. Unfortunately N_2O also causes deactivation of the catalyst by coke formation. In addition this oxidant molecule is not easily available.

In the second process molecular oxygen is the oxidant both in the gas and liquid phase. Some examples are reported by Niwa et al: in situ-hydroxylation over Pd with O_2/H_2, that gives phenol selectivity of 77% and yield of 20% [26,27]; alternatively, ion-exchange resins[28] or polyoxometalates are used as catalysts[29].

The third process is the liquid-phase hydroxylation using H_2O_2 (HP) as the oxidant, which can eventually be produced in situ. For this application there are

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[22] F M. Ricci, D. Bianchi, R. Bortolo, in "*Sustainable industrial chemistry. Priciples, tools and industrial examples*" F. Cavani, G. Centi, S. Perathoner, F. Trifirò EDS. Wiley-VCH, Weiheim, 2009, 507-528

[23] D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, *Ang. Chem. Int. Ed.*, 39 (2000) 4321.

[24] Jia, K.S. Pillai, W.M.H. Sachtler, *J. Catal.*, 221 (2004) 119.

[25] . Yuranov, D.A. Bulushev, A. Renken, L.K. Minsker, *J. Catal.*, 227 (2004) 138.

[26] . Itoh, S. Niwa, F. Mizukami, T. Inoue, A. Igarashi, T. Namba, *Catal. Comm.*, 4 (2003) 243.

[27] S. Niwa, M. Eswaramoorthy, J. Nair, A. Ray, N. Itoh, H. Shoji, T.Namba, F. Mizukami, *Science*, 295 (2002) 105.

[28] W. Laufer, W.F. Hoelderich, *Chem. Comm.*, 16 (2002) 1684.

[29] S. Shinachi, M. Matsushita, K. Yamaguchi, N. Mizuno, *J. Catal.*, 233 (2005) 81.

various heterogeneous catalysts, such as supported VOx [30], TS-1 [31], and V-MCM-41 [32]. With V-MCM-41, the phenol selectivity is 40%, with 10% benzene conversion. Recently, heteropolyacids were found to be good homogeneous catalysts in this reaction, giving phenol selectivity over 90% and yield over 17% [33]. However, the recovery and reuse of the catalyst is an important problem of these homogeneous systems, and also for this reason heterogeneous catalysis are preferred.

In this part of the thesis, the hydroxylation of benzene with HP was studied in depth. In particular the effect of solvent was studied comparing the results obtained in water and methanol with those obtained in the presence of a co-solvent, for example sulfolane, which could improve phenol yield. Moreover, different TS-1 catalysts were prepared changing the Si/Ti ratio, in order to investigate the effect of this parameter on catalytic behaviour.

Titanium silicalite-1 (TS-1) was developed in 1983 by Enichem[34]. This zeolite shows several interesting properties in heterogeneous oxidation catalysis. In fact good activity and selectivity are shown for TS-1 in alcohols oxidation[35,36], alkanes oxidation[37], alkene epoxidation[38] and ammoximation of cyclohexanone to cyclohexanone oxime[39].

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[30] K. Lemke, H. Ehrich, U. Lohse, H. Berndt, K. Ja¨hnisch, *Appl. Catal. A*,243 (2003) 41.

[31] L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari, R. Ungarelli, *Ang Chem Int. Ed.*, 42 (2003) 4937.

[32] Y. Chen, Y. Lu, *Ind. Eng. Chem. Res.*, 38(1999) 1893.

[33] J. Zhang, Y. Tang, G.Y. Li, C.W. Hu, *Appl. Catal. A*, 278 (2005) 251.

[34] M. Taramasso, G. Perego and B. Notari *US Patent* 4 410 501 (1983)

[35] C. Neri, and F.Buonomo, *Eur Patent* 0 100 117 A1 (1984)

[36] A. Esposito C. Neri, and F.Buonomo, *Eur Patent* 0 102 655 A2 (1984)

[37] D.R.C. Huybrechts, L. De Bruyer and P.A. Jacbos, *Nature* (London) 345, (1990) 242-243.

[38] C. Neri, and F.Buonomo, *Eur Patent* 0 102 097 b1 (1986)

[39] P. Roffia, M. Padovan, *Eur. Patent* 0 208 311 A2 (1987)

CHAPTER 2: RESULTS AND DISCUSSION

2.1 LIQUID-PHASE OXIDATION OF BENZENE TO PHENOL WITH HYDROGEN PEROXIDE AND TS-1

2.1.1 Micro plant description

The laboratory scale micro-plant used for the oxidation of benzene to phenol in the liquid phase is an autoclave, and it contains two zones (Fig. 1):

1) The feeding Zone: it is necessary to feed slowly the HP aqueous solution using a syringe pump.
2) Reaction Zone: it is a 250 mL batch glass autoclave equipped with a stirrer; heating was provided by means of electric resistances (upper limits 250°C, 10 bar) where the catalyst is present and the reaction occurs. A safety disk is set to 10 bar.

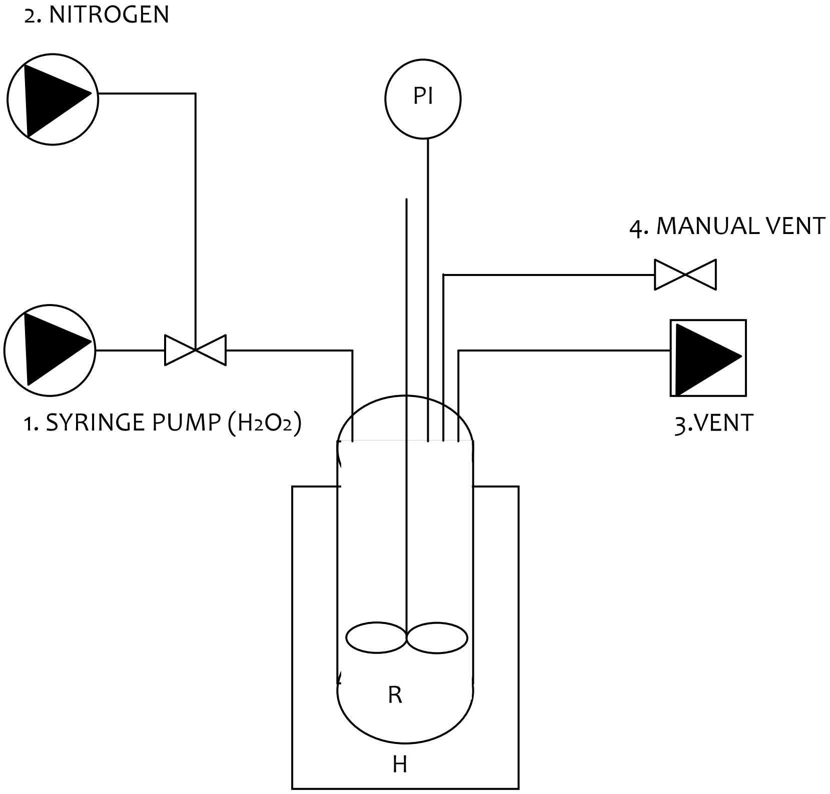

Fig. 1: Autoclave scheme: 1) a syringe pump to add slowly HP, 2) nitrogen mass flow meter to clean the HP feeding line, R: autoclave; H: heating system; PI: pressure indicator; 3) safety disk; 4) manual valve to vent the autoclave.

Catalytic tests were performed using the following procedure: first, the reactor was loaded with benzene, the solvent and the TS-1 catalyst. Then the mixture was heated up to the desired reaction temperature; at this point, the HP aqueous solution was fed to the reactor under stirring, during 30 minutes, by means of the syringe pump; after this, the reaction was left proceed for 1.5 hours more, for an overall reaction time that under standard conditions was 2 h. During this time, the HP was also completely consumed, as confirmed by iodometric titration; this is also important to avoid reactions due to residual unconverted HP when injecting the solution containing the reaction products for GC analysis[40,41], that may cause misleading determination of the products selectivity. As long as

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[40] T. Yokoi, P. Wu, T. Tatsumi, *Catal. Comm.* 4 (2003) 11-15.
[41] N. Ma, Z. Ma, Y. Yue, Z. Gao, *J. Mol. Catal. A* 184 (2002) 361-370.

there is no residual HP in the sample, GC analysis gives the result with high accuracy as by means of HPLC.

The following amounts of reactants, solvent and catalysts were used, unless otherwise specified: solvent volume (either methanol, or methanol + water, or sulfolane + methanol) 52 mL; HP aqueous solution (35%) 8.7 mL; benzene 0.1 mol; catalyst 1.17 g. The reactor operated at autogeneous pressure (about 3 atm for the reaction carried out at 80°C). We decided to use a sealed reactor (after preliminary tests carried out in an open system, equipped with a refrigerated condenser), because we soon realized that it was not possible to avoid benzene evaporation during reaction. This caused errors in the determination of benzene conversion and hence made not possible the determination of C balances. In the case of tests carried out under three-phase conditions, that also led to non-negligible formation of tars, we evaluated the amount of tars produced by means of a thin film evaporator, that allowed removal of monoaromatic compounds and calculate the weight yield of tars formed. This method is also systematically applied for the determination of tars in phenol hydroxilation to diphenols (Part C).

When the reaction mixture was triphasic, before analysis we add methanol to the cold slurry containing the reaction components, in order to obtain a single liquid-phase; the catalyst was separated by means of filtration. The reaction products were analyzed by means of GC, using a Thermo instrument equipped with FID and a semi-capillary column HP-5; oven temperature was programmed from 50 to 250°C.

2.1.2 Catalytic system: TS-1

In this work we report our attempts to selectively oxidize benzene (B) to phenol (PH) using hydrogen peroxide (HP) as the oxidant and TS-1 catalyst. In TS-1 titanium isomorphously replaces silicon in a tetrahedral site of the MFI silicalite lattice. This means that titanium is in four-fold coordination, but has a very strong tendency to go into six-fold coordination increasing the stability of the metal. The activity of TS-1 in HP activation is based on this concept. In addition, the spatial selectivity and specific local geometry of the molecular sieve structure provides some unique properties.

In literature two different mechanisms for the aromatic activation by TS-1 had been hypothesized: a radical mechanism and an electrophilic attack.

HP interacting with TS-1 forms a Ti-hydroperoxo group, Ti-OOH. Presuming a radical mechanism, the homolithic scission of the hydroperoxo specie could generate Ti-O• and •OH radical; the former species activate benzene, which then rearranges to yield phenol. Another possibility is that hydroxyl radicals attack the activated benzene releasing Ti-OH group. However a free radical chain pathway would show a statistical ratio of the products in phenol hydroxylation; on the contrary, yields and selectivity reported are an indication of spatial restrictions that inducing the attack on the aromatic ring by a Ti-centred species in the confined environment, finally leads to a para/ortho ratio which is close to 1[42].

On the other hand, the Ti-hydroperoxo group could have another role. In the heterolythic mechanism, the key species is an O atom (in the Ti-OOH moiety) that has a partial positive charge (δ+). As a consequence of this, the terminal OH of the titanium hydroperoxo group is the electrophilic species that attacks the aromatic ring[43]. This mechanism is well exemplified by van Steen et al[44] for phenol hydroxylation, but the same may occur also with benzene, with the difference that the electrophilic attack on the ring is less favoured because the positive charge cannot be delocalised on the OH phenolic group.

Usually, if the reaction rate is insensitive to radical scavengers (e.g., AIBN or benzoquinone), a non-radical mechanism is assumed, but considering the hydroxylation of benzene or phenol, indeed radical scavengers are produced in the reaction. Moreover, in phenol hydroxylation, hydroquinone is formed more selectively in a polar solvent, showing a strong influence of H-bonding effects; in apolar solvents, catechol may be the preferred product. On the basis of UV-Vis and EPR spectra, Ratnasamy identified two different Ti-superoxo species in equilibrium with the Ti-hydroperoxo species, Ti-OO$\bullet^-$ formed by reaction of Ti(IV) with HP, one associated to Ti incorporated in the framework and one associated to defective Ti sites[45]. The various species were claimed to be active in different types of reaction, either olefins epoxidation or aromatics hydroxylation. This

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[42] M.G. Clerici, *Top. Catal.* 15 (2001) 257-263

[43] J.S. Reddy, P.A. Jacobs, P. A., *Catal. Lett.* 37 (1996) 213

[44] U. Wilkenhoner, G. Langhendries, F. van Laar, G.V. Baron, D.W. Gammon, P.A. Jacobs, E. van Steen, *J. Catal.*, 203 (2001) 201-212

[45] V.N. Shetti, P. Manikandan, D. Srinivas, P. Ratnasamy, *J. Catal.*, 216 (2003) 461–467.

suggests that indeed various types of mechanisms can overlap, in function of the nature of active sites that form during reaction.

We prepared a series of TS-1 samples, using different conditions. The alkoxide precursors (silicon an titanium sources) were tetraethylorthosilicate (TEOS) and tetraethylorthotitanate (TEOTi). The templating agent was TPAOH (tetrapropyl ammonium hydroxide) in aqueous solution. After stirring, the resulting synthesis gel composition was: SiO_2- $xTiO_2$- 1.63 TPAOH- 23 H_2O. In a typical experiment, TEOTi was dissolved in TEOS. The clear yellow solution obtained was stirred for 15-20 minutes, and then TPAOH was added. The batch was kept in a water bath at 80°C for 4 hours, then the mixture was topped up to original volume with deionised water, transferred in a Teflon lined, stainless steel autoclave and heated at 170°C for 48 hours under autogeneous pressure. The autoclave was then cooled and the white gelatinous solution formed was centrifuged at 10000 rpm for 10 minutes. The surnatant liquid was discarded, deionised water was added and the process was repeated 4-5 times until the pH of the surnatant solution was close to neutral. A thermal treatment after synthesis was carried out in air at 550°C.

Table 1 summarizes the Si/Ti ratio of samples prepared.

Table 1. TS-1 samples prepared.

Samples labels	Si/Ti w/w ratio
TS-1 A	7.3
TS-1 B	4.2
TS-1 C	3.0
TS-1 D	2.3

The XRD powder patterns of the catalysts (Fig 2) were taken with Ni-filtered CuKα radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator. In all cases, clear evidence of the MFI structure as well as of high crystallinity was observed.

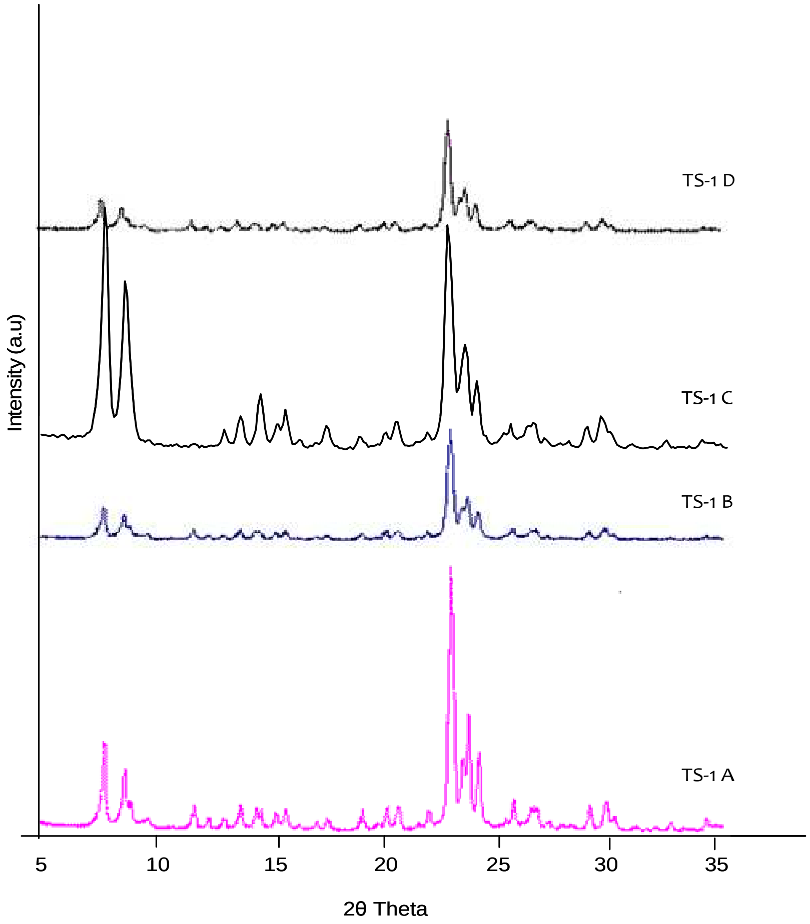

Fig. 2: X Ray diffraction pattern of samples TS-1 A; TS-1 B; TS-1 C; TS-1 D.

The crystal morphology and dimensions of TS-1 samples were recorded by means of Scanning Electron Microscopy (SEM) JEOL-JSM-T330-A (Fig 3). The crystal size was 0.5 ÷1 µm and the picture shows a uniform distribution of crystals. After thermal treatment no variation in the morphology or crystal size of the samples was observed. TS-1C shows a spherical form due to the spray-dryer treatment simulating the industrial use, so also particle size for this sample was higher. SEM images for samples A and B were quite similar, but it is important to underline that samples B has a higher amount of titanium. However sample D shows an aggregated nanophase around the TS-1.

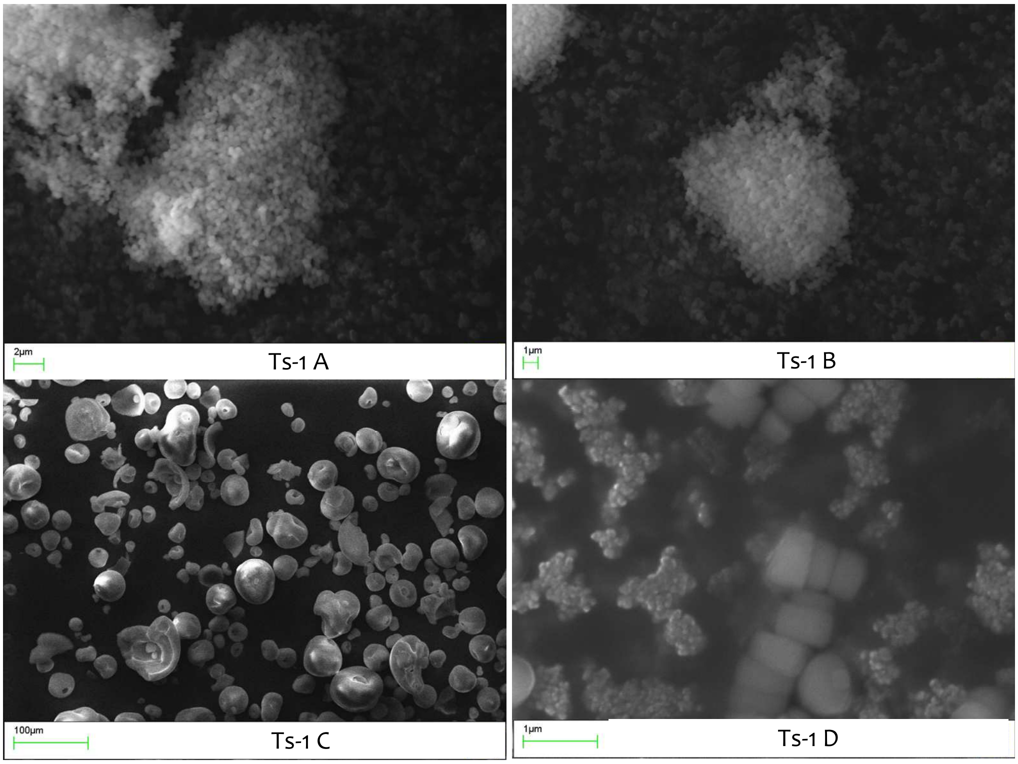

Fig. 3 SEM images of different TS-1: samples A, B, C, D.

Specific surface area assessment (Table 2) was carried out with a Micromeritics ASAP 2020 instrument. Calcined solids were heated up to 250 °C until a pressure of 30 μmHg was reached, then kept 120 min at this temperature and finally heated up to 250 °C and maintained for 30 min. This instrument measures the adsorption and desorption isothermal curve (at 77 K) by the volume of adsorbed/desorbed N_2, as a function of relative pressure. It is evident that sample TS-1 C has the lower surface area but also a different porosity distribution: mesoporosity is more accentuated then microporosity.

Table 2. Main morphological features of TS-1 samples.

	TS-1 A	TS-1 B	TS-1 C	TS-1 D
Si/Ti (w/w) ratio	7.3	4.2	3.0	2.3
Micropores diameter (Å)	5.80	5.95	6.00	5.80
Mesopores diameter (Å)	97	97	205	55
Specific Surface Area BET m^2/g	615	534	500	516
Micropores area m^2/g	486	420	387	412

External micropores area m^2/g	128	114	113	104
Micropores volume cc/g	0.200	0.175	0.160	0.170
Mesopores volume cc/g	0.142	0.132	0.346	0.055

Uv-Vis spectra were recorded in diffuse reflectance using a Perkin Elmer UV/VIS/NIR Lambda 19 instrument, equipped with an integrating sphere, between 190 and 1500 nm, with a scansion rate of 480 nm/min. After recording, spectra were transformed in F(R) by means of the Kubelka-Munk law. UV spectra (Fig 4) show the typical band at approx. 210 nm that is an indication of tetrahedral coordination of Ti atom incorporated in the framework structure. In sample TS-1 C, a band at 320 nm is also present. This band is due to the presence of an "anatase-like phase", with octahedral units of TiO_2, which is not active for oxidation reactions with HP. In particular, titanium dioxide decomposes HP decreasing the catalyst activity.

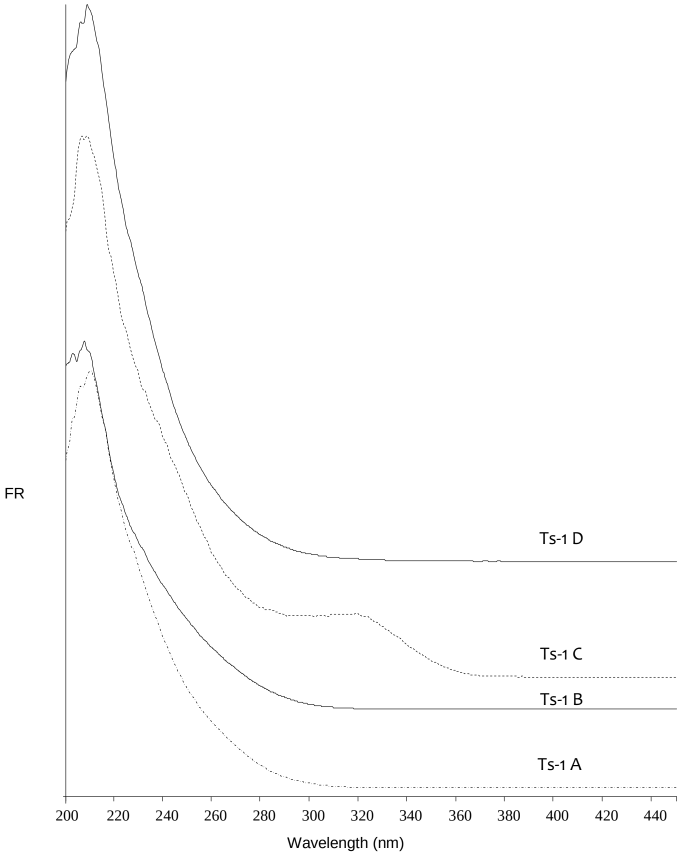

Fig. 4: UV-Vis DR spectra of samples TS-1 A; TS-1 B; TS-1 C; TS-1 D.

2.1.3 Reactivity tests

The catalytic tests with the TS-1 samples were carried out in a an autoclave at 80°C with benzene/HP (mol/mol) ratio 1, reaction time 2h, with methanol as the solvent and using a 35% HP aqueous solution. Results are summarized in Table 3.

Table 3. Results of catalytic tests

	Phenol Yield (%)	BQ Yield (%)	CT Yield (%)	HQ Yield (%)	Phenol Selectivity (%)
TS-1 A	1.7	0.2	0.03	0	90
TS-1 B	3.9	0.4	0	0	90
TS-1 C	4.8	0.8	0.4	0.4	75
TS-1 D	2.4	0.3	0.03	0	88

It is possible to observe that sample TS-1 C gave the highest activity, with a benzene conversion of 6.4%, but the selectivity was relatively low. Phenol yield improved increasing the amount of titanium in the chemical structure: TS-1 A < TS-1 B < TS-1 C. The aggregated nanophase may affect the activity of sample TS-1 D. This is not evident for TS-1 C, which holds anatase. Probably the high mesoporosity, induced by spray-dryer treatment, helps to keep the activity high in the transformation of benzene to phenol. In the same way the high yield to BQ may be due to the mesoporosity of this sample, that increases the possibility for phenol to interact with internal sites of TS-1, quickly reacting to BQ. TS-1 A and B show high selectivity, but low phenol yield.

These preliminary experiments suggest that mesoporosity may influence both activity and selectivity; therefore, it is necessary to find a good compromise between the titanium content and the mesoporosity. TS-1 C was then used for other experiments aimed at understanding the reaction network and the role of reaction parameters.

THE SOLVENT ROLE: WHICH IS BEST, BIFASIC OR TRIPHASIC ?

The literature agrees that the nature of the solvent is fundamental, and is the major parameter affecting catalytic performance[46]. In general, more polar solvents have little affinity with the hydrophobic surface of TS-1, especially in samples having lesser amount of defects and surface hydroxyl groups. Therefore, with polar solvents the pores are preferentially filled with apolar hydrocarbons (e.g., benzene), whereas more polar molecules diffuse more slowly because preferentially dissolve into the polar reaction medium. The opposite is true with less polar solvents (e.g, t-butanol); the partition coefficient is modified, and the concentration of apolar hydrocarbons inside pores is lower, that may imply a lower reaction rate.

Another important point is the interaction between the solvent and the active sites. For example, it is well known that methanol itself, although diffusing slowly due to its predominantly polar characteristics, may interact with Ti(IV), and contribute to the formation of a penta-coordinated site in which the positive charge on the O atom of the hydroperoxo species develops by interaction with the methanol proton[47].

However, the more controversial point concerns how the presence of either a triphasic or a biphasic system affects the performance. Kumar et al [48,49,50,51] report that the presence of a triphase system (two liquid phases and the solid catalyst) yields an excellent performance. Other authors, however, did not confirm on this effect [52]. In order to give an answer to the question on the role of solvent, we planned specifically designed experiments. Figure 5 shows the results of tests carried out keeping the benzene-to-HP molar ratio fixed, and the overall solvent volume too, while varying the relative amount of methanol and water in the solvent mixture. In all cases shown, the conversion of HP was higher than 92-95%. The system was biphasic in the left part of the Figure (where methanol was the prevailing solvent), but was triphasic in the right part (water as the prevailing

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[46] M. Ricci, D. Bianchi, R. Bortolo, in "*Sustainable industrial chemistry. Priciples, tools and industrial examples*" F. cavani, G. Centi, S. Perathoner, F. trifirò EDS. Wiley-VCH, Weiheim, 2009, 507-528

[47] M.G. Clerici, *Topics Catal.*, 15 (2001) 257-263.

[48] P. Mukherjee, A. Bhaumik, R. Kumar, *Ind. Eng. Chem. Res.* 46 (2007)8657-8664.

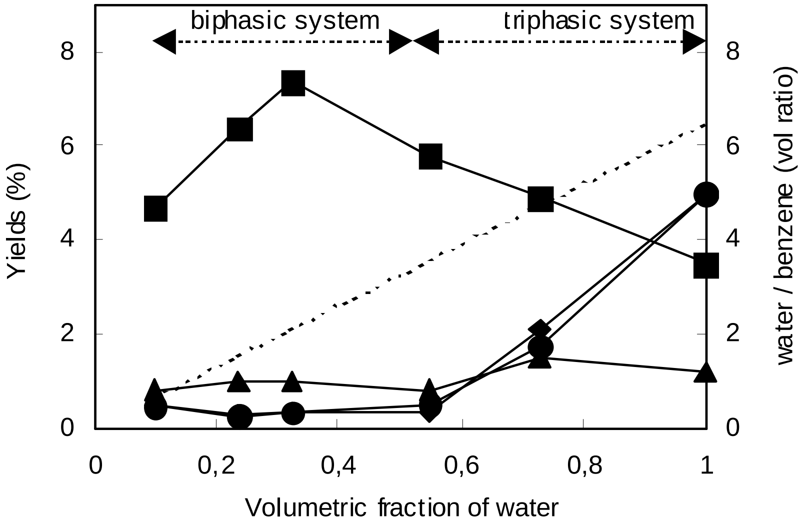
[49] R. Kumar, P. Mukherjee, A. Bhaumik, *Catal. Today*, 49 (1999) 185-191.

[50] A. Bhaumik, P. Mukherjee, R. Kumar, *J. Catal.*, 178 (1998) 101-107.

[51] R. Kumar, A. Bhaumik, *Microp. Mesop. Mater.*, 21 (1998) 497-504.

[52] D. Bianchi, L. Balducci, R. Bortolo, R. D'Aloisio, M. Ricci, G. Spanò, R. Tassinari, C. Tonini, R. Ungarelli, *Adv. Synth. Catal.*, 349 (2007) 979-986.

solvent).



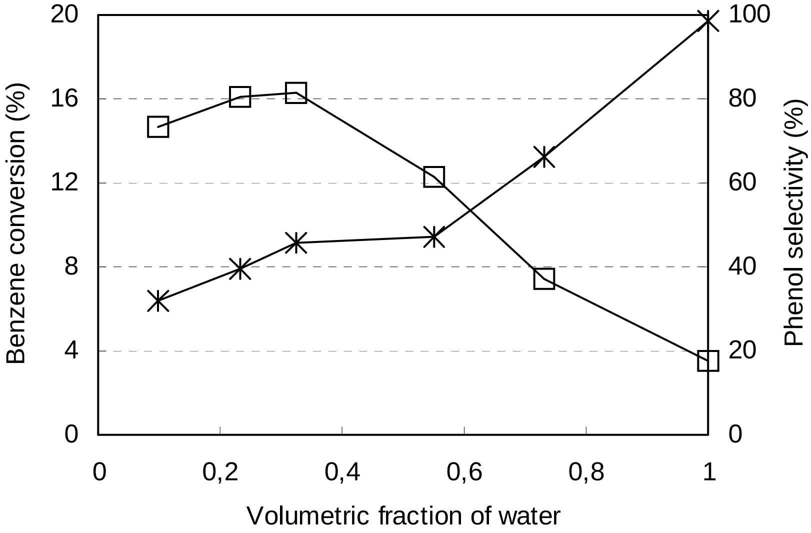


Fig. 5: Effect of the volumetric fraction of water in water+methanol solvent mixture on catalytic performance (water from the HP solution is included). Top Figure: Yield to phenol (■), CT (◆), HQ (●) and BQ (▲). Dotted line (right hand scale): volumetric water/benzene ratio (included water from HP solution). Bottom Figure: benzene conversion (✳), selectivity to phenol (□). Reaction condtions: HP sol (35%, 8.7 mL); benzene 0.1 mol (8.9 mL, 7.8 g); solvent (water+methanol): 41.4 g (52 mL); catalyst amount 1.17 g. Temperature 80°C; reaction time 2 h; benzene/HP 1/1 (molar ratio). Reaction system: sealed reactor.

An increasing amount of water led first to an increase of phenol yield, whereas the yield to by-products remained substantially constant (that clearly implies an increase of both benzene conversion and phenol selectivity); the maximum yield achieved was 7%. After that, i.e., when the system became triphasic, there was a dramatic increase of the yield to by-products, especially to hydroquinone (HQ) and catechol (CT), and a fall of the yield (and selectivity as well) to phenol; the reaction was also accompanied by the relevant formation of tars. Therefore, under the conditions examined, the presence of a tri-phase system has negative effects on catalytic behaviour. The most reasonable explanation for this effect is that in the absence of solvent molecules able to solvate the phenol produced and facilitate its counterdiffusion from inside the pores towards the external bulk liquid phase, consecutive hydroxilation has time to occur (in other words, the effective intraparticle contact time is very high); moreover, the high local concentration of aromatics may favour bimolecular condensation reactions yielding heavy compounds.

For what concerns the reaction in the biphasic zone, it is evident that there is an optimal relative amount of methanol and water. With low water content, the yield to phenol was low, and it increased when the molar fraction of methanol was decreased within the biphasic zone. This effect can be attributed to the fact that methanol adsorbed on the Ti site either hinders the generation of the Ti-OOH species, or it may affect the hydroperoxo reactivity, in agreement with Clerici et al[53].

An additional effect was on the selectivity to phenol; in fact, the yield to diphenols remained substantially unchanged when water was added to the system, hence the selectivity to phenol increased from the initial value of 73% up to 82%. This effect cannot simply be attributed to a kinetic effect (for example, as a consequence of the different relative concentration of reactants, either benzene or HP), since an increase of conversion (experimentally observed in correspondence of higher water molar fractions, inside the biphasic zone) should have led to a decrease of the selectivity to phenol, and not to an increase of it. Indeed, a more polar solution (because of an increased molar fraction of water) may increase the concentration of benzene inside pores, because of the lower competition for diffusion by the solvent molecules; this in principle might lead to an higher rate of benzene conversion and phenol formation (provided HP does

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[53] M.G. Clerici, Top. Catal. 15 (2001) 257-263

not become the limiting reactant), but this should obviously lead to a constant yield, and not to an increase of it.

Therefore, the effect shown is in favour of a modification of the active site reactivity; the Ti site at which both methanol and HP adsorb, oxidizes benzene to phenol, and oxidizes phenol to diphenols and benzoquinone (BQ) as well. However, when the molar fraction of methanol is decreased, the active site generated (no longer interacting with methanol, because of its decreased concentration), is more active in regard to benzene but less active in regard to the more polar phenol, which implies an increase of benzene conversion and a higher selectivity to phenol. One possible hypothesis is that without methanol, the active species generated by interaction between the Ti site and HP is a non-protonated, bridged $Ti(O_2)$ species, in equilibrium with a Ti(OH)(OOH) site, whereas in the presence of methanol the active site is Ti(ROH)(OOH), in which the interaction with phenol leads to its further oxidation.

The hypotheses made are further supported by the results of experiments shown in Fig. 6. In that case, we examined again the effect of an increased water-to-benzene ratio on catalytic behaviour, but experiments were carried out by keeping constant the volume of methanol solvent (differently from what we had done in the case of tests shown in Fig. 5), that is the methanol-to-catalyst ratio, and the benzene-to-HP molar ratio as well, while the amount of water added (and the overall volume solvent) was increased. In such a way, since the amount of methanol loaded was in all cases anyway sufficient for the interaction with the Ti sites, we expected a less pronounced effect on catalytic behaviour for an increased water amount. Furthermore, with these experiments it was possible to highlight the role of water, while maintaining a biphasic system (because of the presence of an amount of methanol sufficient to dissolve all components); indeed, in experiments of Figure 5 the formation of the triphasic system, for intermediate values of water molar fraction, may interfere with the effect of solvent variation.

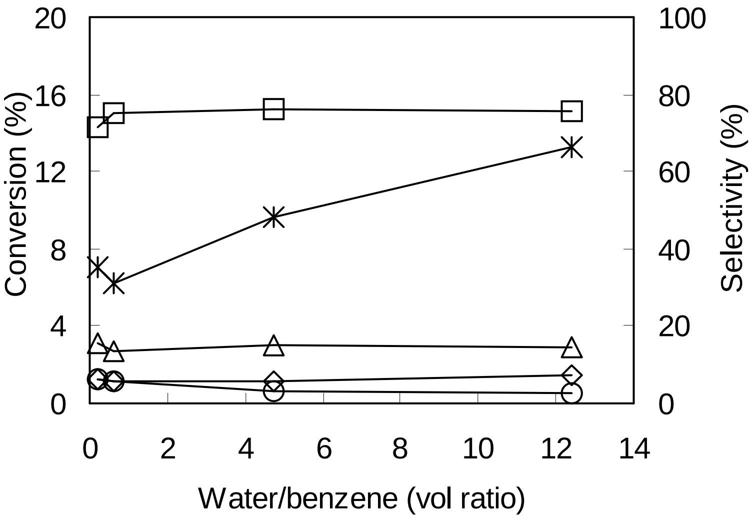

Fig. 6: Effect of the water/benzene volumetric ratio on catalytic performance. Temperature 80°C. Benzene 0.1 mol; methanol 52 mL; catalyst 1.17 g; the amount of water was increased (therefore, the total volume changed); benzene/HP molar ratio = 1. Biphasic system. Symbols: Benzene conversion (✳), selectivity to phenol (□), CT (◇), HQ (○) and BQ (△). Reaction system: sealed reactor.

Once again, the benzene conversion increased; worth of note, for a similar interval of variation of the water-to-benzene ratio (i.e., from 1 to 3), the increase of conversion was only of a few %, that is, lower than that observed for tests in Figure 5; also in this case, the phenomenon observed cannot be attributed to a simple kinetic effect, since an increase of the water-to-benzene ratio in this case implied a decrease of HP concentration (that was not the case for tests of Figure 5), that should have led to a decrease of the rate of benzene conversion, and not to an increase of it. Also the effect on selectivity was less pronounced than in the case of tests of Figure 5.

These results confirm that one relevant aspect for the catalytic performance is the relative amount of the three organic components of the reaction mixture: (a) methanol, that although diffusing slowly inside pores interacts with the Ti sites and affects the characteristics of the site; (b) water, the more polar component, that is the component with the lower affinity with the TS-1 porosity, but that may anyway react with tetrahedral Ti sites and hydrolyze the Ti-O-Si site, so rendering the Ti more prone to generate the active species by interaction with HP, and (c) benzene, the less polar component, and also that one having the greater affinity for the hydrophobic intraparticle surface of the catalyst.

AN ANALYSIS OF THE REACTION NETWORK

Data plotted in Figures 5 and 6 show that by-products of the reaction were HQ, CT and BQ, as well known from the literature. Under triphasic conditions, there was also the formation of tars. BQ formed in amount greater than diphenols, but the opposite was true when the reaction was carried out in triphasic conditions. It is also evident from tests reported in Figure 5 that the relative contribution of the consecutive reactions of phenol hydroxylation to diphenols and the oxidation of HQ to BQ is not simply a function of benzene conversion, but is also affected by the presence of methanol solvent and hence by the characteristics of the active site. It is reported in the literature that in phenol hydroxylation the formation of HQ occurs preferentially on intraparticle Ti sites, whereas CT forms mainly on external sites, because of steric restrictions in the pores. However, results shown in Figures 5 and 6 evidence similar behaviours for the two isomers in response to changes in solvent composition, that would suggest that the formation of both compounds occurs over the same types of sites, either intraparticle or interparticle sites.

Since the formation of BQ should normally occur by phenol two-step oxidation (first to HQ and then to BQ), it may be reasonable to expect that the concentration of HP affect the distribution of products. Therefore, tests were carried out by using various concentrations of HP; the molar ratio between benzene and HP was changed, but the overall volume of the aqueous solution of HP was maintained constant. The reaction time and temperature (2h and 60°C) were chosen so as to obtain low benzene conversion and better highlight the effect of HP concentration on selectivity to the products of primary oxidation. Moreover, the overall amount of water was kept low, in order to develop biphasic systems throughout all the experiments.

Figure 7 reports the results of these experiments. Surprisingly, at these conditions there was no formation of CT and HQ, but only that of BQ; the selectivity to this latter compound increased when the molar ratio between benzene and HP was decreased, and corresponding the selectivity to phenol declined. The increase of HP concentration also accelerated the benzene transformation, and in fact the overall benzene conversion increased.

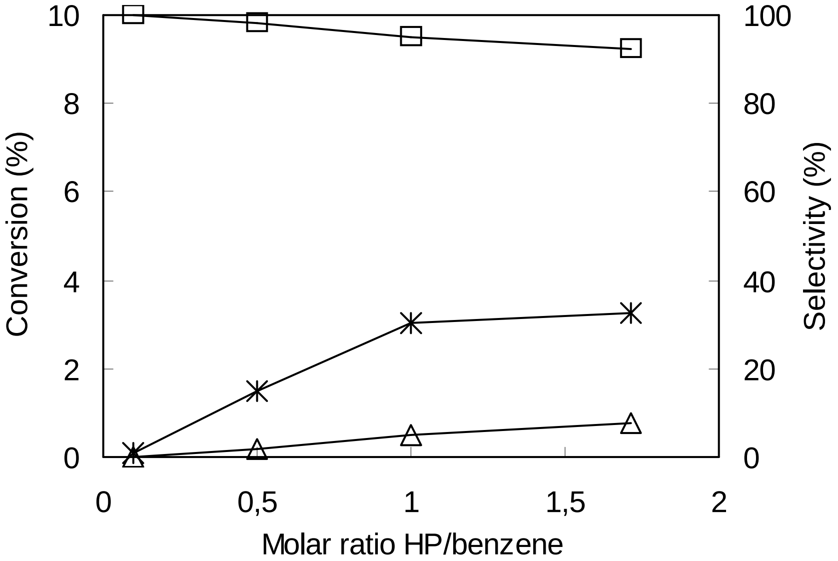

Fig. 7: Effect of the HP/benzene molar ratio on catalytic performance. Temperature 60°C; reaction time 2h; benzene 0.1 mol; HP sol. 8.75 mL (at varying concentration); solvent: methanol 52 mL; TS-1 1.17 g. Note that the ratio between water and benzene is changed, but due to the large excess of methanol the system is always biphasic (single liquid phase). Symbols: Benzene conversion (✳), selectivity to phenol (☐) and BQ (△).

These experiments suggest that phenol is oxidized to HQ inside the pores, and the latter is very quickly transformed into BQ, before it may counterdiffuse towards the bulk phase. In other words, the reactivity of HQ is so high that there is no chance to save it from consecutive oxidation, as long as it is inside the TS-1 pores. In order to confirm this hypothesis, we carried out tests at increasing reaction time, 60°C, and using an HP concentration at which there was only the formation of phenol (the first experimental point in Figure 7), to distinguish between truly primary and secondary products. Figure 8 shows the results of this experiment, that is, the effect of the reaction time on selectivity to CT, HQ and BQ.

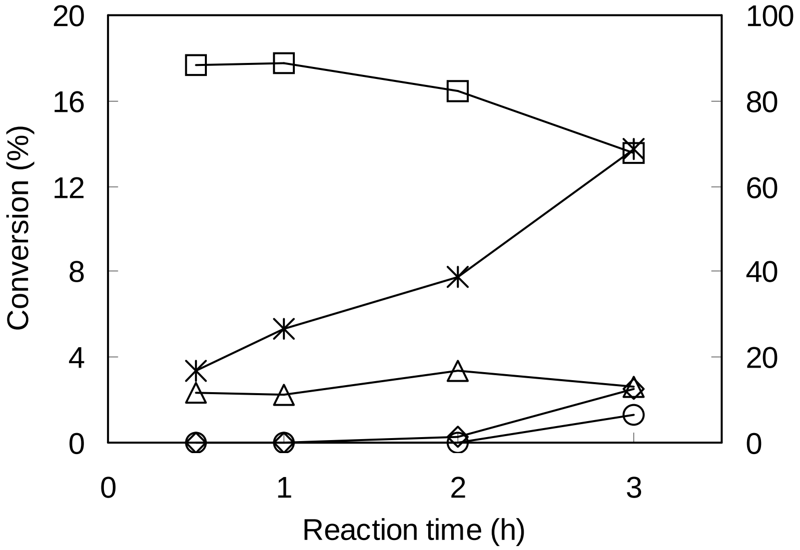

Fig. 8: Effect of reaction time on catalytic performance in benzene hydroxylation with diluted solution of HP (3 wt% in water). Symbols: Benzene conversion (✳), selectivity to phenol (□), CT (◇), HQ (○) and BQ (△). Solvent methanol. Temperature 80°C, reaction time: 2h, HP 3 % p/p (50 mL); benzene 0.1 mol (8.9 mL, 7.8 g); benzene/HP =1 (molar ratio); solvent: methanol 41.4 g (52 mL); TS-1 amount 1.17 g. Reaction system: sealed reactor.

These data definitely confirmed the hypothesis made: CT and HQ showed both the classical behaviour of a kinetically secondary product, obtained by consecutive oxidation of phenol; BQ instead was clearly a primary product of oxidation. This confirms that a fraction of phenol, once formed, is very quickly oxidized to HQ and then to BQ before it may get out of the porous TS1 structure. Concerning HQ and CT, one possible hypothesis is that phenol, after it has counterdiffused in the bulk liquid phase, it may either diffuse again into the porous structure, or more likely react over the external sites, yielding the two dihydroxylated isomers. In fact, if the consecutive oxidation of phenol to HQ occurs inside pores, the latter should be once again oxidized quickly into BQ. Indeed, as a matter of fact, results clearly indicate that there is no kinetic relationship between HQ and BQ. This hypothesis is also supported by the fact that the hydrophobic environment in TS-1 porosity makes intraparticle diffusion of benzene quite easy, whereas the opposite is true for the more polar (and more water-soluble) compounds, that is, HQ and CT. As reported in literature[54], with

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[54] U. Wilkenhoner, W.L. Duncun, K.P. Moller, E. van Steen, *Microp. Mesop. Mater*. 69 (2004) 181-186.

methanol as a solvent the diffusivity of phenol in TS-1 is larger than that of CT and HQ, which are approximately identical.

Worth of note, a similar behaviour was recently reported for the same reaction catalyzed by TS-1 PQ [55], with an initial selectivity to phenol and BQ that was higher than zero; however, this result was not discussed in that paper.

Important implication for this result is that indeed the only intracrystalline products of reaction are phenol and BQ, whereas CT and HQ likely are intercrystalline products. Hence it is expected that the crystal size of the TS-1 may affect the ratio between phenol and BQ, since a more crystalline materials, in which the effective residence time of reactants and products is higher, will lead to a lower initial selectivity ratio between the two kinetically primary product, being the chemically consecutive reaction of phenol transformation to HQ and BQ more favoured. On the other hand, the formation of the kinetically secondary products, HQ and CT, is expected to be principally a function of benzene conversion and of the characteristics of surface sites.

An alternative interpretation is that indeed the formation of HQ and CT occurs in the bulk liquid phase by means of radicalic reactions between phenol and ·OH radicals (see the part on mechanisms for benzene and phenol hydroxylation), because phenol is much more reactive than benzene. Both dihydric alcohols are not oxidized in the bulk because the oxidation of, say, HQ to BQ does not imply an attack of the hydroxy radical on the ring, but a different mechanism, likely including the homolithic scission of the HO-ϕ-O-H bond to generate HO-ϕ-O·. This reaction may instead occur inside the TS-1 pores catalysed by, e.g., the TiO· moiety, with rapid oxidation of the HQ formed (CT being instead unfavoured because of steric reasons) to BQ.

In conclusion, these data indicate that key points to increase the selectivity to phenol in benzene oxidation are:

1. To shorten the mean path of phenol inside pores (or to accelerate its counterdiffusion), in order to save it from consecutive oxidation to HQ and then to BQ.
2. To limit the reaction in the bulk liquid of phenol with radicals generated by HP decomposition. One possibility might be to use a

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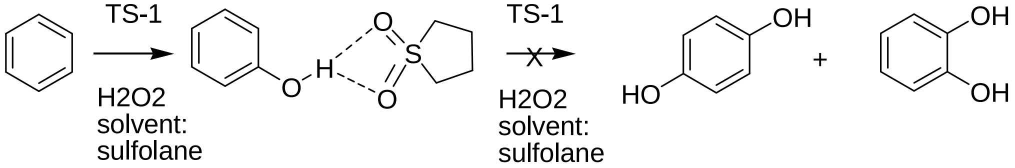
[55] P. Chammingkwan, W.F. Hoelderich, T. MongkHonsi, P. Kanchanawanichakul, *Appl. Catal. A*, 352 (2009) 1-9.

solvent that dissolves phenol, that does not dissolve HP and that does not enter the TS-1 porosity. In such a way, once phenol has left the hydrophobic environment of TS-1, it would be dissolved in a separate phase from HP. The use of a radical scavenger (RS) also might be useful, but indeed it is necessary to use a RS that is more efficient in trapping radicals than diphenols themselves.

THE USE OF SULFOLANE CO-SOLVENT

In the literature, the use of sulfolane is claimed to have beneficial effects on selectivity to phenol[56]. In other words, it is claimed that the coordination of phenol inside the TS-1 pores saves it from any consecutive transformation to CT and HQ.



The authors hypothesize that the increased selectivity may be due to the formation of a sterically hindered species that cannot enter the TS-1 pores, thus allowing phenol to remain relatively protected towards further oxidation. However, this hypothesis seems incorrect, for the following reason: if a sterically hindered complex is hypothesized, it shouldn't form inside TS-1 pores, which means that sulfolane should have no effect on phenol consecutive oxidation to HQ (a reaction that in the literature is reported to occur inside the TS-1 pores). On the other hand, the hypothesis of a bulky complex would fit with our results in the case sulfolane had an effect only on CT and HQ (formed outside of the TS-1 crystalites), and not on BQ (formed inside TS-1 porosity). In other words, we hypothesize that the coordinative effect of sulfolane plays its effect in the bulk liquid phase, NOT inside the TS-1 pores, saving phenol from consecutive oxidation to either CT or HQ. This is not so much due to steric reasons, but probably because sulfolane is a polar molecule (notwithstanding the apolar C4 part), soluble in water, and probably its access in TS-1 hydrophobic pores is not allowed,

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[56] L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari, R. Ungarelli, *Angew. Chem. Int. Ed.*, 42 (2003) 4937-4940.

at least when less polar molecules (e.g., methanol) are present in the reaction medium; these latter molecules have preferential access to the TS-1 pores, and sulfolane then would remain in the bulk liquid. On the other hand, it cannot be excluded that in the presence of a large amount of water solvent (e.g., at low benzene-to-water ratio), also sulfolane may access to TS-1 porosity.

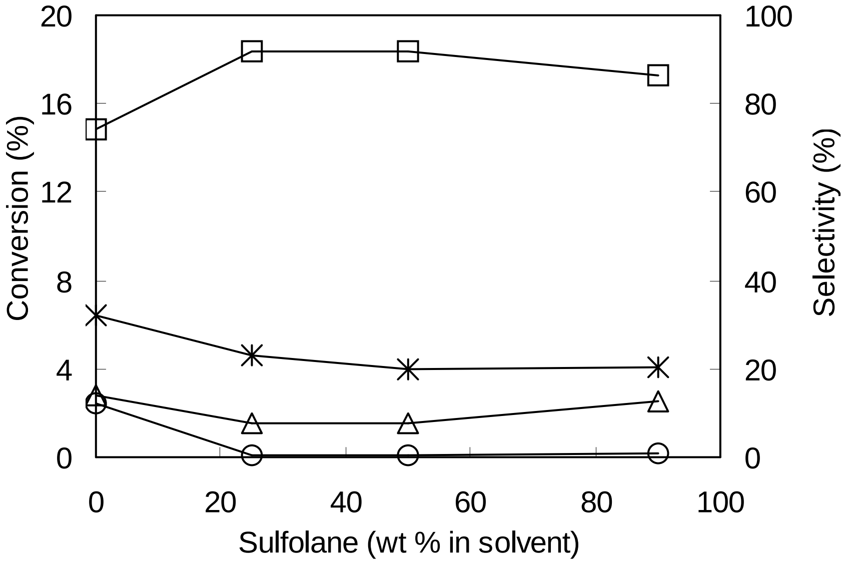

Fig. 9: Effect of the sulfolane content in sulfolane/methanol solvent mixture on catalytic performance in benzene hydroxylation with 35% HP. Symbols: Benzene conversion (✳), selectivity to phenol (☐), CT + HQ (○), and BQ (△). Temperature 80°C, reaction time: 2h; benzene 0.1 mol (8.9 mL, 7.8 g); benzene/HP =1 (molar ratio); initial solvent volume: 52mL; TS-1 amount 1.17 g. Reaction system: sealed reactor.

Results shown in Figure 9 definitely support our hypothesis. Tests were carried out by changing the sulfolane content in the sulfolane/methanol solvent mixture; it is shown that the effect on BQ selectivity was minimal, whereas the selectivity to diphenols went down to almost zero. The selectivity to phenol was the higher with 25-50 wt% sulfolane in the solvent mixture. There was an effect on conversion, that decreased, too; however, this change was not great enough to be the only reason for the drastic fall in selectivity to diphenols.

Results of Figure 9 were obtained under conditions inhibiting the access of sulfolane to the TS-1 porous system, because concentrated HP was used, and the amount of methanol solvent was largely prevailing over the amount of water. It is interesting to look at data obtained under conditions that in principle should favour the access of sulfolane to pores, e.g., when diluted HP solutions are used (while the HP-to-benzene ratio is kept constant). These results are illustrated in Figures 10 (HP solution 7.6%) and 11 (HP solution 3%); in these experiments, the benzene-to-HP ratio was always 1, whereas the ratio water-to-benzene was increased, due to the use of the diluted HP solution.

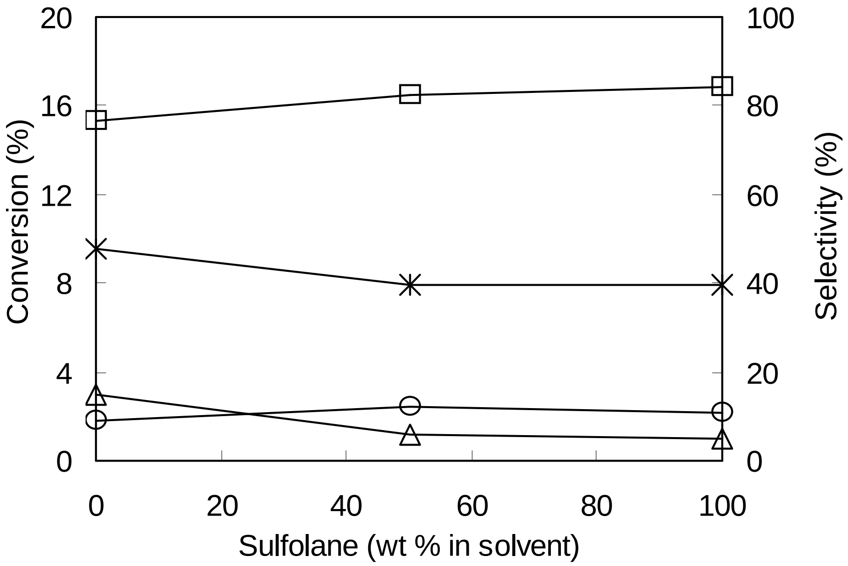

Fig. 10: Effect of the sulfolane content in weight in sulfolane/methanol solvent mixture on catalytic performance in benzene hydroxylation with 7.5% HP. Symbols: Benzene conversion (∗), selectivity to phenol (□), CT + HQ (○), and BQ (△). Temperature 80°C, reaction time: 2h; benzene 0.1 mol (8.9 mL, 7.8 g); benzene/HP =1 (molar ratio); initial solvent volume: 52mL; TS-1 amount 1.17 g. Reaction system: sealed reactor

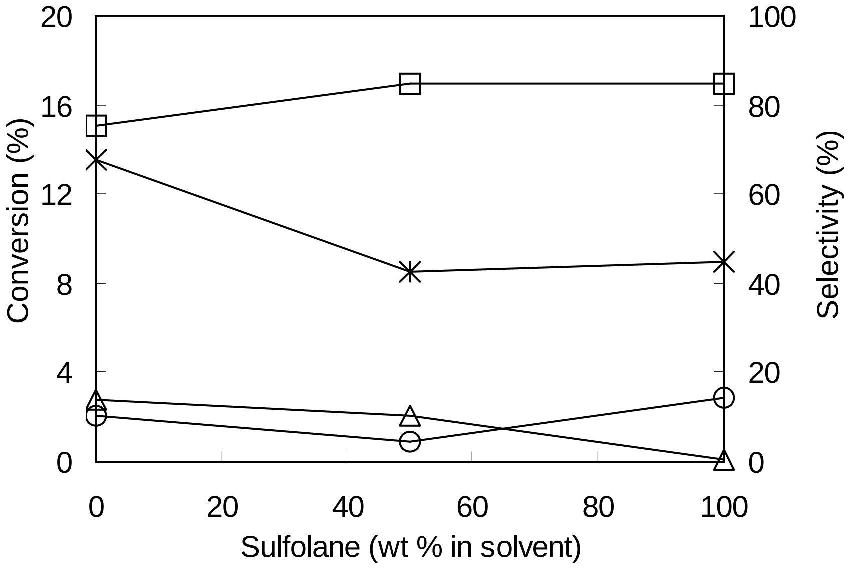

Fig. 11: Effect of the sulfolane content in weight in sulfolane/methanol solvent mixture on catalytic performance in benzene hydroxylation with 3% HP. Symbols: Benzene conversion (∗), selectivity to phenol (□), CT + HQ (○), and BQ (△). Temperature 80°C, reaction time: 2h; benzene 0.1 mol (8.9 mL, 7.8 g); benzene/HP =1 (molar ratio); initial solvent volume: 52 mL; TS-1 amount 1.17 g. Reaction system: sealed reactor

The effect of sulfolane with the diluted HP solition (7.5% HP) was the opposite of that obtained with the concentrated HP solution (Figure 9); in fact there was a remarkable effect on BQ selectivity (that instead decreased when the 50% sulfolane mixture was used), whereas there was no effect on selectivity to CT + HQ. This provides a clear indication that under reaction conditions at which the diffusion of sulfolane into TS-1 pores is more favoured, sulfolane yields to an enhancement effect on the selectivity to by-products formed within pores, and a less marked effect on those formed outside the TS-1 crystalites.

Less clear is the effect of sulfolane with extremely diluted HP solutions, that is, under conditions leading to the three-phase system. In this case, the presence of 50% sulfolane leads to a drastic fall of benzene conversion, and to an increase of the selectivity to phenol, with a corresponding decrease of selectivity to both BQ and CT+HQ; with only sulfolane solvent, however, the selectivity to BQ becomes nil, and that to diphenols increases remarkably

Finally, Figure 12 sums up the results achieved with 100% sulfolane solvent (that is, without methanol at all), and increasing the HP concentration (that is, increasing the benzene-to-water ratio, while keeping constant the HP-to-benzene molar ratio). It is interesting to compare this Figure with results plotted in Figure 6, where the effect of the same parameter on reactivity behaviour is reported, for tests carried out in methanol solvent. It is shown that in both cases an increase of the ratio led to an increase of benzene conversion; in the case of methanol solvent, this was attributed to the interaction between methanol and Ti sites that was affected by the water content in the reaction medium. A similar effect is shown in Figure 12; at high water-to-benzene ratio (low HP concentration), sulfolane likely diffuses inside TS-1 pores, and may interact with Ti sites; moreover, the selectivity to BQ is strongly lowered, because of the protecting effect on phenol. At low water-to-benzene ratio, the diffusion of sulfolane is less facilitated; in this case the main effect is on the selectivity to diphenols (formed out of the TS-1 crystalites), that becomes very low.

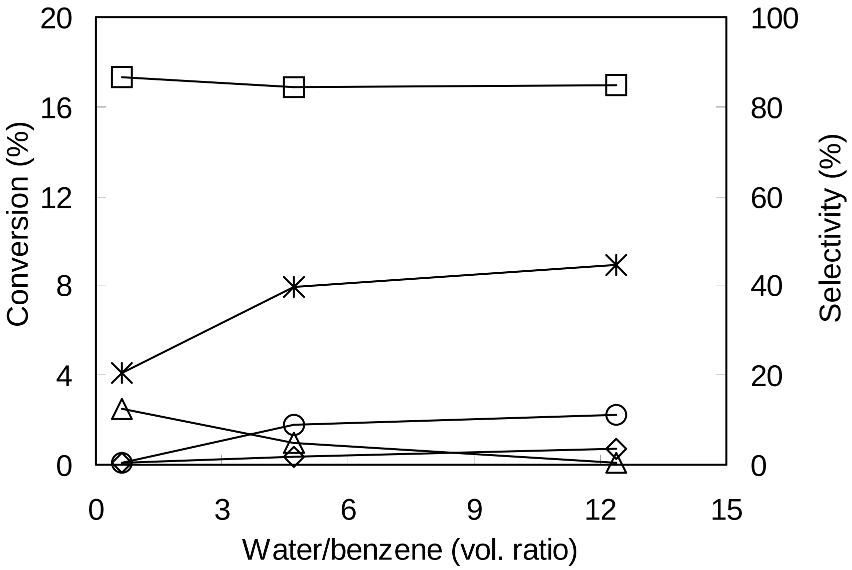

Fig. 12: Effect of the water/benzene volumetric ratio on catalytic performance. Temperature 80°C. Benzene 0.1 mol; sulfolane 32 mL; catalyst 1.17 g; the amount of water was increased (therefore, the total volume changed); benzene/HP molar ratio = 1. Biphasic system. Symbols: Benzene conversion (∗), selectivity to phenol (□), CT (◇), HQ (○) and BQ (△). Reaction system: sealed reactor.

CHAPTER 3: CONCLUSIONS

Titanium silicalite (TS-1) is one of the most studied catalysts in last decades. During my work, different TS-1 samples were synthesized and tested in benzene hydroxylation to phenol; this led us to conclude that morphological and structural characteristics of the catalyst may greatly affect the catalytic behaviour.

After identification of the best catalyst in terms of activity, experiments were carried out trying to focus on the reaction network. The nature of the solvent is important, since it does interact with the Ti active site, but also affects the diffusivity of reactants inside pores. We propose an original reaction network, in which the key point is the diffusion rate of phenol from the TS-1 pores towards the bulk liquid phase. Moreover, results of experiments allowed us to conclude that radicalic reactions occurring in the bulk may also affect the catalytic performance.

PART C: The oxidation of phenol to diphenols with hydrogen peroxide and TS-1

CHAPTER 1: INTRODUCTION

Due to their several applications, ranging from photography, to pharmaceutical and polymers industries, hydroquinone and catechol and synthetic procedures aimed at producing them are widely studied. Nowadays, there are three processes that synthesize diphenols: the Rhône Poulenc (now Rhodia), the Brichima and the EniChem (now Borregaard) processes. The oxidizing agent for all of them is hydrogen peroxide (HP), but with different catalytic systems.

The Rhône Poulenc process operates at 90°C in an acidic medium, using concentrated HP and phenol with a molar ratio of 1/20. Perchloric acid is the catalyst (electrophylic catalysis) while phosphoric acid is used as a masking agent to prevent degradation via radical mechanism. A peroxonium ion is formed $[HOO(H_2)^+]$, which is considered the real oxidizing species. The Brichima process is based on Fenton-like radical reaction that uses ferrocene or cobalt salts as catalysts, forming hydroxyl radicals that react with phenol (radical catalysis). The EniChem process uses the titanium silicalite-1 (TS-1) as catalyst, containing Ti(IV) (in a silica matrix), that form peroxo complexes with HP.

Among the various available methods, phenol hydroxylation using TS-1 catalyst is considered the most profitable one, offering advantages over the other processes. A great benefit of TS-1 is that it gives higher phenol conversion and para-hydroxylation selectivity, which is commonly interpreted as a shape selectivity effect; the performance however is affected by several parameters, such as the nature of solvent[57,58], reaction conditions[59] and preparation methods[60]. In general, HP conversion in phenol hydroxylation with TS-1 is higher than 85% whilst catechol-to-hydroquinone ratio is between 0.5 – 1.5, and their selectivity based on phenol is higher than 92%.

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[57] A.Tuel, S. Moussa-Khouzami, Y. Ben Taarit, C. Naccache, *J. Mol. Catal.*, 68 (1991) 45-52.

[58] U. Wilkonhöner, G. Langhendries, F. van Laar, G. Baroni, D. W. Gammon, P. A. Jacobs, E. van Steen, *J. Catal.*, 203 (2001) 201-212.

[59] A. Thangaraj, R. Kumar, S.P. Mirajkar, P. Ratnasamy, *J. Catal.*, 131 (1991) 294.

[60] A.J.H.P. van der Pol, J.H.C. van Hoof, *Appl. Catal.*, 92 (1992) 93.

Catechol itself is used as a photographic developer, analytical reagent and oxidant scavenger, but its derivates are more important than catechol itself; examples include guaiacol (reagent for the synthesis of vanillin, 4-hydroxy-3-methoxybenzaldehyde), veratrole but also ethylvanillin (3-ethoxy-4-hydroxybenzaldehyde), eugenol (2-methoxy-4-allylphenol), safrole (5-allyl-1,3-benzodioxole) and piperonal, that are fragrances in perfumery. In medicine some of its derivatives are used as antihypertensive, vasodilator, antispasmodic drugs and for antiparkinsonism. Bayer developed also some insecticides from catechol. On the other hand hydroquinone is another important molecule for the chemical industry; in fact it is used in photographic applications (principally for black and white films, photochemical machining, microfilms and X-ray films), in the rubber industry (for the production of antioxidants and antioxonans), and also as a monomer inhibitor in the vinyl industry, to avoid free radical polymerisation during the process and the storage.

The two structural isomers have different uses and markets; therefore it would be economically convenient to produce each one of them with high selectivity in a specifically dedicated process. For example, the demand for hydroquinone is larger than that for catechol; therefore, the former compound has a higher market value.

The hydroxylation of phenol with the EniChem method already produces more hydroquinone than the other processes, but the catechol formation is relevant also in this case. This was the main reason that pushed research activities (and production of papers and patents) aimed at the enhancement of the para selectivity in phenol hydroxylation with TS-1. Examples of factors investigated include the solvent effect and the role of post-synthesis modifications of TS-1.

For example, it was demonstrated that there is a different interaction of the solvent with the active sites in TS-1, in function of the nature of the solvent itself, either protic or aprotic. In fact Wilkhonhöner et al suggest that in presence of methanol or water as the solvent, the coordination sphere of Ti sites in TS-1 increases from 4 to 5 or 6. A five –member ring with hydrogen bonds between methanol and peroxo group at the Ti site has often proposed as the active intermediate complex for TS-1 catalysed reactions. In this case phenol (hydrogen bonded to the solvent OH groups), will approach the titanium site, with the OH group pointing away from the titanium site and finally yielding hydroquinone. On the other hand, in non-protic solvent, phenol can take the role of the protic solvent molecule and the formation of catechol is favoured.

Lin et al [61] declared that changing the morphology of TS-1 it is possible to improve the catalytic performance creating a titanium-silicalite molecular sieve possessing hollow cavities. In fact a post-synthesis treatment of a calcined TS-1 with tetrapropyl ammonium hydroxide led to hollow TS-1 crystals. In this way it is possible to obtain crystals with the same chemical composition and approximately the same size as those of the original ones, but with a different distribution of Ti species. The result of recristallyzation process, that make an hollow catalyst, is an higher activity in comparison with the dense one, and in some cases, also an higher selectivity to hydroquinone.

As far as the effect of light intensity during phenol hydroxylation with TS-1 is concerned, Klaewkla et al[62] reported that at 60°C, under 500W light intensity, in 2 h the phenol conversion reached 50% and hydroquinone selectivity increased while catechol formation decreased. This effect is due to the more efficient formation of hydroxyl radicals from HP.

In this work the effects of solvent and co-solvent, particle size and operative temperature have been investigated in a batch reactor, in order to favour the hydroquinone formation instead of catechol while keeping constant the phenol conversion. Water as solvent was found to lead to the lower catechol/hydroquinone ratio, but its practical use may cause problems during catalyst filtration. Therefore it was decided to use an extruded catalyst based on TS-1 and test it in a fixed bed reactor, so avoiding the filtration step.

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[61] M. Lin, X. Shu, X. Wang, B.Zhu, *Pub N° US* 2001/0021369

[62] R. Klaewkla, T. Rirksomboon, S. Kulprathipanja, L. Nemeth, P. Rangsunvigit, *Catal. Comm.*, 7 (2006) 260-263.

CHAPTER 2: RESULTS AND DISCUSSION

2.1 THE LIQUID PHASE OXIDATION OF PHENOL TO DIPHENOLS WITH HYDROGEN PEROXIDE AND TS-1

2.1.1 Micro plant description: semi-batch system in a continuous stirred reactor

This semi-batch system is a flask (three-necked glass reactor) equipped with a refrigerant to avoid the loss of solvent, a thermometer to control the temperature inside the liquid phase and an inlet line to feed the aqueous solution of HP. In this case the catalyst was used in powder form and it was mixed with the reagent mixture containing phenol and solvents. A magnetic hot plate stirred the mixture and heated an ethylene glycol bath until the temperature of the mixture reached the boiling point; then the HP was added slowly using a syringe pump. Usually the reaction time was 5 hours, but in some cases it was changed (as detailed in Figures captions). About 1 h of digestion time was necessary to convert the unreacted HP, in order to avoid problems during GC analysis using a GC5890 SeriesII with Rtx5 column and heating from 50°C to 250°C. The amount of unreacted HP was checked by iodometric titration, while conversion and selectivity were measured by GC using the internal standard method (veratrole is the internal standard), after filtration of the catalyst.

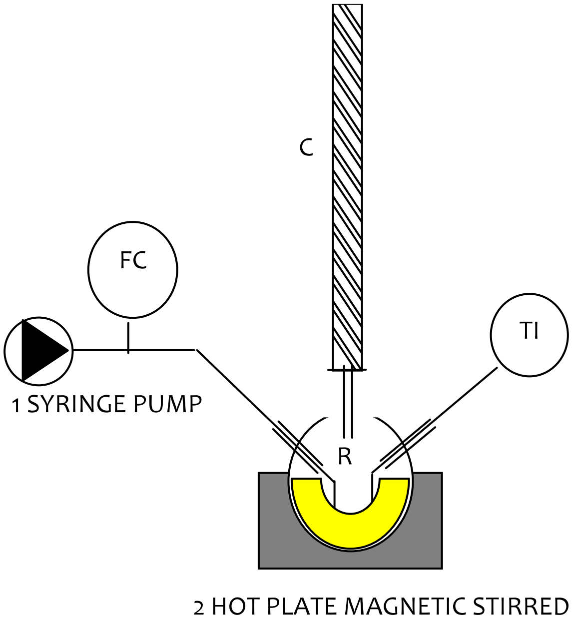

Fig. 1: Laboratory Micro-plan scheme: FC flow controller is the syringe pump; R reactor: volumetric flask; TI temperature indicator: thermometer; C refrigerant.

2.1.2 Micro plant description: semi-batch system in a fixed-bed down-flow reactor

This system is more complex than the previous one. It is a fixed-bed where the liquid phase containing phenol, solvents and products recirculate continuously, while HP is fed slowly during the reaction time. This plant was realized with the aim of avoiding the filtration of TS-1 and at the same time of simulating a CSTR, in order to compare the results obtained in the fixed-bed reactor with those of the stirred batch one. This system includes 3 zones:

1. Feeding Zone: it is necessary to feed an aqueous solution of HP slowly; also in this case a syringe pump is used.
2. Reaction zone: is a glass reactor that contains the extruded catalyst, in a fixed-bed. The HP solution is fed directly on the catalyst, while the re-circulating phenol solution is fed at the top of the reactor. The temperature of the catalytic bed is increased by means of a thermostat (heating fluid ethylene glycol), and the catalyst temperature is measured by means of a thermocouple. In order to work safely, we set up an indirect level controller, precisely a tube connecting the head of the reactor with the hold-up zone.
3. Hold-up zone: this is a hot and stirred flask where the mixture is collected and mixed before recycling. It is also a sampling point, and a system to maintain the atmospheric pressure at the head of reactor (overpressures could be due to HP rapid decomposition inside the reactor). A refrigerant is needed to condense the vapour from the reaction mixture and eventually also from the head of the reactor. In this way, if obstruction in the reactor causes an overflow, the liquid in excess goes to the collection tank. The temperature in the tank is controlled by a thermometer and regulated by a stirred hot plate that works independently from the thermostat.

The operative conditions were quite similar to those used with the stirred batch reactor; however, the temperature in the fixed bed was kept lower, to avoid the boiling of the solution in the catalyst bed, and also the temperature of the tank was kept lower in order to limit the by-products formation. The recycling flow can be regulated (160-330 ml/min), but anyway it was kept much higher than the inlet feed of the HP solution (0,023 ml/min), in order to better simulate a CST reactor. The start-up procedure requires that the mixture containing phenol and solvent is first loaded in the tank and heated. When the desired temperature is reached, the recycle flow is started. After the hot liquid mixture has flood the catalytic bed, it is possible to stabilize the temperature of the solid using the thermostat. Only after all the temperatures have been stabilized, the HP solution is fed and the reaction starts.

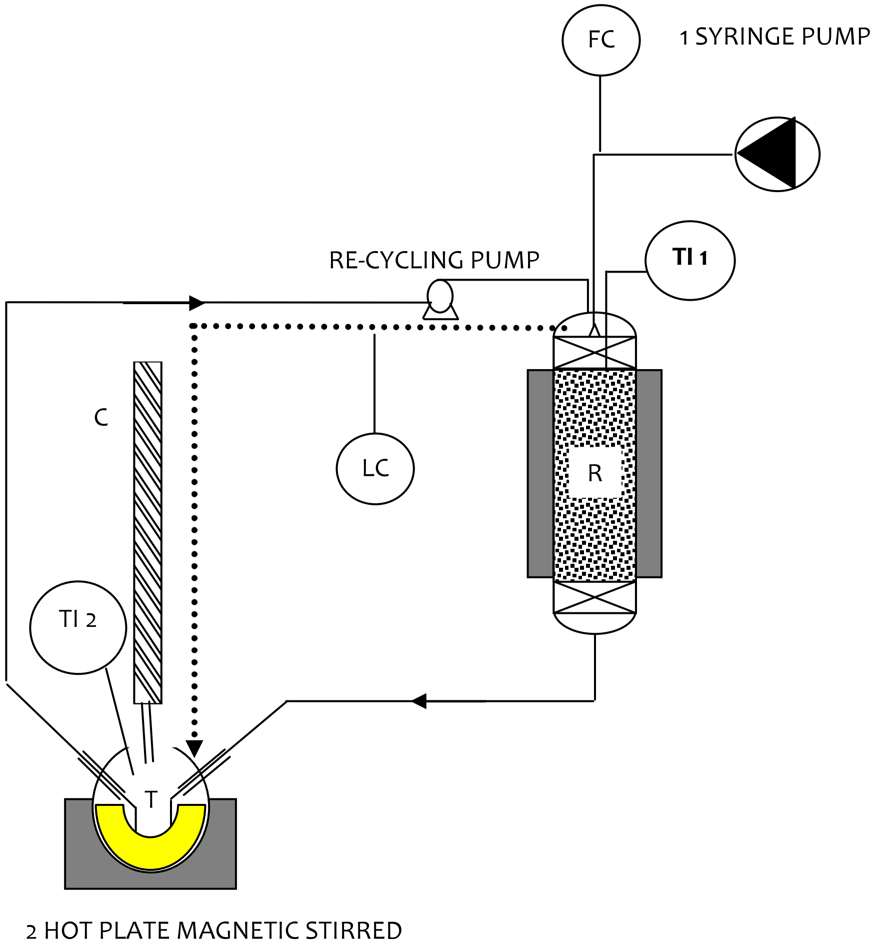

Fig. 2: Laboratory Micro-plan scheme: FC the flow controller is the syringe pump; R glass reactor with a fixed bed of catalyst; TI 1 temperature indicator: thermocouple; C refrigerant; TI 2 temperature indicator: thermometer; T tank used as a liquid hold-up; LC level controller for vapour or liquid in the top of reactor.

2.1.3 Catalytic system

The catalysts used in the batch stirred reactor is the powered form of a TS-1Ref synthesized following Tamarasso et al[63] procedure. In particular, this catalyst was shaped in the form of extrudates.

In literature, different methods are reported for the preparation of extruded catalysts based on TS-1[64,65]; in fact, this catalyst is used for propene epoxidation, which is industrially carried out in a fixed bed reactor. In particular, it is possible to use different inorganic binders for the extrusion, such as bentonite (Sud Chemie), montmorillonite (Across), sepiolite Pansil (Tolsa), sepiolite Pangel (Tolsa), silica PQ (Grace Division) silica gel (J.T. Baker) and silica spheres (Saint Gobain Norpro)[66]. The extrusion process needs a homogeneous paste constituted by (i) the inorganic binder, which provides the suitable physical strength; (ii) methylcellulose polymer as organic binder, providing the appropriate plasticity to the paste; (iii) the TS-1 powder; and (iv) distilled water. There are 3 different procedures to prepare the paste. For example in the first method the paste is obtained by means of dry-mixing the sepiolite, methylcellulose and TS-1 powder, and only at the end adding water. The second method consists in the preparation of a TS-1 water suspension; then the clay is added and finally also methylcellulose. The third method consists in using ultrasounds to suspend TS-1 in an excess of water and then following the second procedure. The extrusion procedure used to prepare the catalysts reported here is not described in detail, because of confidentiality reasons.

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[63] M. Tamarasso, G. Perego, B. Notari, *US Patent*. 4,410,501.

[64] W. Cheng, X. Wang, G. Li, X. Guo, B. Du; *Catal. Lett.*, 95 (2004) 185-190.

[65] U. Muller, G. Krug, P. Bassier, H.G. Gobbel, P. Rudolf, J.H. Teles; *Pub. N°* US2004/0054199.

[66] D.P. Serrano, R. Sanz, P. Pizarro, I. Moreno, P. de Frutos, S. Blazquez, *Catal. Today*, 143 (2009) 151-157.

2.1.4 Catalytic tests

SOLVENT EFFECT

HP was fed in water solution (60%), therefore water was always present in the reaction mixture. With only water as solvent, a pseudo-three-phase system develops: an aqueous, an organic and a solid phase. It is well know that TS-1, being principally formed by silica, is a hydrophobic catalyst; in the presence of water, phenol preferentially fills the TS-1 pores. In fact, as a consequence of that, the catechol/hydroquinone ratio is very low (0,8) but also diphenols yield with respect to HP is low (63%) while undesired products are formed with a weight yield of 4%, at a phenol conversion of 15-17%.

Acetone is a good solvent for diphenols and also for the heavy compounds that are produced by consecutive oxidative reactions or condensation. Adding acetone to the initial mixture (that already contained phenol and water) in a little amount, phenol conversion increased and diphenols and heavy compounds yields increased too. However, acetone also caused an increase of the catechol/hydroquinone ratio. The effect of acetone was demonstrated by progressively changing the amount of acetone in place of water, up to the phenol/water/acetone ratio (in the initial mixture) equal to 70/17/13 w/w (Fig 3-5). To avoid the acetone peroxide formation (an explosive molecule), it is necessary to work with excess water.

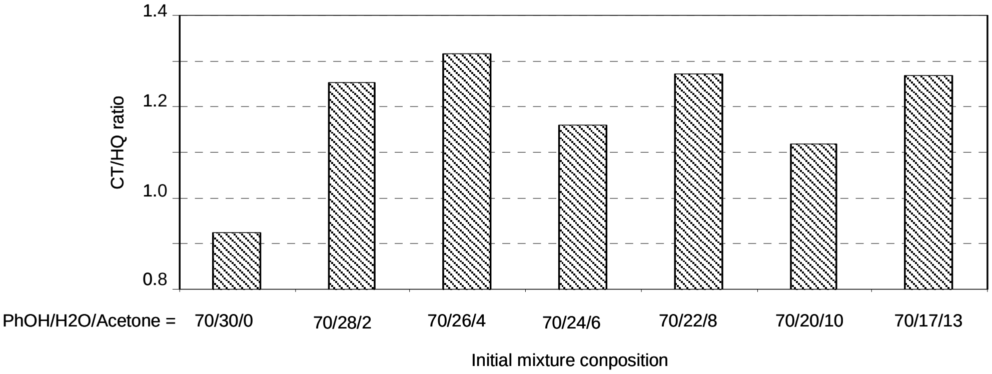

Fig. 3: Effect of initial mixture composition, changed by replacing water with acetone, on the catechol/hydroquinone ratio in the batch stirred reactor. T= boiling point; catalyst TS-1 0,625g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture weight 100 g, reaction time 300 min, plus 60 min keeping hot the products mixture, and 60 min for cooling.

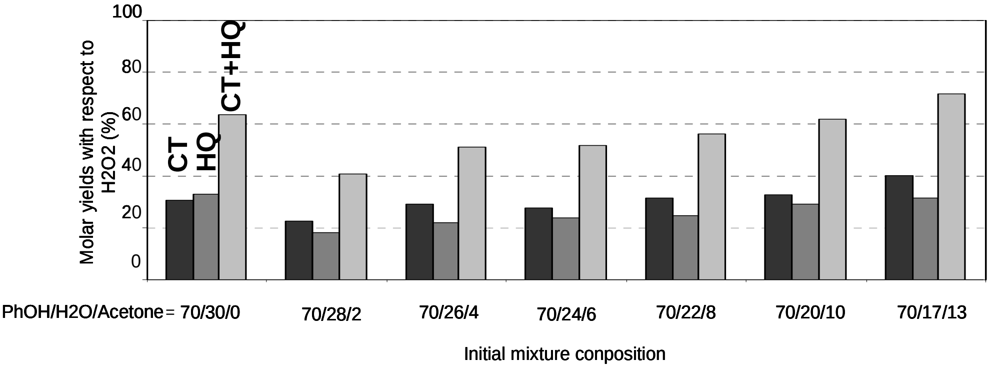

Fig. 4: Effect of initial mixture composition, changed by replacing water with acetone, on the yield to diphenols (with respect to HP), in the batch stirred reactor. T= boiling point; catalyst TS-1 0,625g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture weight 100 g, reaction time 300 min, plus 60 min keeping hot the products mixture, and 60 min for cooling. The first bar is catechol yield, the second bar is hydroquinone yield and the third bar is the sum of catechol and hydroquinone also called diphenols yield.

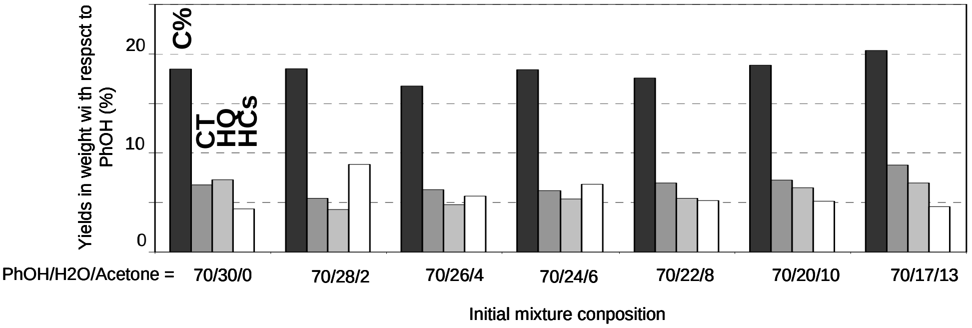

Fig. 5: Effect of initial mixture composition, changed by replacing water with acetone, on phenol conversion, and on yields to diphenols (with respect to phenol) and to heavy compounds in the batch stirred reactor. T= boiling point; catalyst TS-1 0,625g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture weight 100 g, reaction time 300 min, plus 60 min keeping hot the products mixture, and 60 min for cooling. The first bar is the phenol conversion (C%), the second bar is catechol yield (CT), the third one is hydroquinone (HQ) yields and the last bar is heavy compounds (HCs) yield.

There are two different hypotheses that can explain this experimental behaviour. The first, in accordance with Tuel et al.[67], is that outside the TS-1 porosity, the major product formed is catechol, but in addition to catechol the external catalytic sites also produce tar compounds, responsible for the deactivation of the surface. However, using appropriate solvents, such as

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[67] A. Tuel, S. Moussa-Khouzami, Y. Ben Taarit, C. Naccache, *J. Mol. Catal.* 68 (1991) 45-52.

acetone, it is possible to keep the catalytic surface clean, in particular the external one, so favouring catechol formation and increasing diphenols yields and phenol conversion too. On the other hand, Wilkenhöner et al.[68] reported that the type of product preferentially formed on the external surface depends on solvent type: catechol is preferred in acetone solvent while hydroquinone in a protic solvent. This is caused by a particular interaction between the active sites and the solvent.

CO-SOLVENT EFFECT

The characteristic shape-selectivity effect shown by TS-1 is due to microporous channel system, typical for a zeolitic catalyst. It is important to consider also the typical hydrophobicity of TS-1, which favours the contact between phenol and the active sites inside the pores, in order to produce hydroquinone instead of catechol. The affinity of TS-1 with polar molecules (like phenol also) is quite low; therefore phenol adsorption is in competition with non-polar solvents, and if the solvent is a small molecule (that diffuses quickly inside the pores), the nature of Ti sites located inside the catalyst pores can also be affected. So with the aim of improving the hydroquinone production, the adsorption of phenol inside the TS-1 channels has to be favoured.

Comparing the results obtained using a mixture of water and acetone, and adding to this also a co-solvent (Table 1), it is shown that on increasing the acidity of the liquid phase, by addition of a mineral acid such as phosphoric acid, the catechol/hydroquinone ratio decreased, whereas in presence of a basic molecule, such as formamide, the catechol/hydroquinone ratio increased. Being Ti a Lewis acid, the interaction with small basic molecules inhibited the hydroxylation of phenol. On the other hand, acid co-solvents favoured the hyroquinone formation and also the heavy compounds production. Adding a linear non-polar molecule, such as octane, the yield to hydroquinone, calculated with respect to HP, decreased while, at the same time, heavy compounds formed because of consecutive transformations (e.g., overoxidation) of catechol and hydroquinone.

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[68] U. Wilkonhöner, G. Langhendries, F. van Laar, G. Baroni, D. W. Gammon, P. A. Jacobs, E. van Steen, *J. Catal.*, 203 (2001) 201-212.

Table 1: Results obtained with different co-solvent using TS-1Ref

CO-SOLVENT	SOLVENT MIXTURE	CT / HQ RATIO	PHENOL CONVERSION %	DIPHENOLS MOLAR YIELD with respect to HP	HEAVY COMPOUNDS WT YIELD with respect to PhOH
Any	Water/acetone	1,26	25	71	5
Formammide	Water/acetone	1,70	10	60	7
Octane	Water/acetone	1,71	20	58	3
Phsphoric acid	Water/acetone	1,02	14	50	9
Boric acid	Water/acetone	1,19	10	51	7

In conclusion, there are different phenomena that contribute to the catalytic behaviour observed:

1. When a hydrophilic solvent is used, the diffusion of phenol inside pores is favoured, but phenol competes for adsorption over the active sites with other polar molecules, such as the co-solvent.
2. Diphenols are more easily oxidized than phenol; this implies that a high yield to diphenols also increases the rate of heavy compounds formation; the latter are soluble in acetone (as diphenols also) but, however, they can block the active sites, leading to an inhibition phenomenon. This phenomenon is observed when increasing amounts of phosphoric acid are added as co-solvent. Phosphoric acid has a positive effect on the formation of hydroquinone (lower catechol/hydroquinone ratio), also in presence of acetone, but it causes a decrease of diphenols yield.
3. Linear non-polar molecules have a preferential affinity for the hydrophobic zeolite, and fill the pores hindering the catalytic reaction inside pores. This finally leads to the preferential formation of catechol.

POST-SYNTHESIS "ACIDIC" TREATMENT

In the last years, several methods have been studied to improve the catalytic performance of TS-1 by synthesizing materials containing only Ti in tetrahedral coordination; an alternative approach is post-treatment, aimed at the removal of less active Ti species. In 2001 Polimeri Europa patented an "activation" procedure for TS-1 that consists in a modification of the catalyst by means of treatment with dicarboxylic ammonium salts[69]. The treatment is carried out by the adequate stirring of a catalyst suspension in an aqueous or aqueous-organic solution of the salt, and by raising the temperature up to the reflux value of the suspension. After the treatment, the catalyst is separated from the solution by filtration; it is not washed, and then calcined by heating at 5°C/min up to 550°C, finally keeping this temperature for 5h. UV-spectra of post-treated catalysts are not reported in the patent; however a structural change was detected by means of XRD analysis.

We have selected various salts for the treatment of TS-1Ref, such as ammonium salts of acetic, citric, phthalic and cis-5 norbonene endo-2,3-dicarboxylic acids; this allowed to compare the effect of a monocarboxylic acid with that of a dicarboxylic acid, and the steric effect as well.

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[69] V. Arca, A. Boscolo, N. Fracasso, P. Furlan, L. Meda; *Int. Pub.* N° WO 03/002254.

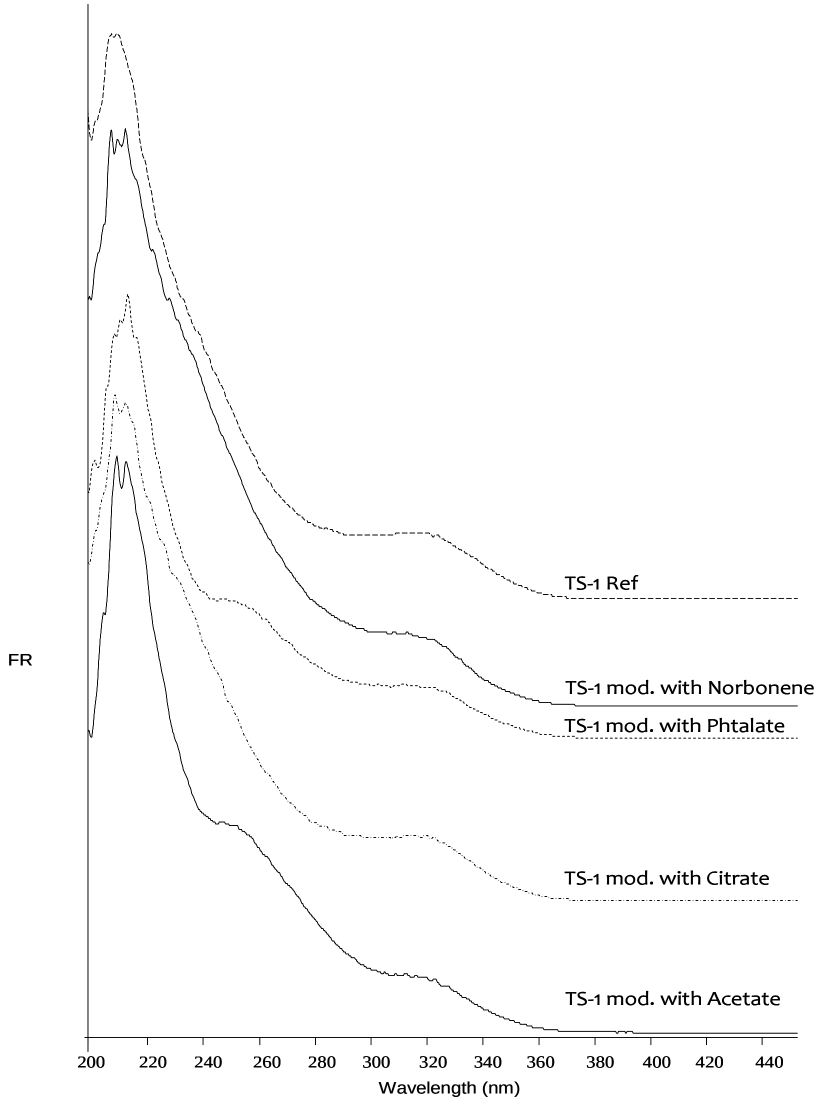

Fig. 6: UV spectra of different TS-1 samples.

The UV spectra of the treated TS-1 (Fig 6) show the band at approx 210 nm typical of Ti ion in tetrahedral coordination, but there is also a band at 320 nm. This band is due to the presence of octahedral units of TiO_2, specifically of an "anatase-like phase", which is not active for oxidation reactions with HP. In fact, this species decomposes HP, decreasing the catalyst activity. Another signal is present at 250 nm. This indicates that the catalysts also contain isolated monomeric Ti with coordination number greater than four.[70] After treatment with the acetate and phthalate salts, the broad band at 250 nm became evident; this suggests that a part of Ti, either in the anatase or incorporated inside the structure, was removed by the treatment and generated a new species, most likely having penta-coordinated environment.

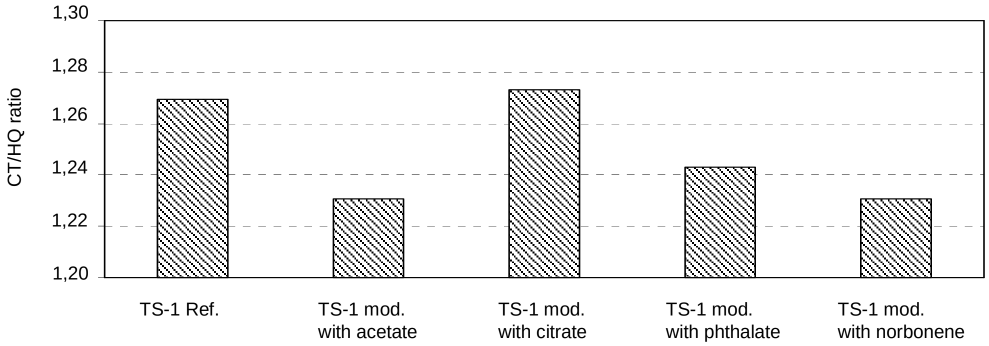

Fig. 7: Effect of acidic treatment of TS-1 on the catechol/hydroquinone ratio in the batch stirred reactor. T= boiling point; catalyst TS-1 0,625g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture weight 100 g, reaction time 300 min, plus 60 min keeping hot the products mixture, and 60 min for cooling.

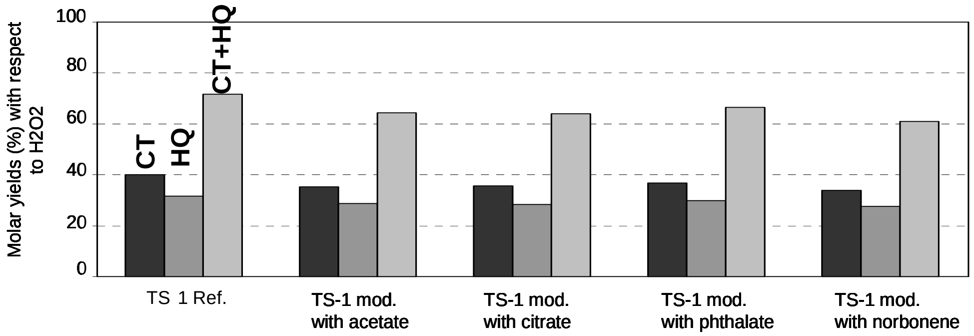

Fig. 8: Effect of acidic treatment of TS-1 on the molar yield to diphenols in a batch stirred reactor. T= boiling point; catalyst TS-1 0,625g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture weight 100 g, reaction time 300 min, plus 60 min keeping hot the products mixture, and 60 min for cooling. The first bar is catechol (CT) yield, the second one is hydroquinone (HQ) yield and the third one is the sum of catechol and hydroquinone, also called diphenols yield.

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[70] P. Chammingkwan, W. F. Hoelderich, T. Mongkhonsi, P. Kanchanawanichakul *Appl.Catal. A*, 352 (2009) 1-9.

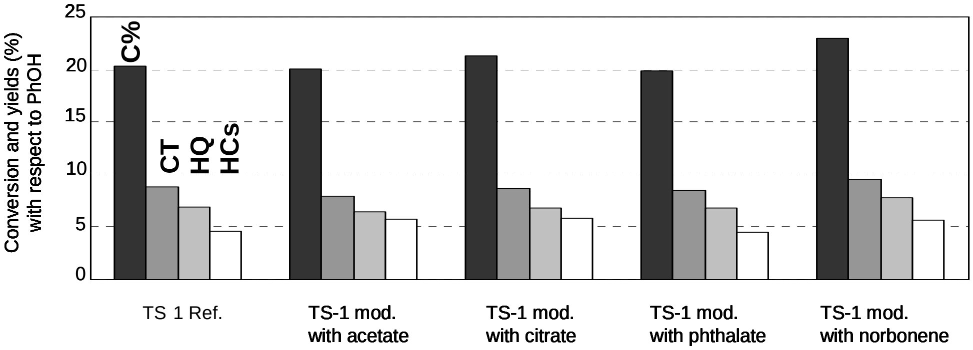

Fig. 9: Effect of acidic treatment on TS-1Ref on the weight yields (with respect to phenol), in the batch stirred reactor. T= boiling point; catalyst TS-1 0,625g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture weight 100 g, reaction time 300 min, plus 60 min keeping hot the products mixture, and 60 min for cooling. The first bar is the phenol conversion (C%), the second one is catechol yield (CT), the third one is hydroquinone (HQ) yields and the last one is heavy compounds (HCs) yield.

It is shown that there was no appreciable effect due to the acidic treatment, and small differences observed were not meaningful.

PARTICLE SIZE AND OTHER PARAMETERS

Industrial catalyst is usually spray-dried starting from a solution that contains the crystals of TS-1. By modifying the operative conditions of our lab spray-dryer apparatus, it was possible to produce samples with different particle size. Furthermore, increasing the diameter of the nozzle, the fragility of the solid decreased. Considering that the catalyst was then used in a batch stirred reactor, this result has some important implications; a fragile catalyst is easily crumbled under continuous stirring, and the effective particle size during the reaction will be different from the initial one. The particle size analysis is made by sedigraph MICROMERITCS 5100 instrument that calculates the size of sediment particles by measuring the attenuation of a finely collimated X-ray beam through a settling suspension (sample, CALGON, and mineral water) as a function of height above the base of the sedimentation tube and time. The diameter of the 50% of particles in the sample is considered the average diameter. In the same way also fragility is measured, but the samples is pre-treated with ultrasounds for 1 h at room temperature. The fragility is expressed as the percent of particles that have particle size < 5μm after the ultrasounds treatment in comparison with the no-treated sample.

Table 2: Characterization of samples.

Samples labels	Average Diameter (μm)	Fragility (%)
TS-1 D9-F57	9,179	57
TS-1 D7-F18	7,62	18
TS-1 Ref	22,13	3

This means that for TS-1 D9-F57, the probability to have after reaction particles smaller that 9 μm is very high.

Figs 10-12 compare the results obtained with the catalysts produced in laboratory. A decrease of the particle size caused a small decrease of the yield (calculated with respect to HP). More fragile samples gave higher phenol conversion.

The catechol/hydroquinone ratio decreased with samples having smaller particle size; this indicates that particle size is one possible parameter for the improvement of hydroquinone production. Unfortunately, filtering smaller catalyst particles may be difficult during industrial operation; therefore at the end this system is impracticable.

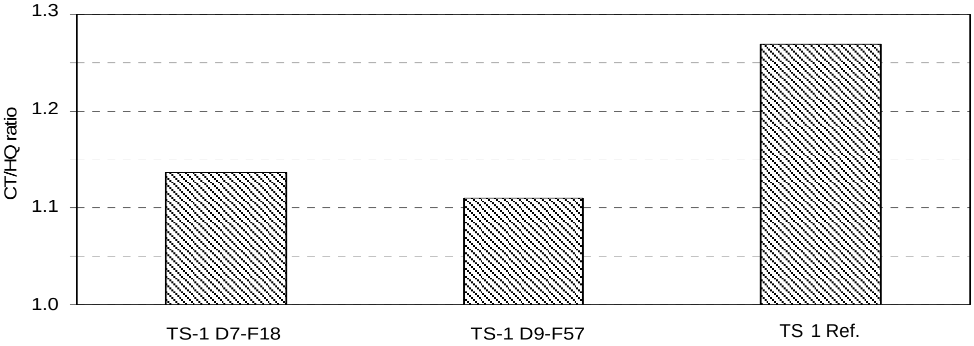

Fig. 10: Effect of particle size (Dx) and fragility (Fy). on the catechol/hydroquinone ratio in a batch stirred reactor. T= boiling point; catalyst 0,625g Volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g, time 300 minutes plus 60 minutes keeping hot the products mixture and 60 minutes of cooling. TS-1Ref as reference.

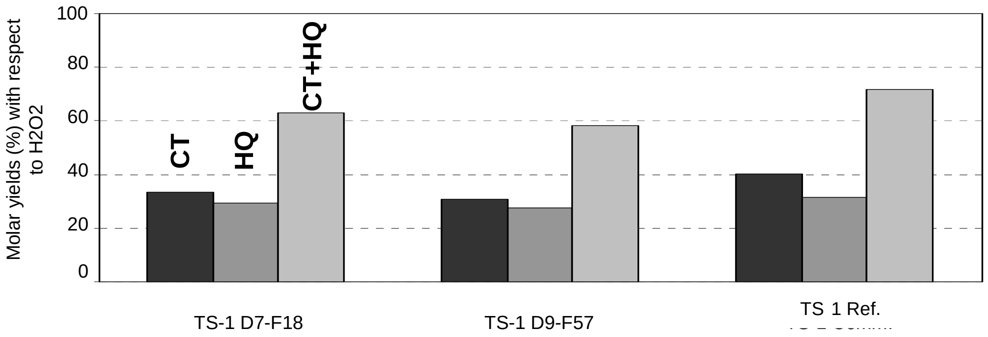

Fig. 11: Effect of particle size (Dx) and fragility (Fy) on the molar yields with respect to HP in a batch stirred reactor. T= boiling point; catalyst 0,625g Volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g, time 300 minutes plus 60 minutes keeping hot the products mixture and 60 minutes of cooling. The first bar is catechol (CT) yield, the second one is hydroquinone (HQ) yield and the third one is the sum of catechol and hydroquinone also called diphenols yield. TS-1Ref as reference.

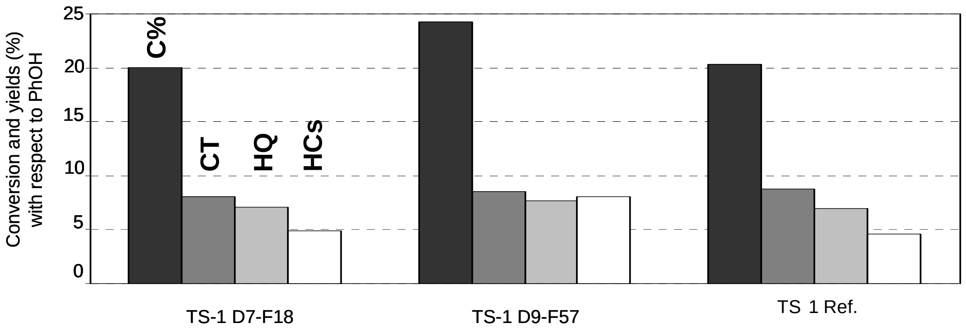

Fig. 12: Effect of particle size (Dx) and fragility (Fy). on the yields with respect to phenol in weight in a batch stirred reactor. T= boiling point; catalyst 0,625g Volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g, time 300 minutes plus 60 minutes keeping hot the products mixture and 60 minutes of cooling. The first bar is the phenol conversion (C%), the second one is catechol yield (CT), the third one is hydroquinone (HQ) yields and the last one is heavy compounds (HCs) yield. TS-1Ref as reference.

TEMPERATURE EFFECT

The activity and the selectivity can be modified changing other operative parameters, such as the working temperature (Fig 13-15). With the TS-1Ref, we observed that on increasing the reaction temperature, both diphenols yield (calculated with respect to HP) and yield to heavy compounds (with respect to phenol), increased. Therefore, at high temperature the kinetics of both reactions was favoured. In the T range 65-95°C, the catechol/hydroquinone ratio first decreased and then increased. These tests demonstrate that the optimal temperature to get the lower catechol/hydroquinone ratio is approx 85°C, but the best one to obtain the best selectivity to diphenols (with the minimal formation of heavy compounds) is lower than 75°C. A possible strategy would be that of carrying out the reaction in two different steps; in the first step, a partial conversion of phenol could be achieved, with an optimal ratio between the two diphenols, primary products of the reaction; then, the conversion of phenol and HP could be completed in a second step, carried out at lower temperature, to limit the formation of heavy by-products. Since the formation of heavy compounds may also occur in the bulk liquid phase, the temperature of the liquid, under optimal conditions, should be kept lower than that of the catalytic bed.

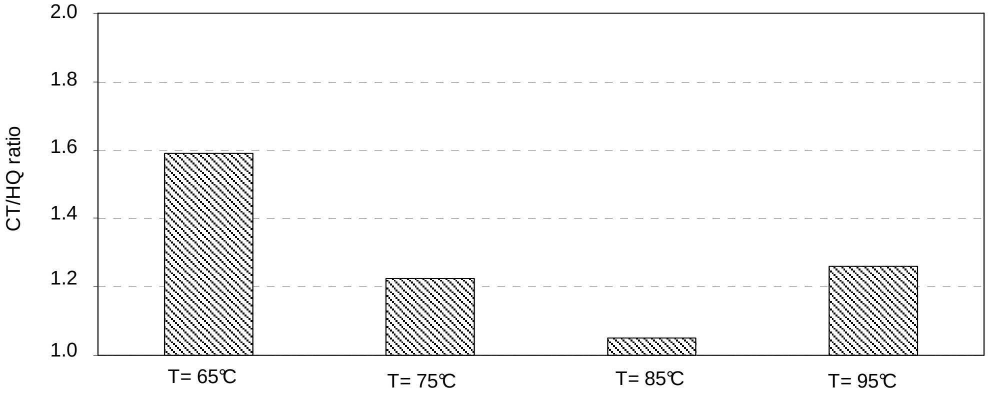

Fig. 13: Effect of temperature on the catechol/hydroquinone ratio in a batch stirred reactor. T= boiling point; catalyst TS-1Ref 0,625g Volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g, time 300 minutes plus 60 minutes keeping hot the products mixture and 60 minutes of cooling.

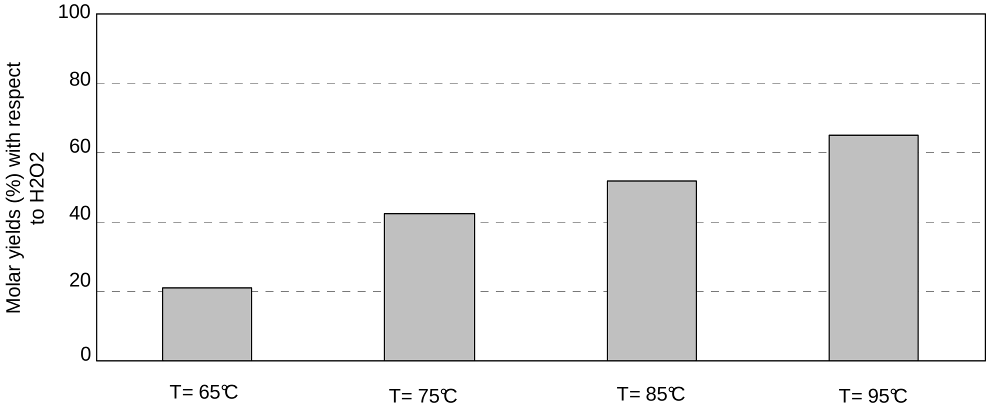

Fig. 14: Effect of temperature on the diphenols (CT+HQ) molar yields (with respect to HP) in a batch stirred reactor. T= boiling point; catalyst TS-1Ref 0,625g Volumetric flow

HP (60%) 0,023 ml/min, Initial mixture 100 g, time 300 minutes plus 60 minutes keeping hot the products mixture and 60 minutes of cooling.

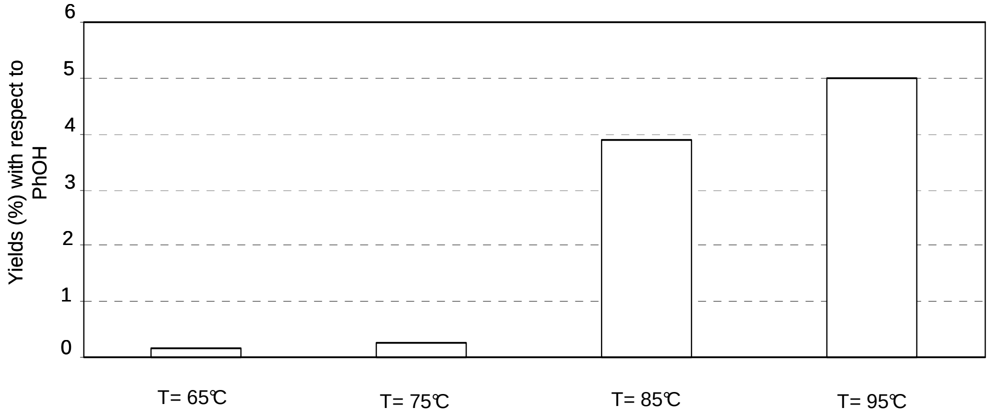

Fig. 15: Effect of temperature on the weight yields of heavy compounds (HCs) (with respect to phenol) in a batch stirred reactor. T= boiling point; catalyst TS-1Ref 0,625g Volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g, time 300 minutes plus 60 minutes keeping hot the products mixture and 60 minutes of cooling.

EXTRUDED SAMPLES, LOADED IN A CONTINUOUS-FEED REACTOR

After several tests with different solvents and using different operative conditions, it was possible to conclude that the best solvent to produce preferably hydroquinone, at the same time keeping high diphenols yields and phenol conversion with only a little amount of heavy compounds formed, is water. However, in order to use water without any co-solvent, in an industrial plant, it is necessary to find out a new filtration strategy. Alternatively, it could be convenient to change completely the reactor system, and use a fixed-bed reactor instead of a batch, semi-continuous, stirred one. The use of a fixed-bed reactor implies the use of catalyst in the form of extrudates.

In a previous chapter, we already described the main characteristics of this reactor type. Tests, reported above, indicate that, if possible, it would be better to have different temperatures on the catalyst bed and in the bulk liquid phase; this explains the reactor configuration that we adopted, with two separate heating systems in the different zones of the reactor/circulation system.

First of all, it was necessary to check for eventual changes of catalytic behaviour after extrusion. Therefore, we first ground the extruded TS-1 samples and tested the powdered extrudates in the batch stirred reactor. Since these preliminary experiments gave satisfactory results, we loaded the extrudates in the fixed-bed reactor. Figs 16-18 report the effect of the reaction time on catalytic behaviour.

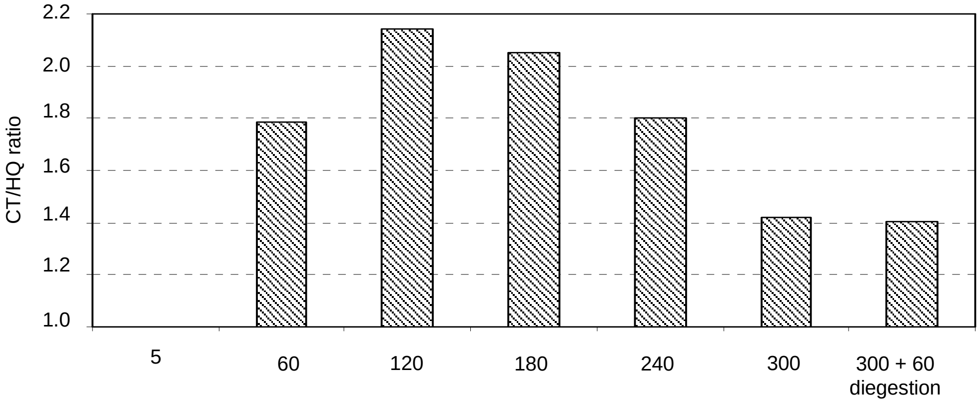

Fig. 16: Effect of feeding time on the catalechol/hydroquinone ratio in the fixed bed reactor. T= 85°C on the catalyst; catalyst TS-1 extrudates 2,5g ; volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g PhOH/H2O/Acetone=70/17/13.

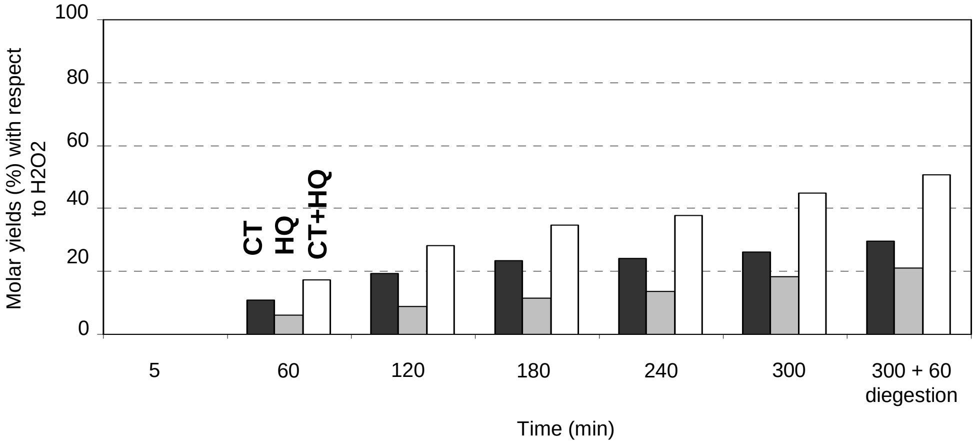

Fig. 17: Effect of feeding time on the molar yields (with respect to HP) in a the fixed bed reactor. T= 85°C; catalyst TS-1 extrudates 2,5g; volumetric flow HP (60%) 0,023 ml/min, initial mixture 100 g, PhOH/H2O/Acetone=70/17/13. The first bar is catechol (CT) yield, the second one is hydroquinone (HQ) yield and the third one is the sum of catechol and hydroquinone also called diphenols yield.

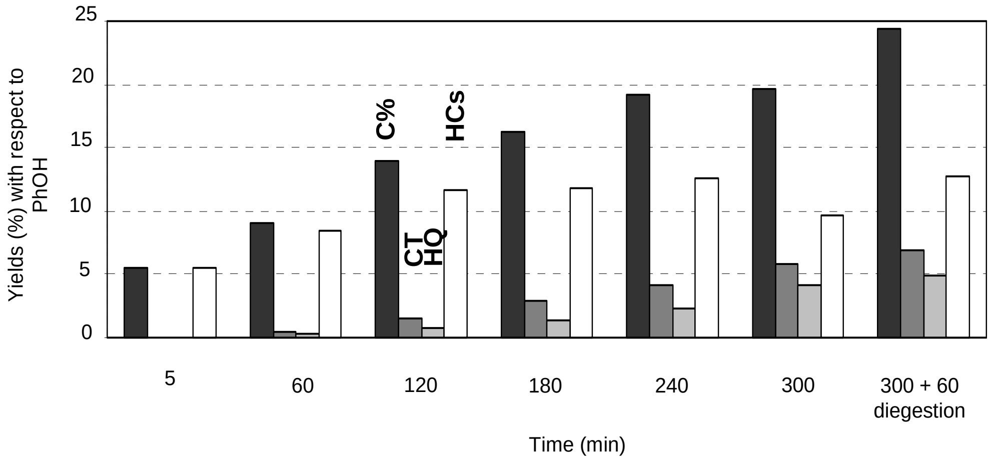

Fig. 18: Effect of feeding time on the weight yields (with respect to phenol) in a fixed bed reactor. T= 85°C; catalyst TS-1 extrudates 2,5g. Volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g PhOH/H2O/Acetone=70/17/13. The first bar is the phenol conversion (C%), the second one is catechol yield (CT), the third one is hydroquinone (HQ) yields and the last one is heavy compounds (HCs) yield.

In this case, using the standard reaction mixture (acetone + water and phenol), it was possible to achieve the same results obtained in the batch stirred reactor, but using a higher amount of catalyst. A fixed-bed reactor may present some drawbacks: for example problems due to diffusion of reactants inside the porosity generated in the catalyst by the extrusion process, or an inefficient contact of reactants with the solid; the latter can be improved by keeping a high re-circulating flow in comparison with the fresh feed one. On the other hand, a high recirculation leads to a more homogeneous temperature in the entire system, which in our case was not desired.

Tests were carried out by slowly adding the fresh HP solution, and by sampling every 60 minutes the liquid phase, in order to analyse the product mixture. After 300 minutes the HP feed was stopped, and the product mixture (still containing some unconverted HP) was kept hot for one hour more, in order to consume completely the oxidant, and finally cooled simulating the procedure used in the batch stirred reactor. When only water was used as the solvent, a catechol/hydroquinone ratio equal to 1.0 was obtained, and also diphenols yield was the same as that obtained in the stirred reactor at the same operative conditions.

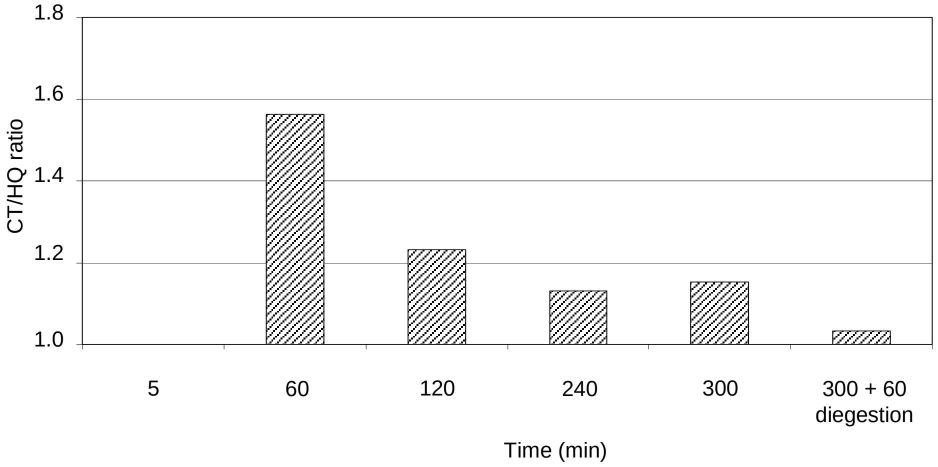

Fig. 16: : Effect of feeding time on the catechol/hydroquinone ratio in the fixed bed reactor. T= 85°C on the catalyst; catalyst TS-1 extrudates 2,5g ; volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g PhOH/H2O=70/30.

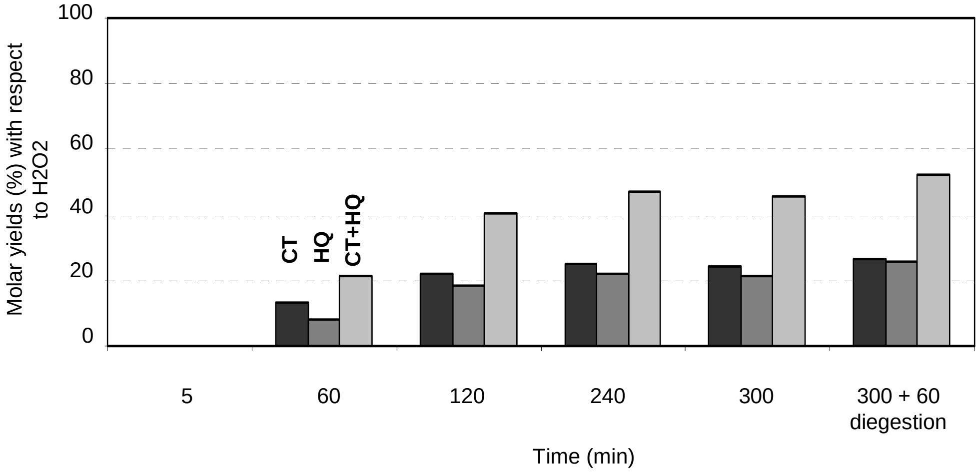

Fig. 17: Effect of feeding time on the molar yields (with respect to HP) in the fixed bed reactor. T= 85°C on the catalyst; catalyst TS-1 extrudates 2,5g ; volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g PhOH/H2O=70/30.

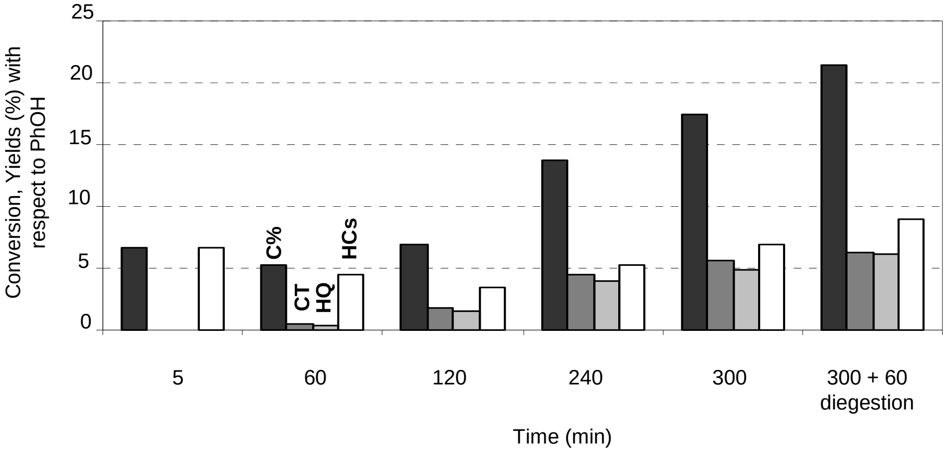

Fig. 18: Effect of feeding time on the weight yields (with respect to phenol) in the fixed bed reactor. T= 85°C on the catalyst; catalyst TS-1 extrudates 2,5g ; volumetric flow HP (60%) 0,023 ml/min, Initial mixture 100 g PhOH/H_2O=70/30.

Another advantage was that with water the final amount of unconverted HP (before the final ageing) was lower than that obtained with the acetone+water mixture.

CHAPTER 3: CONCLUSIONS

This chapter reports about an in-depth study of the reactivity of TS-1 in phenol hydroxylation. This process is already industrially applied; therefore our goal was to find alternative process conditions that might lead to a lower catechol/hydroquinone ratio, that is, in favour of hydroquinone formation. Several possible solutions for this problem were found: reduce the particle size, decrease the operative temperature (80°) or change the solvent. Each one of these alternative approaches offers both advantages (reduction of the catechol/hydroquinone ratio) and disadvantages (decrease of either diphenols yield or conversion, or increase of heavy compounds)

Water was found to be an optimal solvent for the reaction, but this implies a modification of the industrial process. Moreover, the role of water was not completely elucidated; one hypothesis is that the presence of only water as the solvent increases the access to Ti sites located inside the zeolitic TS-1 channels. The use of water led us to use a different type of reactor configuration, a continuous fixed-bed instead of a batch semi-continuous reactor, which also implied the use of extrudates instead of a powdered catalyst. The process of extrusion did not negatively affect the catalytic behaviour.

Comparing the results obtained with water solvent in these two different reactor configurations (batch stirred and fixed-bed), allowed us to conclude that it is possible to increase the production of hydroquinone at the expense of catechol, without other negative implications on the performance.

PART D: Glycerol transformation to acrolein and acrylic acid

CHAPTER 1: INTRODUCTION

The commercial production of fats and oils has increased rapidly during the last century and still is increasing; its production is estimated to be around 350 million tons for the year 2015 (in comparison with only 144 Mt in the 2010)[71]. However, it must be reminded that only a small part of this material is converted within the chemical industry: about 81% of the worldwide oil production is used for the food industry, 14% in the chemical industry and 7% for feed. Nonetheless, renewable oils are being used for energy applications also, substituting the fossil raw materials. The community is starting to understand the importance of a green global effort in order to contrast the climate changes favouring, with financial supports, the use of alternative raw materials for energy, instead of the classical production derived from oil. Actually, this is the driving force for the production of biodiesel, which is estimated to be around 18 Million tons for 2010 in the European Union. However, supporting the biodiesel as automotive fuel, so applying a eco-friendly lifestyle, has caused an overcapacity of glycerol (the co-product of transesterification) on the market; in fact, the market of biodiesel is strictly connected with the glycerol one and to its price, so the question arises how this additional glycerol produced could be used.

Biodiesel is the well-known term for the fatty acids methyl esters formed from the transesterification of triglycerides with methanol, and it is easy to understand that an higher production of biodiesel necessitates finding new valued-products from glycerol -as alternatives to glycerol incineration- that would improve the economic viability of biodiesel manufacture and the biodiesel supply chain. The current application of glycerol is mainly confined to pharmaceuticals and cosmetics (hair and skin care), soaps and toothpastes, but evidently this is not enough.

For all these reasons, glycerol can be considered a promising low-cost feedstock or platform molecule for producing a wide variety of value-added

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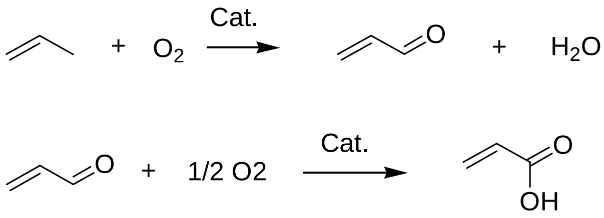
[71] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem*. 10 (2008) 13-30.

special and fine chemicals. For example, the chemical utilization of glycerol might include the synthesis of chemicals such as acrolein, propanediols or epichlorohydrin, by means of catalytic processes such as reforming, oxidation, hydrogenolysis, etherification and esterification.

The dehydration of glycerol to acrolein is an important route for the utilisation of the fast-growing glycerol resource, also providing a sustainable alternative to the present acrolein production based on petroleum-derived propylene. In particular acrolein is an intermediate for acrylic acid production, whose global market is deeply influenced by Chinese and Indian economical and industrial development.

Currently, acrylic acid is produced by oxidation of propene, using heterogeneous catalysis in vapour phase, with air, in two separate steps:



Each step requires specific reaction conditions and a specific catalyst to obtain the optimal conversion and selectivity[72]. It is also possible to obtain directly acrylic acid by a single-step oxidation of propylene, but in this case the yield is at the best 50-60%; another drawback is the limited lifetime of catalyst, which is a multicomponent system, made of Mo/V/W mixed oxides.

Nowadays, much research effort is being devoted to the conversion of glycerol to acrolein by catalytic processes; in fact several catalysts with Brϕnsted-type acid properties have been reported to achieve excellent performance in glycerol dehydration, yielding total glycerol conversion and selectivity to acrolein of 70 to 90%, as shown in the recent review by Katryniok et al.[73] Catalysts offering the best performance include WO_3/ZrO_2[74,75], supported Keggin

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[72] *Ullmann's Encyclopedia of Industrial Chemistry* vol A1 161-175.

[73] B. Katryniok, S. Paul, M. Capron and F. Dumeignil, *ChemSusChem*, 2 (2009) 719 – 730.

[74] J.-L. Dubois, C. Duquenne and W. Hölderich, *Eur Patent* n° 1,874,720 A1, (2006), assigned to Arkema.

[75] A. Ulgen and W. Hoelderich, *Catal. Lett.*, , **131** (2009) 122–128.

polyoxometalates,[76,77,78] V/P/O,[79,80] rare earth pyrophosphates,[81] and H-ZSM5.[82,83,84]

In general, a strong acidity is required ($-8.2 \leq H_0 \leq -3.0$), in order to facilitate the double intramolecular dehydration of the reactant. With even more acid systems the selectivity obtained is claimed to be lower, and this has been attributed mainly to the consecutive transformations occurring on acrolein, that is converted into heavier compounds; the latter also contribute to catalyst deactivation, because accumulate on the catalyst surface. Thus, acidity is the primary feature affecting the performance of catalysts, in terms of glycerol conversion, selectivity to acrolein and catalyst durability. Other important factors include textural properties, such as the porosity of the support, because if steric limitations do not allow the rapid counterdiffusion of the products, formation of heavy products by bimolecular condensation and of coke may lead to catalyst deactivation. Another important factor affecting the catalytic behaviour is the density of surface acid sites, as in the case of supported polyoxometalates, and HZSM-5.

One further characteristics of this reaction is that with many of the strongly acidic catalysts investigated in the literature, the co-feed of oxygen helps in keeping the catalytic surface cleaner limiting the formation of heavy deposits that may lead to catalyst deactivation[85]. The co-feed of oxygen in gas-phase, acid-catalyzed reactions indeed is an unusual feature of this reaction, since it is generally believed that the addition of oxygen impurities may enhance, and not hinder, the formation of higher boiling, oxygenated compounds, that make deactivation quicker than it is without oxygen (unless a metal promoter is added that may facilitate the combustion of residues).

Amongst the various systems investigated, little attention has been given

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[76] H. Atia, U. Armbruster and A. Martin, *J. Catal.*, 2008, **258**, 71–82.

[77] S.-H. Chai, H.-P. Wang, Y. Liang and B.-Q. Xu, *Appl. Catal. A*, 2009, **353**, 213–222.

[78] S.-H. Chai, H.-P. Wang, Y. Liang and B.-Q. Xu, *Green Chem.*, 2008, **10**, 1087–1093.

[79] F. Wang, J.-L. Dubois and W. Ueda, *J. Catal.*, 2009, **268**, 260–267.

[80] F. Wang, J.-L. Dubois and W. Ueda, *Appl. Catal. A*, in press

[81] Q. Liu, Z. Zhang, Y. Du, J. Li and X. Yang, *Catal. Lett.*, 2009, **127**, 419–428

[82] C.-J. Jia, Y. Liu, W. Schmidt, A.-H. Lu and F. Schüth, *J. Catal.*, 2010, **269**, 71–79

[83] A. Corma, G.W. Huber, L. Sauvanaud and P. O'Connor, *J. Catal.*, 2008, **257**, 163–171

[84] Y.T. Kim, K.-D. Jung and E. Duck Park, *Microp. Mesop. Mater.*, 2009 in press.

[85] J.-L. Dubois, C. Duquenne, W. Hölderich and J. Kervenal, *WO* 2006/087084, 2006, assigned to Arkema.

to sulphated zirconia.[86] We decided to investigate the catalytic behaviour of sulphated zirconia, as a model system in which the density of surface acid sites can be properly controlled through a change of the amount of loaded sulphate, and also to understand how the interplay of acidity and reaction parameters affect the selectivity to the desired product. Finally, sulphated zirconia might in principle be the most suitable catalyst for this reaction when conducted in the presence of molecular oxygen, since it combines acid and redox properties that may help in accelerating the removal of heavy compounds incipiently formed on catalyst surface.[87,88,89,90] Moreover, the redox properties of sulphated zirconia may be further implemented by depositing over it another active phase holding enhanced redox properties for the oxidation of the formed acrolein into acrylic acid. This might allow the development of a multifunctional catalyst for the single-step transformation of glycerol into acrylic acid. Following this idea, also Keggin-type polyoxometalates, either in the unsupported or supported form, were studied as catalysts for glycerol transformation into both acrolein and acrylic acid.

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[86] S.-H. Chai, H.-P. Wang, Y. Liang and B.-Q. Xu, *Green Chem.*, 2007, **9**, 1130–1136.

[87] J.H. Wang and C.Y. Mou, *Appl. Catal. A*, 2005, **286**, 128-136.

[88] C.-C. Hwang and C.-Y. Mou, *J. Phys. Chem. C*, 2009, **113**, 5212–5221.

[89] C. Breitkopf, H. Papp, X. Li, R. Olindo, J.A. Lercher, R. Lloyd, S. Wrabetz, F.C. Jentoft, K. Meinel, S. Förster, K.-M. Schindler, H. Neddermeyer, W. Widdra, A. Hofmann and J. Sauer, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3600–3618.

[90] X. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, A. Hofmann, and J. Sauer, *J. Am. Chem. Soc.*, 2005, **127**, 16159-16166.

CHAPTER 2: RESULTS AND DISCUSSION

2.1 THE LIQUID-PHASE TRANSFORMATION OF GLYCEROL

REACTIVITY IN LIQUID PHASE

Initially, tests in the liquid phase were carried out using the semi-batch stirred reactor described in paragraph 2.1.1. Part C. The oxidizing agent was hydrogen peroxide (HP) and the catalytic system was TS-1 C already described in Part B. The operative conditions were the following: initial aqueous solution of glycerol (20% w/w), 0,625g TS-1 C, temperature 100°C, reaction time 5h, HP flow 0.023 mL/min, HP 60% (m/m), digestion time 1 h, products solution analyzed by means of GC with the internal standard (valeric acid) method, and GC-MS for the identification of all products.

The results were not satisfactory, because glycerol conversion was only 28%, with 10% selectivity to acetic acid, 5% to formic acid, 9% to hydroxyacetone, 1% to di-hydroxyacetone; relevant amount of formate esters and heavy compounds also formed. This test confirms the hypothesis that TS-1 generates radical in the reaction environment, favouring overoxidation and molecular cracking.

2.2 THE GAS-PHASE TRANSFORMATION OF GLYCEROL

2.2.1 Micro-plant description.

The micro-plant scale laboratory used for the gas-phase dehydration of glycerol includes three zones (fig. 1):

1) The Feeding Zone contains the following components: two mass flow-controllers, to regulate the inert flow (He) and the oxygen flow (when used), directly to the feeding pipeline; a

flow-meter, to measure the inlet and outlet total gas flow; an high-precision syringe pump, to feed the aqueous solution of glycerol; a P gauge to control the pressure in the entire plant. Glycerol is fed directly onto the catalytic bed and the dedicated pipeline is not pre-heated. With the aim of limiting decomposition reactions on glycerol occurring in the feed-vaporization zone, it was necessary to feed very slowly and in presence of inert gas, to facilitate the vaporization of the glycerol-water mixture. An alternative option could be filling the reactor, before the catalytic bed, with solid inert.

2) Reaction Zone: where the catalyst is loaded, in pellet shape, and where the reaction occurs. The reactor is a tubular fixed-bed made in glass. The catalyst is placed in the isothermal part of the reactor; the temperature is measured by a thermocouple directly over the bed, while the reactor is heated increasing the temperature of the furnace.

3) Collector Zone: the effluent gas stream passes through two cold traps (0 – 4°C), filled with water; the solution, that is obtained dissolving the products in water, is analysed by gas-cromatography (GC), using the internal standard method and a FID (Flame Ionisation Detector). The incondensable gases, passing after the cold traps, are analysed on-line by GC, using a TCD (Thermal Conductivity Detector). From time to time, gases after the cold traps are sampled with a syringe and analysed by GC-FID, to check for the effective absence of any condensable product (e.g., acrolein).

The operative conditions for the transformation of glycerol are the follows (unless otherwise specified):

Glycerol = 20% (w/w) in water
Volumetric flow of organic liquid feeding mixture = 0,0166ml/min
Volumetric inert (He) flow = 25 ml/min in presence of oxygen, at low linear velocity, or 27 ml/min in anaerobic conditions.
Volumetric oxygen flow = 2 ml/min (when used).
Temperature in the feeding gaseous pipeline= 290°C

Temperature on the fixed-bed = 290-410°C
Pressure in the system = atmospheric pressure
Pellets size: 30-60 mesh
Catalyst volume 0,2 cm^3 at ordinary contact time.
Temperature of the glycol bath: 0-4°C

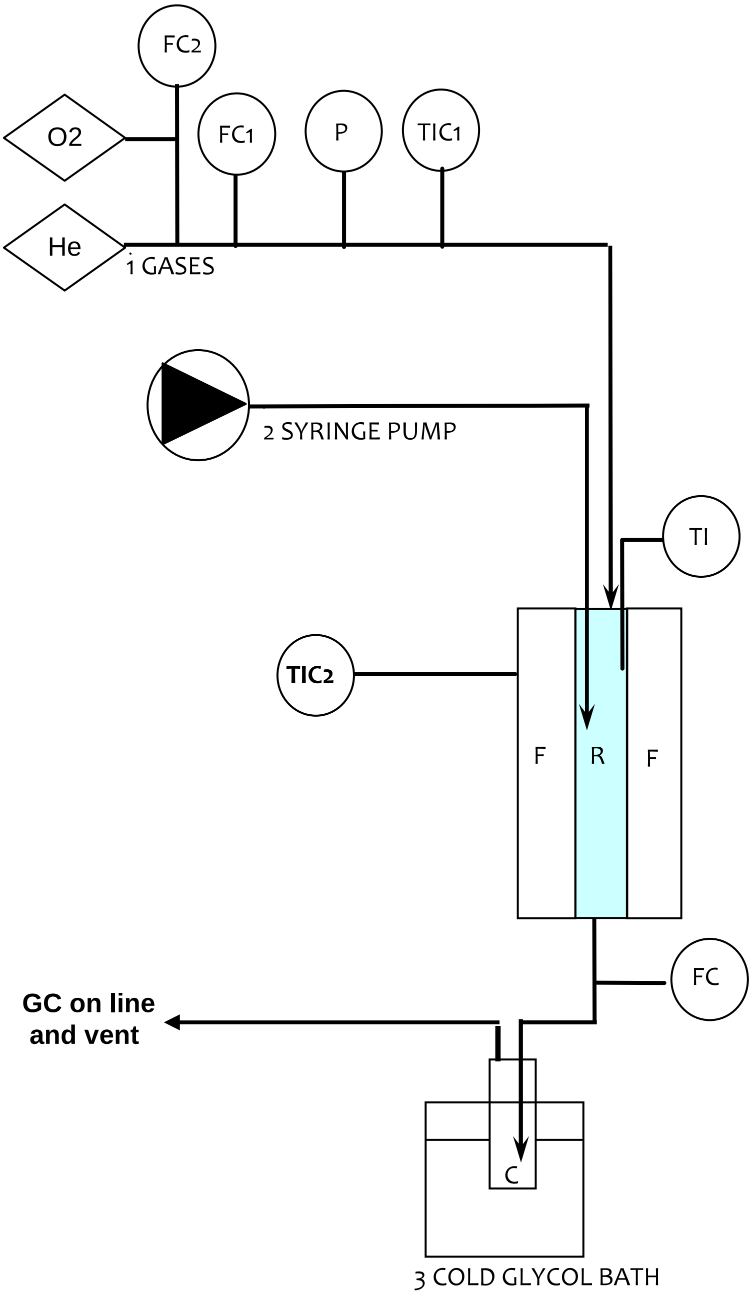

Fig. 1: Laboratory micro-plant scheme. FC1 He mass flow; FC2 O_2 mass flow, PI pressure indicator; TIC1 temperature indicator and controller for the gaseous feeding pipeline; TI temperature indicator thermocouple; F furnace; R reactor; TIC2 temperature indicator and controller for the furnace; FC rotameter to control the total gases flow; C cold traps; only one is shown in the Figure, but indeed usually two or more were used.

2.2.2 Reactivity tests

REACTIVITY WITHOUT CATALYST

Preliminary experiments were carried out in function of temperature, but without any catalyst in the reactor, in order to check for the contribution of thermal homogeneous reactions to glycerol conversion. Results of these experiments are shown in Figure 2, for tests carried out both in the absence and in the presence of co-fed oxygen. It is shown that in the 290-390°C temperature range the conversion of glycerol was less than 15%; since conversion measured was estimated to be systematically around 5-10% higher than the true one, it can be assumed that in the interval of temperature considered, the amount of glycerol converted because of thermal reactions was negligible (however, it was not nil, since some very low amounts of products formed, with an overall yield of less than 3-4 %). On the other hand, when 2% oxygen was added in the stream, the conversion became non-negligible at above 330°C.

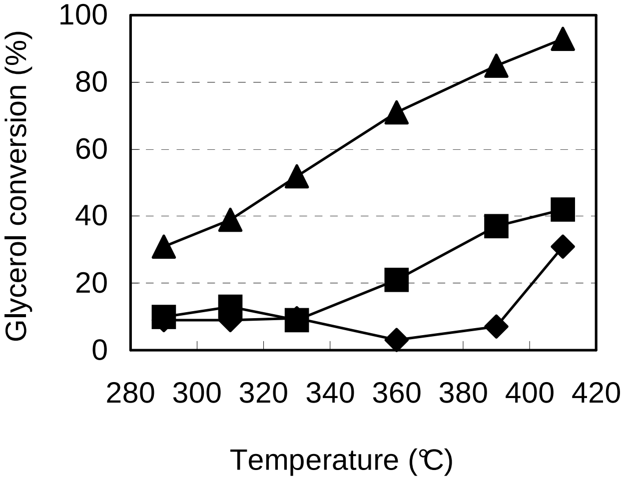

Fig. 2: Conversion of glycerol as a function of temperature. No catalyst, no O_2 in feed (◆), no catalyst, O_2 (2%) in feed (■) and ZrO_2 catalyst, O_2 in feed (▲). Feed composition (without O_2): glycerol / water / helium=2/40/58 (molar ratios). Feed composition (with O_2): glycerol / oxygen / water / helium = 2/4/40/54 (molar ratios).

Main products found under these conditions were acrolein, acetaldehyde, hydroxyacetone, acetone, allylic alcohol, ethanol and propanal, and in the presence of oxygen also CO_2 (the predominant product at above 360°C) and acetic acid. The formation of heavy compounds, both in the presence and in the absence of oxygen, was very likely but could not be ascertained, because due to the very low conversion achieved the C balance could not be properly evaluated.

In the same Figure it is also shown the conversion achieved with non-sulphated zirconia (tests in the presence of oxygen). Despite the absence of any Brϕnsted acidity (see below), the catalyst produced a relevant conversion of glycerol, but with very low selectivity to acrolein; the latter was less than 5% at low temperature, but when the temperature was raised it increased, up to a maximum of 8-10% due to the contribution of homogeneous reactions. Several by-products formed, the same also observed in the absence of catalyst, with yields that also were similar to those obtained with no catalyst at all. In fact, almost all of the converted glycerol was transformed into heavy compounds. These preliminary results confirm indications from the literature, that a weak acidity (H0 > 3.0) is not suitable for the dehydration of glycerol,[91] and that parallel undesired reactions are responsible for the relevant formation of by-products.

2.2.3 Catalytic systems: Main characteristics of sulphated zirconia

Sulphated zirconia has been studied by several authors owing to its high activity in acid-catalyzed reactions, such as the activation of short alkanes at low temperature[92]. However, the scientific community still doesn't agree about its surface chemical properties, the nature of acid sites, the sulphate species and the influence of the zirconia support. At the same time, it is clear that a wide variety of sulphate species exists on sulphated zirconia, and that there is a relationship between the species on the catalyst surface and the catalytic performance. In literature, different theories about the nature of active sites are reported: bi-dentate[93,94], tri-dentate[95] and also penta-coordinated[96] species. Monodentate bisulphate species (HSO_4^-) were proposed by Kustov et al[97] and Adeeva et al[98]; bi-dentate bisulphate-like species were also related to the formation of Brϕnsted

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[91] S-H. Chai, H-P. Wang, Y. Liang and B-Q. Xu, *Green Chem.*, 9 (2007) 1130-1136

[92] X. Song, A. Sayari, *Catal. Rev. Sci. Eng.*, 38 (1996) 329.

[93] T. Yamaguchi, *Appl. Catal.*, 61 (1990) 1.

[94] K. Arata, M. Hino, *Appl. Catal.*, 59 (1990) 197.

[95] M. Bensitel, O. Saur, J.C. Lavalley, B.A. Morrow, *Mater. Chem. Phys.*, 19 (1988) 147

[96] R.L. White, E.C. Sikabwe, M.A. Coelho, D.E. Resasco, *J. Catal.*, 157 (1995) 755.

[97] L.M. Kustov, V.B. Kazansky, F. Figueras, D. Tichit, *J Catal.*, 150 (1994) 143.

[98] V. Adeeva, J.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler, R.A. Van Santen, *J. Catal.*, 151 (1995) 364.

sites in the structure model proposed by Clearfield et al[99] and by Morterra et al[100]. This problem is also complicated by the fact that sulphated zirconia is a very sensitive material, and many variants may influence its preparation and its characteristics, despite the fact that this system is used industrially for alkylation, isomerisation, and esterification [101].

We investigated the reactivity of this strong acid catalyst in the dehydration of glycerol, considering that the latter is stable in presence of steam and its decomposition temperature it is quite high (650°C). Despite this, the characteristics of sulphated zirconia were more interesting that we would have expected; therefore, we also carried out an investigation on the chemical-physical properties of these materials.

Catalysts were prepared by the University of Venezia (prof. M. Signoretto) via a conventional precipitation method[102]. ZrOCl2·8H2O (99%, FLUKA) was dissolved in distilled water and added with a peristaltic pump under vigorous stirring to an ammonia (30%, AnalaR) solution. During the entire course of the precipitation, the pH value was kept constant at 10.0± 0.1 by the continuous addition of a 5N ammonia solution. After the complete addition of the salt solution, the hydroxide suspension was aged for 20 h at 90°C under reflux conditions. The aged hydroxide was filtered and washed with warm distilled water until it was free from chloride ions (AgNO3 test). The Zr hydroxide was dried at 110°C and then impregnated with (NH4)2SO4 by an incipient wetness method. The sample was finally calcined at 650°C for 3 h in flowing air.

The preparative conditions were standardized, in order to obtain reproducible samples. For this reason, the main parameters were set as follows: (i) pH 10 (the pH values can influence the surface area); (ii) a long aging treatment at room temperature (that produces a solid with low particle size, in comparison with other treatments at higher temperature and under reflux conditions); and (iii) a calcination temperature of 650°C (higher temperature could cause the collapse of the microporous structure, the decrease of surface area and the loss of surface sulphate groups).

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[99] A. Clearfield, G.P.D. Serrete, A.H. Khazi-Syed, *Catal. Today*, 20 (1994) 295.

[100] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, *J. Phys. Chem.*, 98 (1994) 12373.

[101] T. Kimura, *Catal. Today* 81 (2003) 57.

[102] M. Signoretto, S. Melada, F. Pinna, S. Polizzi, G. Cerrato and C. Morterra, *Microp. Mesop. Mater.*, 2005, **81**, 19-29

Table 1 summarizes the main characteristics of samples prepared.

Table 1: Main characteristics of samples prepared.

Samples labels	**Description**	**Specific Surface Area**
Z0	**ZrO2**	**80 m2/g**
SZ2.0	**ZrO2 with 2.0 % of (SO4)2 w/w-**	**125 m2/g**
SZ3.8	**ZrO2 with 3.8 % of (SO4)2- w/w-**	**117 m2/g**
SZ4.4	**ZrO2 with 4.4 % of (SO4)2- w/w-**	**122 m2/g**

The content of sulphates in the catalysts was analyzed by Ion Exchange Chromatography; the specific surface area were obtained from N_2 adsorption/desorption isotherms at -196°C with a Micromeritcs ASAP 2000 instrument, using the BET equation. Calcined samples were outgassed at 300°C before test.

The presence of sulphated was also detected by FTIR (PerkinElmer One) instrument in ATR configuration (Attenuated Total Reflectance), using samples in form of powders, obtaining spectra at 2 cm^{-1} resolution. In this case it is possible to observe the typical bands for sulphated zirconia calcined at 650 C (Fig. 3).

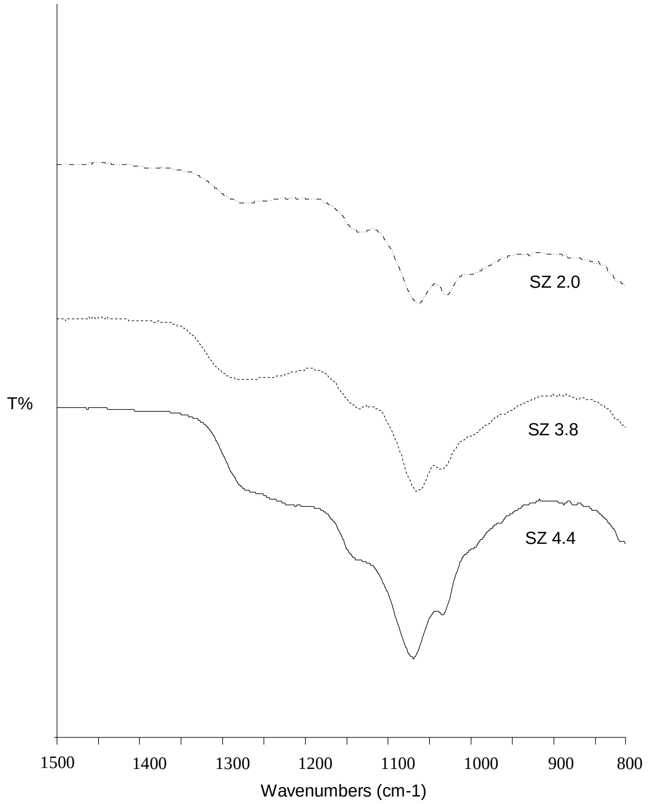

Fig. 3: FTIR spectra of calcined sulphated zirconia samples: SZ 2.0; SZ 3.8; SZ4.4.

The FT-IR spectra show the IR bands of SO_4^{2-} group in the region of 1200–900 cm^{-1}, with peaks at 1242, 1142, 1073, 1045 and 998 cm^{-1}, which are assigned to the asymmetric and symmetric stretching frequencies of single and partially double bounds. The partially ionic nature of the S-O bond is responsible for the Brϕnsted acid sites in sulphated zirconia. In addition, a broad peak at around 3400 cm^{-1} and an intense peak at 1632–1628 cm^{-1} were also observed and were attributed to the stretching and bending O-H mode of water, respectively, associated with zirconia and sulphate groups.

2.2.4 Reactivity tests: Sulphated Zirconia

THE REACTIVITY OF SZ4.4 (SULPHATED ZIRCONIA WITH 4.4 WT% SO_4^{2-}): ANAEROBIC TESTS

Fig.4 shows the results of experiments carried out using the SZ4.4 sample, without O_2 in feed. Fig.4(left) plots the conversion of glycerol, the selectivity to acrolein and to heavy compounds (quantitatively evaluated as missing C in mass balance); Fig.4(right) plots the detail of main by-products: acetaldehyde, propionaldehyde, hydroxyacetone, acetone and carbon monoxide. Some minor additional by-products, such as allyl alcohol and ethanol, have been grouped into Others; the latter also includes two unidentified compounds.

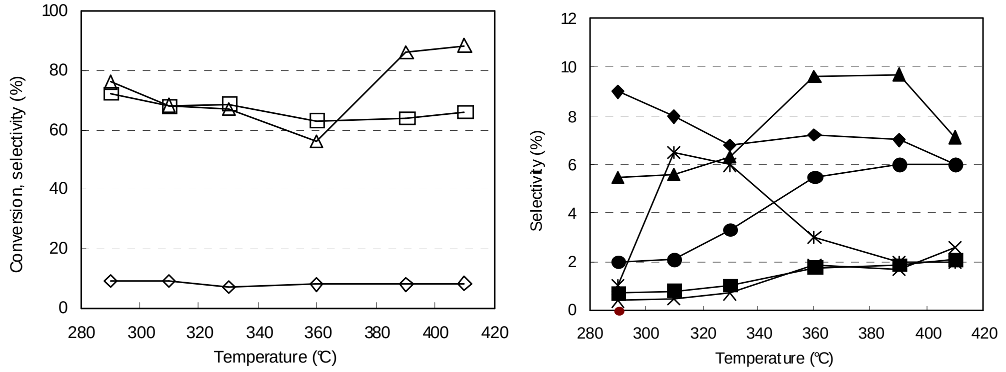

Fig. 4: Effect of temperature on catalytic behaviour of SZ4.4 sample. Feed composition: glycerol / water / helium=2/40/58 (molar ratios). Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), acetone (◆), acetaldehyde (●), propionaldehyde (■), CO (✕), hydroxyacetone (✱) and others (minor identified + unknown) (▲).

Glycerol conversion was close to 80% at 290°C, but then decreased down to 55% when the temperature was raised up to 360°C, likely because of a deactivation phenomenon that contrasted the expected increase of conversion. At higher temperature the relevant conversion increase registered was due to the contribution of homogeneous reactions (see Fig.2). Major products found were acrolein (but with a selectivity lower than 10%), acetone, acrolein, propionaldehyde, acetone, acetaldehyde and CO; the latter formed probably by reforming of organic compounds or aldehydes decarbonylation. However, the very low C balance hinted for the relevant formation of heavy compounds (selectivity between 60 and 80%); these compounds were likely responsible for the deactivation phenomenon experimentally observed.

The presence of a deactivation phenomenon was confirmed by experiments carried out under isothermal conditions, at 310°C, during increasing elapsed reaction time; results of this experiment are shown in Fig. 5 (we reported only the selectivity to products that underwent the major variations during time). The deactivation rapidly led to the decrease of glycerol conversion within a few hours reaction time. This also had important consequences on selectivity to products; in fact, the selectivity to heavy compounds, that on the fresh catalyst was very high, rapidly decreased and after 7 h was about 10%. The selectivity to some products correspondingly increased; the greater variation was observed with hydroxyacetone and acetone. The selectivity to acrolein initially increased, but then remained constant at approximately 18-19%.

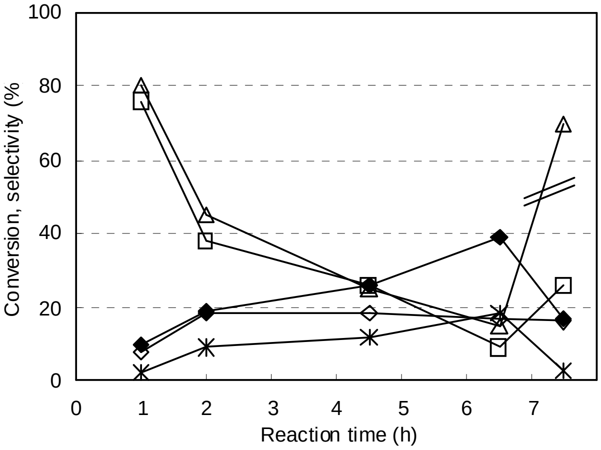

Fig. 5: Effect of the reaction time on the performance of the fresh SZ4.4 catalyst. Feed composition: glycerol / water / helium = 2/40/58 (molar ratios). Temperature 310°C. Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), to acetone (◆), and hydroxyacetone (✱). The last point was taken after a regeneration of the catalyst in air flow for 3 h at 450°C.

The fall of selectivity to heavy compounds observed in concomitance with the decrease of conversion, may be attributed to two different factors: either (a) a decrease of conversion led to a lower contribution of consecutive reactions, that means that heavy compounds mainly form by condensation reactions on products, such as acrolein itself; or (b) the accumulation of coke caused the deactivation of selected sites, those responsible for the formation of the heavy compounds. The three main light products at intermediate glycerol conversion were acetone, acrolein and hydroxyacetone. Acetone, the prevailing product after a few hours reaction time, is reported to form by consecutive transformation of hydroxyacetone;[103,104] in our case, however, there was no relationship between the two compounds, since the selectivity to both acetone and hydroxyacetone increased.

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[103] F. Wang, J-L. Dubois, W. Ueda, *Appl. Catal. A in press*

[104] A. Corma, G.W Huber, L Sauvanaud, P. O'Connor, *J. Catal.*, 257 (2008) 163-171.

The deactivated catalyst was then treated in flowing air for 3 h at 450°C, and the catalytic behaviour was then registered again (last point in Fig. 5). It is shown that the initial activity of the fresh catalyst was not completely recovered after the regeneration treatment; in fact, the initial conversion was 70% (80% for the fresh catalyst).

THE REACTIVITY OF SZ4.4: AEROBIC TESTS

Fig. 6 compares the behaviour of SZ4.4 both in the absence and in the presence of oxygen. The positive effect on performance due to oxygen addition is evident; the conversion of glycerol, which in the absence of oxygen declined in the temperature range between 290 and 360°C, now showed a continuous, albeit slight, increase when the temperature was raised in the presence of oxygen. On the other hand, it is shown that in the latter series of experiments, the conversion increase was only of 8-9 point % over the entire temperature range, suggesting either the possible presence of mass-transfer limitations under the conditions used, or the contribution of residual deactivation phenomena.

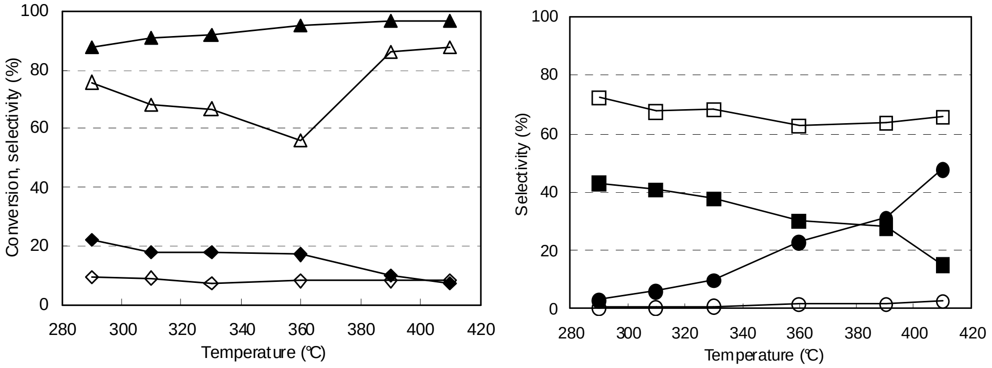

Fig. 6: Effect of temperature on glycerol conversion (▲△), selectivity to acrolein (◆◇), selectivity to heavy compounds (■□) and to $CO+CO_2$ (●○). Feed composition: glycerol / water / helium = 2/40/58 (molar ratios) (open symbols) or glycerol / oxygen / water / helium = 2/4/40/54 (molar ratios) (full symbols). Catalyst SZ4.4.

The selectivity to acrolein was slightly higher in the presence of oxygen, but the main effect was on the amount of heavy compounds, which were considerably decreased; at the same time, the formation of CO and CO_2 became relevant. However, deactivation phenomena were not completely eliminated, as confirmed by tests carried out during increasing reaction time with SZ4.4, under isothermal conditions (310°C) in the presence of oxygen (Figure not shown). After

4 hours reaction time, glycerol conversion was only 13-14% lower than the initial value (decreasing from 74% to 61%, whereas in the absence of oxygen the conversion decline was much greater during a similar value of elapsed reaction time, see Figure 5), but conversion was lowered down to 37% after 24 h reaction time. These data confirm the existence of a deactivation phenomenon, even when oxygen was co-fed with glycerol, likely due to the still present accumulation of heavy compounds.

Another important aspect is that the yield to COx was greater than it should be reasonably expected (already at 290°C there was a non-negligible formation of CO_x, Fig. 6), suggesting a catalytic role possibly played by sulphate groups. These aspects will be examined later, with dedicated experiments aimed at determining the main reasons for catalyst deactivation under anaerobic conditions and the possible catalytic role of sulphates in the presence of oxygen.

THE EFFECT OF SULPHATE LOADING

Fig. 7 compares the conversion of SZ2.0, SZ3.8 and SZ4.4 samples in function of the reaction temperature, under anaerobic conditions. Deactivation phenomena, that were so evident in the case of SZ4.4 sample, were much less relevant with SZ3.8 and apparently minimal with SZ2.0. Despite this, the distribution of products was very similar for the three samples, with a similar amount of heavy compounds, which with all catalysts formed with selectivity comprised between 60 and 80%, and similar acrolein selectivity as well, around 10%.

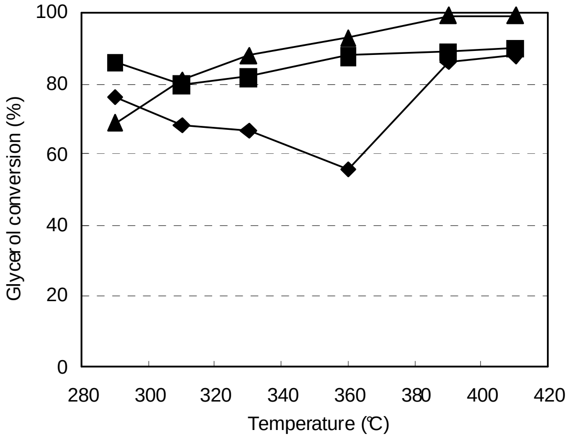

Fig. 7: Conversion of glycerol as a function of temperature for catalysts SZ2.0 (▲), SZ3.8 (■) and SZ4.4 (◆). Feed composition: glycerol / water / helium = 2/40/58 (molar ratios)

The absence of relevant deactivation phenomena for SZ2.0 was confirmed by the comparison of results achieved in the absence and presence of oxygen (Fig. 8). In this case, at variance with what observed with SZ4.4, the effect of oxygen addition on glycerol conversion was minimal. Also the distribution of products showed little variations; the selectivity to heavy compounds was only marginally affected. Moreover, the selectivity to acrolein and to other light by-products decreased, and the selectivity to COx increased. In this case, therefore, the effect on selectivity to acrolein was the opposite of that observed with SZ4.4, and in general it can be concluded that with SZ2.0 the addition of oxygen had no positive effect on catalytic behaviour, and indeed is even detrimental in regard to the formation of acrolein.

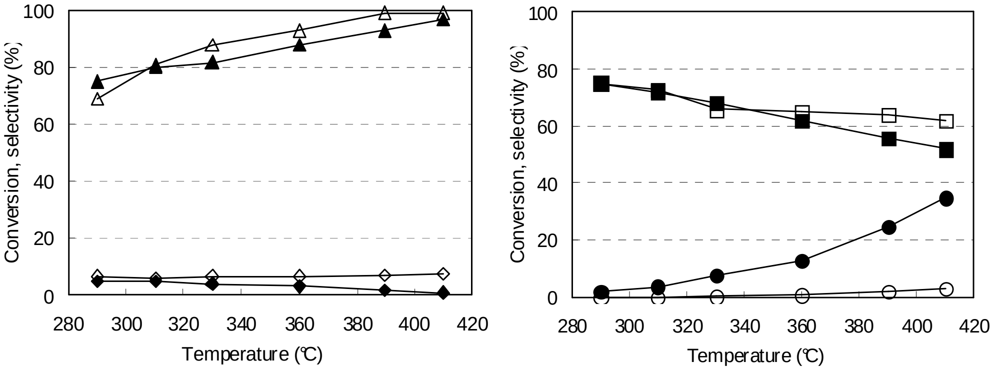

Fig. 8: Effect of temperature on glycerol conversion (▲△), selectivity to acrolein (◆◇), selectivity to heavy compounds (■□) and to $CO+CO_2$ (●○). Feed composition: glycerol / water / helium = 2/40/58 (molar ratios) (open symbols) or glycerol / oxygen / water / helium = 2/4/40/54 (molar ratios) (full symbols). Catalyst SZ2.0.

These experiments suggest that the accumulation of heavy compounds and carbonaceous deposits is not the only reason for the deactivation of these catalysts. Moreover, it is also evident that the behaviour of catalysts is drastically different under aerobic and anaerobic conditions, in function of the amount of sulphate loading. The density of acid sites may play an important role in the phenomena experimentally observed; therefore we decided to investigate more in detail the reasons for the deactivation shown by SZ4.4.

VARIOUS PHENOMENA CONTRIBUTE TO CATALYST DEACTIVATION

Main differences experimentally observed between samples having different sulphate loading are the following:

1. The higher is the S content, the more important are the deactivation phenomena under anaerobic conditions.
2. The addition of oxygen increases conversion and limits deactivation phenomena with the catalyst having the greater S content (SZ4.4), but has marginal effects on the activity of the sample containing the lower amount of S (SZ2.0).
3. The selectivity to acrolein is similar for all samples under anaerobic conditions, regardless of S content in samples. However, the addition of oxygen has opposite effects on acrolein selectivity obtained with SZ2.0 and SZ4.4. The ranking of selectivity to

acrolein at 310°C in the presence of oxygen is SZ4.4 (18%) > SZ2.0 (5%).

4. The addition of oxygen reduces the formation of heavy compounds in SZ4.4 (however, some heavy compounds still form even in the presence of oxygen), whereas it has almost no effect on the formation of heavy compounds with SZ2.0.

On one hand, these data clearly indicate that the deactivation of catalysts, particularly in the case of the S-richer sample (SZ4.4), is not only due to the formation of heavy compounds (that also form with SZ2.0). On the other hand, data highlight the possible role of sulphate groups, especially in the case of SZ4.4, in catalysing the combustion of heavy compounds to CO_x. A redox cycle on S cannot be excluded, in analogy with what reported in the literature when sulphated zirconia are used as catalysts for high-temperature acid-catalysed reactions[105]

In order to confirm the possible role of redox cycles under aerobic conditions, we first checked the self-reducibility of samples under inert atmosphere. Fig. 9 shows the results of these experiments. The m/e signal of H_2O, O_2 and SO_2 released from SZ4.4 and SZ2.0 were recorded while heating the samples in an He flow, from room temperature up to 650°C (TPD experiments); other m/e signals attributable to S containing compounds were searched for, but were not found.

In the case of SZ4.4, the self reduction of S^{6+} into S^{4+} already began at 250-300°C, and was completed at around 450°C, as evident from the signal of O_2; in this temperature range there was no release of any S-containing compound. Then, starting at about 450°C, the release of SO_2 was monitored; therefore, at high temperature the sulphite groups, formed at lower temperature and linked to the zirconia via Zr-O-S moieties, were totally decomposed into gaseous sulphur dioxide.

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[105] X. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Learcher, A. Hofmann, J. Sauer, *J. Am. Chem. Soc.*, 230 (2005) 214-225; and *See reference 87,89 and 90* in this Part D

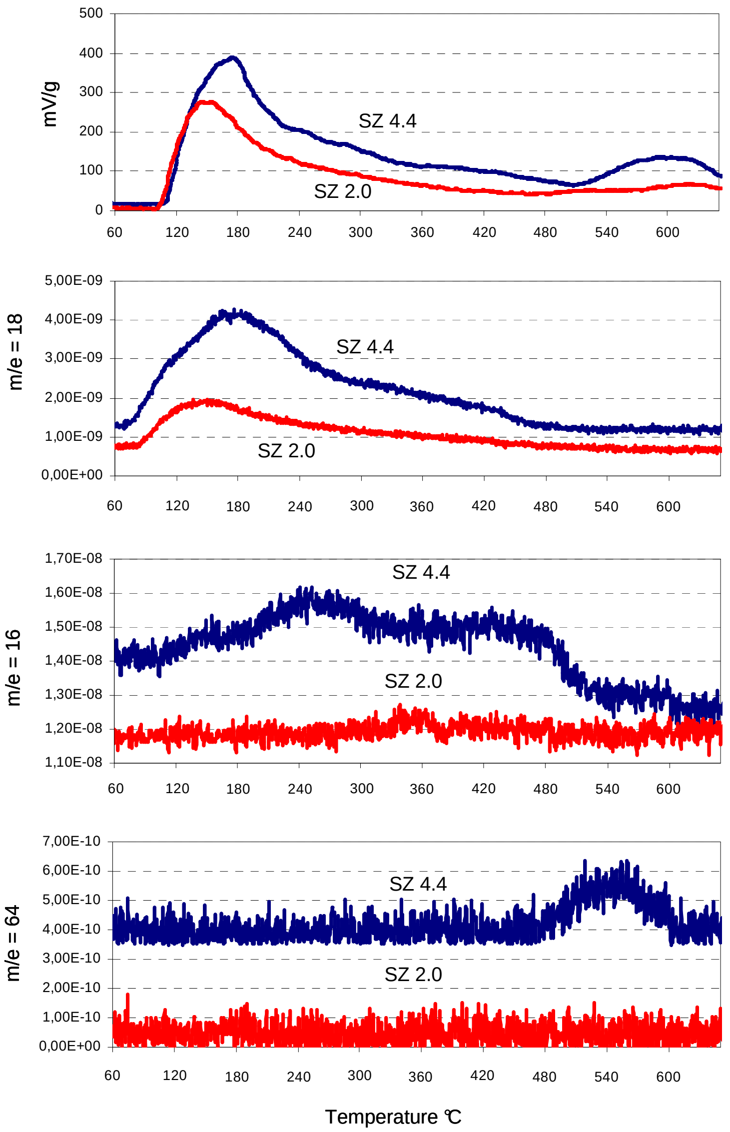

Fig. 9: TCD signal in TPD profiles of SZ4.4 and SZ2.0 samples (top Figure). M/e=18 signal (H_2O, second Figure from top), m/e=16 signal (O_2, third Figure from the top) and m/e=64 signal (SO_2, bottom Figure) registered during TPD experiments.

After this experiment, the sample was cooled down to room temperature and then was heated again under flow of O_2/Ar; no consumption of oxygen was registered, that confirmed that the reduced (S^{4+}) sulphite groups had not remained on the catalyst surface. In another related experiment, the self-reduction of SZ4.4 was stopped at 400°C, that is, before the release of SO_2; then the sample was cooled down to room temperature and heated again in the oxidizing flow. In this case, a consumption of oxygen was registered between 250 and 350°C, because of the reoxidation of sulphite into sulphate groups; a further increase of temperature led again to the release of O_2. Worth of note, the self-reduction also occurred when SZ4.4 was heated in an air flow, but in this case the reduction occurred concomitantly with the release of SO_2, at 650°C. It is important to underline that in this latter case there was no release of any S-containing compound up to 650°C; this means that S desorbs as the corresponding gaseous anhydride only when S is in the 4+ oxidation state.

These experiments demonstrate that with SZ4.4, during reaction in the glycerol stream, the S moieties are likely present in the reduced form when the reaction is carried out under anaerobic conditions, whereas are present in the oxidized state (as sulphate group) when the reaction is carried out under oxidizing conditions. Moreover, if the reaction temperature used is not higher than 450°C, it may be expected that even under anaerobic conditions the S-containing groups remain on the catalyst. In fact, the release of SO_2 only occurs at very high temperature.

Quite different was the behaviour shown by SZ2.0. In this case, in fact, there was no release of either O_2 or SO_2 over the entire temperature range; the only molecule released from the sample during heating was water. Therefore, the spontaneous self-reduction of S did not occur in this case. One possible explanation for this is that a high surface density of sulphate groups is the key requisite for self-reduction. This agrees with literature showing that the redox activity of S^{6+}-containing groups is related to the formation of pyrosulphate groups,[106] the formation of which is obviously more likely in the sample containing a higher amount of S, and hence having a greater surface density of S sites.

With both SZ2.0 and SZ4.4, the signal at $m/e = 18$, due to the desorption of water, showed a main broad peak with maximum at around 150°C, that however covered the entire range of temperature from 100°C to 400°C; this peak can be associated to the loss of water interacting with either Lewis Zr^{4+} sites or S-OH moieties, and to the dehydration of sulphuric groups (Scheme 1).[107] Not only was the overall intensity of the water signal greater for SZ4.4 than for SZ2.0 (because

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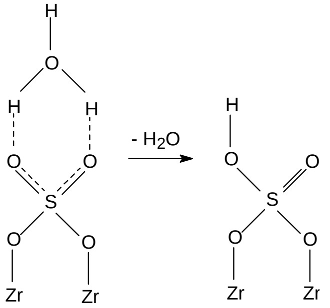
[106] Lercher et al., *Phys. Chem. Chem. Phys.* 9 (2007) 3600-3618.

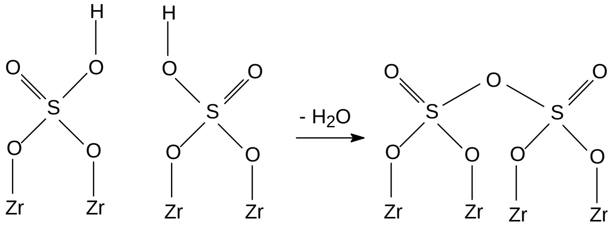
[107] C. Morterra; G. Cerrato, F. Pinna, M. Signoretto, *J. Phys. Chem.*, 98 (2004) 3279-3283.

of the bigger S loading in the former sample), but SZ4.4 also showed an additional peak with maximum at 180-200°C, overlapping the former one, that was either absent or remarkably less intense in SZ2.0.



Scheme 1: Dehydration of isolated sulphuric groups

This can be attributed to the dehydrative condensation of sulphuric groups into pyrosulphate (Scheme 2), a phenomenon that is possible only with neighbouring S sites, and is therefore more favoured with SZ4.4, because of the relatively higher concentration of sulphuric groups.



Scheme 2: Condensation of sulphuric groups

H_2-TPR experiments were done with the aim of finding whether the presence of a reductant species might facilitate the reduction of S^{6+}. It was found that all samples reduce in H_2 with a peak starting at around 450°C, the peak maximum being at approx 650°C (Figure 10). The hydrogen consumption followed the ranking: SZ3.8> SZ2.0 > SZ4.4; this was due to the fact that in SZ4.4, S was present as S^{4+} at the temperature at which reduction by H_2 began, because the spontaneous self-reduction had occurred at a temperature lower than 450°C. On the contrary, in the case of samples having the lower S content, either the self-reduction had only in part occurred (SZ3.8) or it had not occurred at all (SZ2.0).

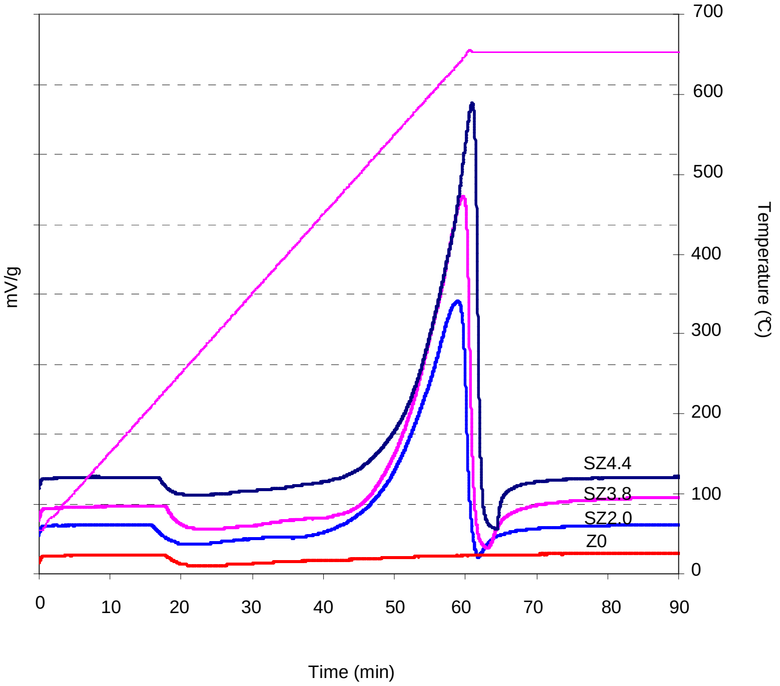


Fig. 10: H_2-TPR profiles (H_2 consumption as revealed by a TCD) of SZx samples

The results of these experiments may provide an explanation for the catalytic behaviour observed during glycerol dehydration. In SZ4.4, the deactivation shown under anaerobic conditions may be at least in part due to the spontaneous reduction of sulphate into sulphite groups; the latter is supposed to develop less strong Brϕnsted sites than the former one, in the presence of steam. However, under aerobic conditions the sulphate group is stable, and no self reduction occurs; at these conditions S^{6+} oxidizes heavy compounds into COx, and the active sites are likely made of pyrosulphate groups, that play the redox cycle and limit (but do not eliminate) the deactivation phenomena due to heavies accumulation. These phenomena do not occur with SZ2.0, because sulphuric groups are made of isolated rather than neighbouring (dimeric) units; in fact, the effect of O_2 addition on catalytic behaviour was much less important than with SZ4.4, glycerol conversion and selectivity to heavy compounds moreover being substantially unaffected. On the other hand, the absence of redox behaviour in SZ2.0 allows keeping the sulphate groups intact (and in fact SZ2.0 is more active than SZ4.4 when used under anaerobic conditions), and deactivation phenomena are much less important than with SZ4.4, even in the absence of oxygen.

Therefore, the presence of oxygen in the gas phase modifies the intrinsic reactivity of the active sites; with SZ4.4, oxygen keeps S oxidized and the acidity of the sulphuric group is preserved, that allows obtaining an higher conversion of glycerol and an higher selectivity to acrolein with respect to the case when the reaction is carried out without oxygen. In other words, the increase of acidity more than compensates the amount of acrolein that is burnt to CO_x because of the redox activity of S^{6+}. With SZ2.0, the addition of oxygen does not alter the acid characteristics of the active site with respect to the anaerobic operation; the selectivity to acrolein decreases because of the contribution of combustion reactions (even though the latter are less important than with SZ4.4).

In order to confirm the hypothesis made about a role of dehydrative condensation and self-reduction on the acidic properties of sulphuric groups in SZ4.4, we estimated the surface acidity by means of pyridine adsorption and recording of IR spectra after pyridine desorption at increasing temperatures. In fact, the pre-treatment at high temperature under vacuum, that is usually carried out in order to set the Brϕnsted and Lewis acid free from adsorbed molecules and contaminants, should lead to the above mentioned phenomena, i.e., the dehydrative condensation of neighbouring sulphuric groups and the self-reduction of sulphate (or pyrosulphate) into sulphite with SZ4.4, but not with SZ2.0. In other words, this characterization method may allow an estimation of the surface acidic properties under conditions that are closer to those used in the reaction. On the other hand, it has to be reminded that the reaction of glycerol dehydration occurs under a very high partial pressure of steam; this might limit the high-temperature dehydrative condensation of sulphuric groups and eventually transform Lewis-type acid sites into Brϕnsted sites after water adsorption (in fact, Figure 9 shows that complete water desorption from catalysts only occurs at above 400°C), but it should have no effect on redox behaviour. Therefore, a lower concentration of Brϕnsted S-OH sites than the expected one should be registered with SZ4.4 from pyridine-adsorption experiments (because of the dehydrative condensation of sulphuric groups), and some effect on the relative strength of these sites should also be observed (in fact, the acid strength of pyrosulphuric acid, H_0 –15, is greater than that of sulphuric acid, H_0 –12). Moreover, an additional effect should be observed on the Lewis-type acid strength of Zr^{4+} sites, due to the presence of neighbouring S^{4+}

sites (deriving from the self-reduction process in SZ4.4). The expected lower electronegativity of S^{4+} as compared to S^{6+} might lead to a decrease of the strength of Lewis-type acid sites in SZ4.4, whereas the same effect should be irrelevant with SZ2.0.

These hypotheses were in part confirmed by results of acidity measurements tests. Figure 11 shows the variation of concentration of surface Brϕnsted and Lewis sites in SZ2.0 and SZ4.4 in function of the desorption temperature, after adsorption of pyridine at room T. Non-sulphated zirconia (SZ0) showed no Brϕnsted acid sites at all. The main results were the following:

1. The concentration of Brϕnsted sites was similar in SZ2.0 and SZ4.4, despite the higher concentration of S in the latter sample. However, the acid strength of these sites was considerably higher in SZ4.4 than in SZ2.0. Both effects are in line with the expected effects due to the dehydrative condensation of sulphuric groups, preferentially occurring with SZ4.4 and not with SZ2.0. On the other hand, it seems that the self-reduction of S^{6+} into S^{4+} had not the expected effect of a decrease of acidity of S-OH groups.
2. The concentration of Lewis sites followed the scale: SZ4.4 > SZ2.0 > SZ0. However, the strength of these fewer sites in SZ2.0 was greater than that of more numerous Lewis sites in SZ4.4, since with the former sample the concentration of pyridine adsorbed was not much affected by temperature. At high temperature, the residual concentration of adsorbed pyridine was similar for the two samples. Moreover, in both cases the acid strength was greater than that of non-sulphated zirconia. These results indicate that the presence of S enhances the Lewis acidity of Zr^{4+}; on the other hand, the presence of S^{4+} in SZ4.4 is the reason for the lower strength registered with this catalyst. Worth of note, with both samples the concentration of Lewis sites is higher than that of Brϕnsted sites; this means that during reaction, in the presence of water, it may be expected that Zr-OH groups generated by water adsorption over stronger Lewis sites play a role in glycerol dehydration.

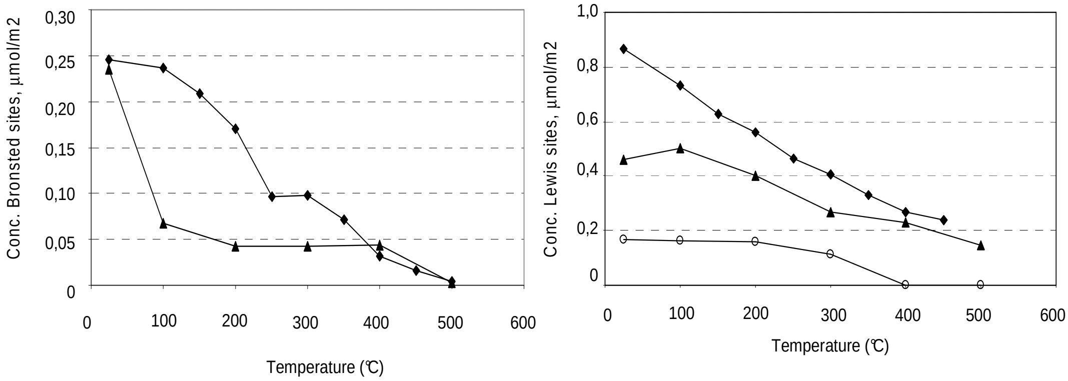


Fig. 11: Concentration of Brϕnsted sites (top) and of Lewis sites (bottom) in function of the temperature of treatment after adsorption of pyridine at room temperature. Samples were pre-treated at 450°C under vacuum before adsorption of pyridine. Symbols: SZ0 (○), SZ2.0 (▲) and SZ4.4 (◆).

In overall, it seems that the combined effect of the two phenomena experimentally observed in SZ4.4, i.e., the dehydrative condensation of sulphuric groups and the self reduction of S, lead to an enhanced acid strength of Brϕnsted sites, but to a decrease of their surface concentration, and to a decreased strength of the more numerous Lewis acid sites.

One additional reason for catalyst deactivation was found to be the release of S from the catalyst. Initially, we thought that the leaching of S were associated to the release of SO_2 at high temperature, a phenomenon more relevant with the SZ4.4 catalyst (Figure 9). However, results shown in Table 2, reporting the amount of residual S in SZ2.0 and SZ4.4 after reaction, demonstrate that S was progressively lost during the increasing reaction time at both low and high T, and with catalysts having both low and high S content. Therefore, the leaching of S was not related to the spontaneous self-reduction of S and to the release of SO_2. Moreover, the loss of S occurred only in the presence of glycerol, whereas the S content in samples was not altered when the catalyst was treated in separate experiments with steam/air at either low or high temperature. The formation of glycerol sulphate esters or other volatile compounds can be hypothesized to be the reason for the loss of S, eventually accelerated by hydrolysis phenomena due to the presence of large amounts of steam in the reaction environment.

Table 2: Chemical analysis of S content in catalysts after various treatments.

	SO_4^{2} content			
Catalyst	**Reaction time 0 h**	**Reaction time 0.5 h**	**Reaction time 6 h**	**Reaction time 15 h**
SZ2.0 reaction at 310°C Glycerol/H_2O/O_2/He	2.0	2.0 (2.85 wt% C)	1.2	nd
SZ2.0 reaction at 400°C Glycerol/H_2O/O_2/He	2.0	2.0	1.3	0.3
SZ2.0 reaction at 290°C H_2O/O_2/He	2.0	2.0	nd	nd
SZ2.0 reaction at 400°C H_2O/O_2/He	2.0	2.0	2.0	nd
SZ4.4 reaction at 310°C Glycerol/H_2O/O_2/He	4.4			0.4
SZ4.4 reaction at 310°C Glycerol/H_2O/He	4.4			0.4
SZ4.4 reaction at 400°C Glycerol/H_2O/O_2/He	4.4			0.5
SZ4.4 reaction at 400°C Glycerol/H_2O/O_2/He + regeneration in air	4.4			0.5

Worth of note, the relevant loss of S did not cause the expected corresponding loss of activity; in fact, the deactivated catalysts still were much more active than non-sulphated zirconia; this also demonstrates that the small residual amount of S (0.3 % in SZ2.0 and 0.5% in SZ4.4) is enough to catalyse the reaction of glycerol dehydration. This is further confirmed by tests shown in Fig. 5; a reoxidation treatment on the deactivated catalyst (after operation under anaerobic conditions) led to an almost total (but not complete) recovery of the initial reactivity behaviour, demonstrating that the loss of the major part of S had not led to a corresponding, proportional loss of activity as compared to the fresh, fully sulphated catalyst.

The third reason for catalyst deactivation is the accumulation of coke and heavy compounds on catalyst surface; for instance, in the case of tests carried out in the presence of oxygen, catalyst SZ2.0 had an amount of coke deposited on the surface of 2.85 wt% after only 0.5 h reaction time.

In conclusion, with sulphated zirconia catalysts, various phenomena contribute to catalyst deactivation, both reversible and irreversible. The reversible one is more evident in the catalyst having the greater S content, and is due to the reduction of sulphate into sulphite, occurring under anaerobic conditions; this phenomenon had opposite effects on the Brϕnsted and Lewis acid sites, with an increase of the strength of the Brϕnsted and a decrease of the strength of the more numerous Lewis sites, as compared to SZ2.0, for which no self-reduction was experimentally registered. Treatment with oxygen allows to reoxidize S (as shown by TPO tests) and recover the greater part of catalyst activity (see Fig. 5). Another reversible deactivation was due to coke accumulation, a less rapid phenomenon (but not completely avoided) when the reaction was carried out in the presence of oxygen. Finally, the irreversible deactivation was due to the progressive loss of S from the catalyst; this however surprisingly gave a minor contribution to catalyst deactivation. This suggests that indeed only a small fraction of the sulphuric groups on the zirconia surface contribute to the catalytic behaviour; an additional evidence for the existence of extra-particle diffusion limitations.

SEARCHING FOR A BETTER SELECTIVITY TO ACROLEIN: THE REACTION NETWORK AND THE ROLE OF MASS AND HEAT TRANSFER LIMITATIONS PHENOMENA

Concerning the reaction mechanisms leading to acrolein and by-products formation, the following can be inferred from the literature:[108] primary reaction products of glycerol dehydration are enol intermediates, that however are very reactive and transform either into the stable hydroxyacetone (acetol), from 1,2-dihydroxypropene, or into 3-hydroxypropanal (via tautomerisation of 1,3-dihydroxypropene). 3-Hydroxypropanal, however, is only a hypothetical intermediate; in fact, it has never been isolated, and this is attributed to the fact that it is very unstable.

Main by-products of the reaction are acetaldehyde, hydroxyacetone,

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[108] B. Katryniok, S. Paul, M. Capron, F. Dumeignil, *ChemSusChem* 2 (2009) 719-730.

propanal (propionaldehyde), allyl alcohol (2-propenol, formed by hydrogenation of acrolein), light alcohols (methanol, ethanol) and in the presence of oxygen also carbon oxides, propionic acid, acrylic acid and acetic acid.[75-83,109,110,111,112] Other products reported are (i) 1,2-propandiol, possibly formed by hydrogenation of acetol with in-situ generated hydrogen,[78,86,77] (ii) phenol,[74,85,109] probably formed from a dimerisation–cyclisation reaction of glycerol followed by a consecutive dehydration, or from acrolein and acetone via a Diels-Alder reaction, and (iii) acetone,[83,84,103] formed by hydroxyacetone hydrogenation and dehydration. All authors, however, report the formation of a certain number of unidentified oxygenated compounds, and in many cases the C balance is lower than 100%, a clear indication of the formation of heavy, undetected compounds. Acetaldehyde is proposed to form, together with methanol, formaldehyde and acetic acid, from the intermediate 3-hydroxypropionaldehyde.[109,86] CO and CO_2 mainly form by decarbonylation and decarboxylation of various molecules,[109,86] and hydrogen forms by dehydrogenation of glycerol and of various intermediates. Other compounds sometimes reported, especially with zeolites, are (i) olefins and aromatics, formed mainly by consecutive reactions starting from acrolein, acetol, acetone and allyl alcohol, and (ii) C_6 cyclic dioxolanes, formed by dimerisation of either glycerol of 3-hydroxypropionaldehyde.[109] Acetol is an unstable product,[9,39] and yields several by-products, including acetone, acetaldehyde, acetic acid, 1-propanal and propionic acid, various furan derivatives by retroaldol dimerisation (compounds that have been also identified from glycerol), and heavy compounds that deposit on the catalyst. Heavy compounds may either form by direct glycerol transformation (to give linear, cyclic and branched oligomers), or as consecutive transformations from both acrolein and acetol[109] to compounds, that may also include oxygenated aromatics, are precursors for coke formation.

The low selectivity to acrolein achieved with the catalysts here described is due to both the formation of several C_2 and C_3 by-products, of CO_x and of heavy compounds as well. In order to gain information on the reaction network, we carried out experiments by varying the contact time, under isothermal conditions,

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[109] W. Yan, G.J. Suppes, *Ind. Eng. Chem. Res.*, 48 (2009) 3279-3283.

[110] W. Suprun, M. Lutecki, T. Haber, H. Papp, *J. Mol. Catal. A.*, 309 (2009) 71-78.

[111] M. Watanabe, T. Lida, Y. Aizawa, T.M. Aida, H. Inomata, *Biores. Tech.*, 98 (2007) 1285-1290.

[112] L. Ott, M. Bicker, H. Vogel, *Green Chem.*, 8 (2006) 214-220.

in the presence of oxygen. Each experiment was carried out with fresh sample, changing the amount of catalyst loaded.

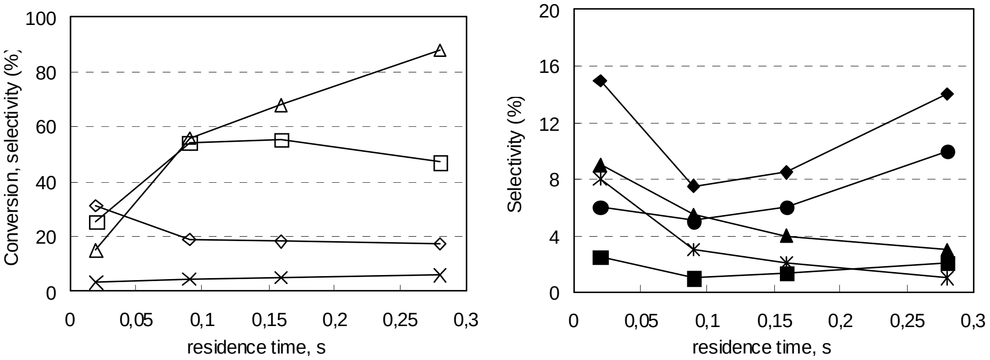

Fig. 12: Effect of residence time on catalytic behaviour of SZ4.4 sample. Feed composition: glycerol / water / oxygen / helium=2/4/40/54 (molar ratios). Temperature 310°C. Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), acetone (◆), acetaldehyde (●), propionaldehyde (■), CO (×), hydroxyacetone (✱) and others (minor identified + unknown) (▲).

The increase of the contact time led to an increase of glycerol conversion (Fig. 12). The selectivity to heavy compounds was low (approx 30%) at low residence time, and increased when the conversion was increased; this provides clear evidence that heavy compounds formed both by direct reaction on glycerol and by consecutive reactions. The selectivity to acrolein, hydroxyacetone and other unknown compounds declined, whereas that to CO_x increased, once again because of the increased contribution of consecutive reactions. The latter were also evident from the results of experiments reported in Fig. 13. An aqueous solution of acrolein (7 wt% acrolein in water) was vaporized and fed over SZ4.4, in the presence of oxygen; the only products identified were acetaldehyde and carbon oxides, with also a relevant formation of undetected heavy compounds, especially at low temperature. Therefore, acrolein is highly reactive with these catalysts, and when the conversion of glycerol is pushed, it is extensively converted to by-products.

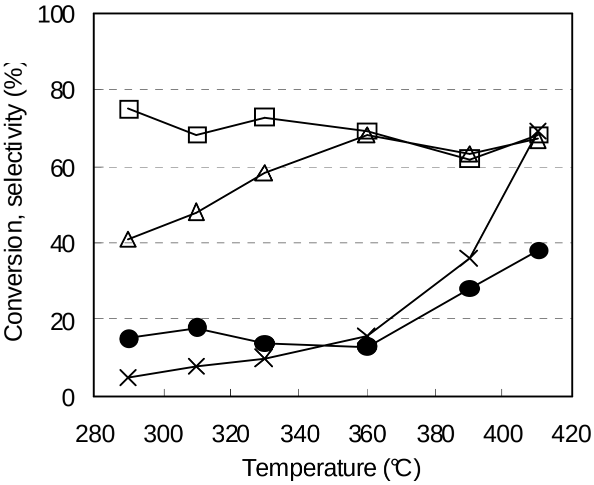

Fig. 13: Effect of temperature on catalytic behaviour of SZ4.4 sample. Feed composition: acrolein / oxygen / water / helium=1/4/43/52 (molar ratios). Contact time 0.2 s. Symbols: conversion of acrolein (△), selectivity to acetaldehyde (●), to heavy compounds (□), and COx (×).

However, Figure 12 shows that still the selectivity to acrolein was low, 31%, even at low glycerol conversion (15%). This was due to both the formation of light by-products (hydroxyacetone, acetone, acetaldehyde and others), and to the formation of heavy by-products (selectivity around 25% at 15% glycerol conversion).

Results of experiments carried out in function of temperature (Figures 6 and 7) highlight that mass transfer phenomena may limit the reaction rate. These phenomena might eventually be responsible for the presence of undesired reactions leading to heavy compounds formation. In order to confirm this hypothesis, we carried out experiments by keeping the same contact time (0.2 s), but using higher linear velocity, i.e., equal to 0.0125 m/s (measured at 20°C, and calculated considering the entire reactor section, as if it had no catalyst loaded within), that is five times greater than that used for experiments shown in Figures 2,4-8 and 12. Worth of note, these experiments were carried out using a total GHSV of 18,000 h^{-1} (360 h^{-1} by glycerol), values that are higher than those typically reported in the literature for this reaction.[6,16] Results of the test carried out at high linear velocity are shown in Fig. 14 (tests were carried out in the presence of oxygen, to limit deactivation phenomena); the comparison with results shown in Fig. 6 (full symbols), made at the same contact time but lower linear velocity, allows making the following considerations:

At high linear velocity, the conversion of glycerol showed a marked increase in function of temperature, with an apparent activation energy that is of 29±2 kcal/mole. The conversion at low temperature was lower than that achieved for the same temperature and contact time, but using lower linear velocity; this difference corresponds to that typically observed when extraparticle mass and heat transfer limitations cause higher local temperature (for exothermal reactions) and hence high conversion rates.

The selectivity to acrolein and to COx was higher than that achieved under conditions of mass transfer limitation, whereas that to other by-products and to heavy compounds was remarkably lower; acetone and propionaldehyde were absent. Worth of note, the selectivity to heavy compounds was lower at both low (compare with Figure 12) and high temperature (compare with Figure 6), a clear indication of the lesser contribution of both parallel and consecutive condensation reactions on glycerol and acrolein, respectively. The preferred occurrence of a bimolecular reaction is also a typical phenomenon encountered when the concentration of products is unusually high in the boundary layer surrounding the catalyst, because of the presence of mass transfer limitations that hinder the counter-diffusion of products towards the bulk reactants phase.

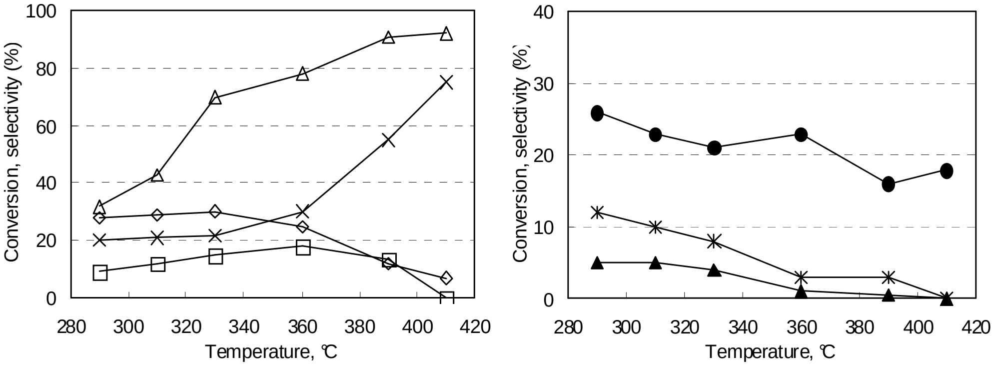

Fig. 14: Effect of temperature on catalytic behaviour of SZ4.4 sample. Feed composition: glycerol / water / oxygen / helium=2/4/40/54 (molar ratios). Contact time 0.2 s; linear velocity 75 cm/min. Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (☐), CO_x (✕), acetaldehyde (●), hydroxyacetone (✱) and others (minor identified + unknown) (▲).

Experiments shown in Fig.14 definitely confirm that one problem met with this reaction is the existence of interparticle mass and heat transfer limitations, contributing to the low selectivity to acrolein. Because this problem has not been reported in earlier literature reports, it is reasonable to assume that a boundary layer made of condensed water (the main component of the reaction medium) may form over the highly hydrophilic catalyst surface of systems used in the present work; relatively high linear velocity (Re_p higher than 10, that in our case is achieved for a linear velocity of approximately 0.4 m/s, calculated taking into consideration the true empty section of the reactor and the temperature of 310°C) are necessary to push the system towards the development of non-laminar regimes, so to minimize diffusion limitations.

Finally, Fig. 15 shows the effect of temperature when the same high linear velocity but a lower residence time (0.1 s instead of 0.2 s) is used, with respect to experiments of Fig.14. As expected, the conversion achieved was lower than that shown in Fig. 14, and the selectivity to acrolein was higher (42% at 49% glycerol conversion); in this case the major by-products were CO_x (with a selectivity that however was lower than that shown in Fig. 14, especially at high temperature) and other light compounds but, remarkably, the formation of heavy compounds was practically nil over the entire range of temperature examined. This means that the combination of a higher linear velocity (that allows minimization of mass and heat transfer limitations) and a higher GHSV value (that however has the drawback of a lower glycerol conversion) allows to kinetically limit both the parallel and consecutive transformations leading to heavy by-products formation, and achieve the higher acrolein selectivity with sulphated zirconia catalysts.

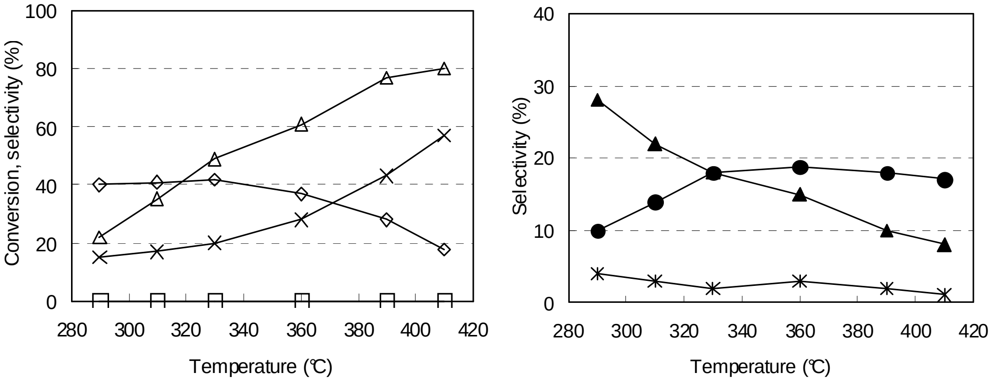

Fig. 15: Effect of temperature on catalytic behaviour of SZ4.4 sample. Feed composition: glycerol / water / oxygen / helium=2 / 4 / 40 / 54 (molar ratios). Contact time 0.1 s; linear velocity 75 Ncm/min. Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), CO_x (✕), acetaldehyde (●), hydroxyacetone (✱) and others (minor identified + unknown) (▲).

2.2.5 Catalytic systems: Main characteristics of Keggin-heteropolycompounds

Polyoxometalates (POMs), or heteropolycompounds (HPCs), are materials with particular characteristics that can be applied in heterogeneous catalysis. They are a remarkable example of intrinsic multifunctionality for catalytic applications[113]. Multifunctional properties are useful for those reactions where different kinds of synthetic steps are needed; one example is glycerol transformation into acrylic acid. Just few words about these compounds are fundamental in order to focus the attention on the reasons why these materials could be suitable for the transformation of glycerol and to understand the guidelines that led us to choose these materials as possible catalysts for glycerol transformation.

Keggin-type POMs are made of heteropolyanions and of cations; when protons are used, these compounds are called heteropolyacids. The most interesting characteristic is that they are very versatile compounds, and chemical-physical properties can be modulated by changing the composition. In particular it is possible to obtain *a priori* the desired features by "tailoring" the composition.

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[113] F. Cavani, *Catal. Today* 41 (1998) 73-86

POMs are crystalline ionic species with a three-dimensional structure, with general formula $X^{n+}M_{12}O_{40}^{(8-n)}$, where M are called addenda atoms, and X is the heteroatom. The addenda atoms are organized in a structure around the heteroatom where usually MO_6 octahedra share corners, edges and in some cases faces. The octahedral group contains one terminal M=O oxo group and five bridging oxo M-O-M groups. The heteroatom X, adopting a tetrahedral coordination, is usually either P^{5+} or Si^{4+}, and M is either Mo^{6+} or $W^{6+,}$ especially in the Keggin structure.

The structural arrangement leads to the formation of a spherical polyanion that it is able to delocalise the surface charge density, leading to a weak interaction between the protons and the anion. Usually the acidity is generated by protons that act as counterions in heteropolyacids and in a mixed acidic salts, or by protons which develop by other phenomena such as the dissociation of water coordinated to metal cations or formed by the reduction of metal ions. The role of addenda atoms is fundamental; in fact POMs containing tungsten (W) instead of molybdenum (Mo) are more acid.

POMs are also multi-electron oxidants and the mechanism of reduction involves the transfer of as many as six electrons to the unit without structural collapse. The reduction increases the basicity and can be accompanied by the protonation of the compound. The redox properties are due to the energy of the lowest unoccupied molecular orbital (LUMO); for Keggin POMs the LUMO is classified as a nonbonding orbital instead of antibonding, so the reduction is easy and reversible. In addition several studies about the redox cycle for this kind of structures demonstrated that the reduction is also fast. The redox properties of POMs are function of the nature of addenda atoms (M), of the heteroatom (X) and also of the counterions.

We tested the reactivity of several POMs; in particular, at the beginning our interest was mainly aimed at investigating the potential multifunctionality of these systems. Therefore we compared the results obtained with $H_4PVMo_{11}O_{40}$, a protonic Keggin HPC, and the corresponding cesium salt, $Cs_4PVMo_{11}O_{40}$, in order to distinguish between acid and redox-properties.

The synthesis of heteropolyvanadates (HPVs), POMs containing also V in the polyanion, as described by Tsigdinos and Hallada[114], starts from an aqueous

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[114] G.A. Tsigdinos, C.J. Hallada, *Inorg. Chem.* 7 (1968) 437-441

solution of sodium molybdate dehydrate as molybdenum source, disodium hydrogen phosphate dehydrate as phosphorous source, and sodium metavanadate to incorporate vanadium. Under vigorous stirring, concentrated sulphuric acid was added dropwise to acidify the solution. The red-coloured solution was cooled down to 273K, and kept for 2h at this temperature before being extracted by diethyl ether. The resulting HPV-etherate complex was dried at 333K overnight to remove the solvent and then recrystallized. This procedure was quite long and the infrared spectra were not satisfactory. The new procedure we used, starts from orthophosphoric acid (H_3PO_4 Sigma Aldrich 85% m/m), molybdenum oxide (MoO_3 Sigma Aldrich 99.5%) and vanadium oxide (V_2O_5 Sigma Aldrich 99.5%), all components being dissolved in a large amount of water. When all the reagents are solubilized, the solvent is evaporated and the solid is dried at 105°C. However, vanadium pentoxide is not soluble in water; therefore, it is necessary to use a dilute aqueous solution of hydrogen peroxide (3%):

$V_2O_5 + H_2O_2$ (in a cold bath) $\longrightarrow$

$VO(O_2)^{++}$ peroxy anions of V (V) $\longrightarrow H_6V_{10}O_{28} + O_2$

Finally the complete procedure is:

$H_3PO_4 + 0.1x\ H_6V_{10}O_{28} + (12\text{-}x)\ MoO_3 + 0.2x\ H_2O) \longrightarrow H_{3+x}PMo_{12-x}V_xO_{40}$

To obtain the corresponding cesium salt, the heteropolyacid was dissolved in water and then a cesium carbonate solution was added dropwise. The pH of the solution has to be low, and during carbonate addition it is possible to observe the CO_2 evolution, and the salt precipitation (cesium Keggin salts are insoluble in water)

$H_{x+y}PV_yMo_{12-y}O_{40} + (x+y)/2\ Cs_2CO_3 \longrightarrow Cs_{x+y}PV_yMo_{12-y}O_{40}\ (s) + (x+y)/2\ H_2CO_3$

$H_2CO_3 \longrightarrow H_2O + CO_2\ (g)$

The solid obtained in this way was dried at 105°C.

Table 3: Main characteristics of POMs prepared

Samples labels	**Description**	**Specific Surface Area**
HV	$H_4PVMo_{11}O_{40}$	3 m^2/g
CsVMo	$Cs_4PVMo_{11}O_{40}$	5 m^2/g

Analyzing the catalysts by FTIR in ATR configuration (Attenuated Total

Reflectance), Fig. 16, it is possible to observe the characteristic bands of the Keggin structure. The well-known bands of POMs are as follows: ν_{as}(P–O) around 1060 cm^{-1}, ν_{as}(Mo=O) at 990–960 cm^{-1}, and ν_{as}(Mo–O–Mo) around 900–870 cm^{-1} [115,116,117,118]. Compared with the spectrum of the V-free $H_3PMo_{12}O_{40}\cdot 13H_2O$ (not shown), the asymmetric P–O and Mo=O stretching bands are broadened and shifted towards lower wavenumber. These effects are due to the decreased oxoanion symmetry (development of a reduced symmetry) caused by the substitution of one Mo in the Keggin anion by V.[119] The band at 1034 cm^{-1}, also observed by means of Raman spectroscopy, can be attributed to the ν(V=O) stretching band of single $V^{5+}O_x$[120]. Together with the aforementioned change of bands attributed to ν_{as}(P–O) and ν_{as}(Mo=O), the appearance of this band clearly indicates that V^{5+} has been eliminated from the Keggin anion. This was observed by recording the spectra of different samples having increasing V/Mo atomic ratio, and comparing the spectra with that of 12-molybdophosphoric acid, either commercial or synthesized.

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[115] J.K. Lee, J. Melsheimer, S. Berndt, G. Mestl, R. Schlögl, K. Köhler, *Appl. Catal. A Gen*, 214 (2001) 125

[116] B.B. Bardin, R.J. Davis, *Appl. Catal. A Gen.*, 185 (1999) 283

[117] N. Mizuno, D.-J. Suh,W. Han, T. Kudo, *J. Mol. Catal. A Chem.*, 114 (1996)309

[118] A. Brückner, G. Scholz, D. Heidemann, M. Schneider, D. Herein, U. Bentrupa, M. Kant, *J. Catal.*, 245 (2007) 369–380

[119] M. Sultan, S. Paul, M. Fournier, D. Vanhove, *Appl. Catal. A Gen.*, 259.(2004) 141.

[120] X.-K. Li, J. Zhao, W.-J. Ji, Z.-B. Zhang, Y. Chen, C.-T. Au, S. Han,H. Hibst, *J. Catal.* 237 (2006) 58.

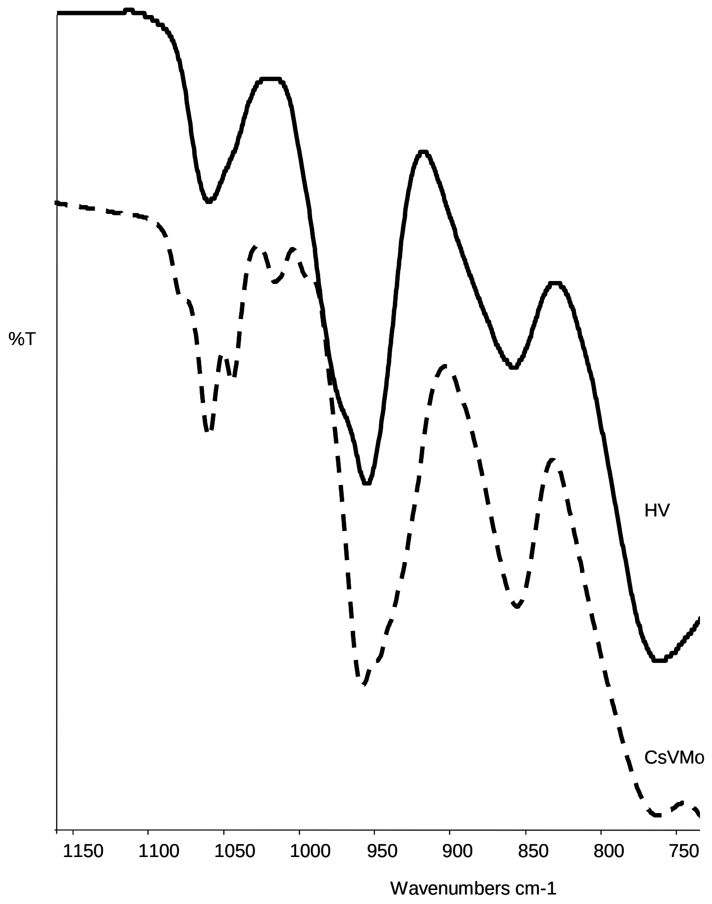

Fig. 16: FT-IR in ATR spectra of samples HV and CsVMo

2.2.6 Reactivity tests: Keggin heteropolycompounds

The results obtained with the heteropolyacid of composition $H_4PVMo_{11}O_{40}$, shown in Fig 17, allow making the following considerations:

1. The conversion at low temperature was higher than in absence of catalyst; therefore there was a catalytic action on the reagent conversion. The conversion trend showed a minimum at 360°C that could be due either to the deposit of heavy compounds on the catalyst surface, or to the structural decomposition of the Keggin structure, or to total oxygen conversion, that limits the glycerol conversion. This last hypothesis is possible considering the stoichiometry of the reactions involved, and the glycerol/oxygen ratio in the feeding gaseous mixture. Tests made by changing the feeding ratio (that is, increasing the oxygen molar

fraction), will allow making other considerations (Fig 19). At high temperature (360-420°C) the glycerol conversion increased, because homogeneous reactions overlapped to the heterogeneous activity.

2. The selectivity to acrolein was higher in presence of the catalyst, confirming the acid features of this Keggin compound. However the production of acrolein was not so high (selectivity 11-12% at low temperature and 16% at high temperature), and there was no formation of acrylic acid. The carbon balance was very low indicating the formation of "heavies", except at 360°C (carbon balance 90%). At high temperature, the homogeneous mechanism became the prevailing one; the C-balance got worse until 410°C, when the selectivity to CO_x and to acrolein reached their maximum value. The by-products were hydroxyacetone, acetic acid, propionaldehyde and allylic alcohol.

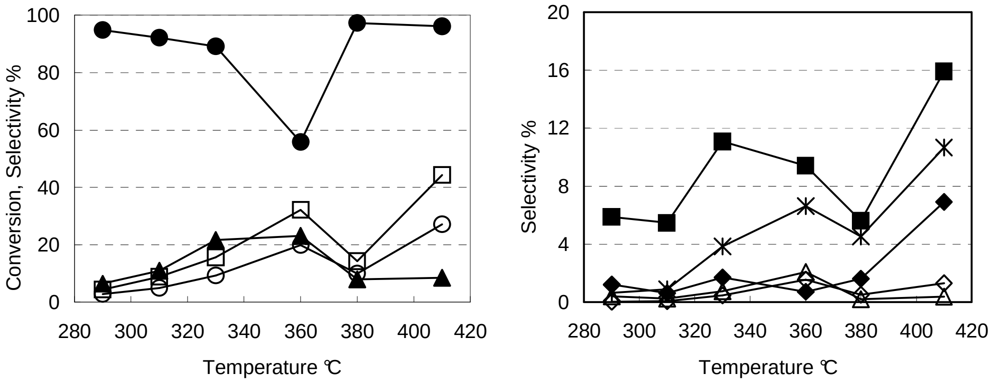

Fig. 17: Temperature effect on glycerol conversion and products selectivitys with $H_4PMo_{11}VO_{40}$ catalyst; feeding mixture: glycerol/oxygen/water/helium=2/4/40/54 (molar ratio). Simbols: ●glycerol conversion; ■ acrolein selectivity; ✱ acetaldehyde selectivity; ○ CO2 selectivity; □ CO selectivity; ◆ acetic acid selectivity; ▲ "Others" selectivity; △ hydroxyacetone selectivity; ◇ allyl alcohol selectivity; × propionaldehyde selectivity.

3. Acrylic acid did not form; this can be due to various reasons: a) the yield to acrolein was too low, and consequently its oxidation was kinetically unfavoured; b) the acrolein produced was quickly transformed into CO_x (the total oxidation was favoured as compared to the partial oxidation, both at low and high temperature); c) the catalyst was not able to selectively catalyze

the oxidation of acrolein into acrylic acid, possibly because of the high amount of water and the low oxygen partial pressure in the feeding mixture.

4. At high temperature (380°C), glycerol conversion was total, suggesting once again the contribution of homogeneous reactions. On the other hand, the products distribution obtained in the absence of catalyst was different from that observed with the catalyst, a clear indication that at these conditions the homogeneous and heterogeneous reactions overlapped. For example, the high selectivity to CO_x was due to the catalytic reaction.

The analysis of the acrolein selectivity in function of temperature, suggests the presence of two different mechanisms for its formation; in fact, the selectivity to acrolein first increased, then decreased down to a minimum, at 380°C, and then increased again. At low temperature, the acidity of the catalyst favoured the formation of heavy compounds (for example, polycondensed molecules of glycerol); at higher temperature, the endothermal dehydration of acrolein was more favoured. Afterwards, the acrolein selectivity decreased because combustion and cracking reactions were more favoured, producing CO_x, "others", acetaldehyde and acetic acid. This is a typical effect of oxidation catalysis where the temperature favours combustion and decomposition instead of partial oxidation. Finally, at 410°C (selectivity to acrolein 16%), there was also an increase of CO_x, acetic acid, and acetaldehyde selectivity, whereas the selectivity to "others" and "heavies" decreased.

In conclusion, the results obtained suggest that Keggin-heteropolyacids, used as bifunctional systems, can catalyze the dehydration of glycerol to acrolein, but selectivity to acrolein is too low to proceed further up to acrylic acid. The low selectivity is caused by the formation of heavy compounds at temperatures between 290°C and 330°C, and by the combustion to carbon oxides in the 330°-360°C temperature range.

The Brϕnsted catalyst acidity plays a key role in the transformation of glycerol at low temperature. In order to better highlight the role of acid sites in polyoxometalates, we used a compound of composition $Cs_4PMo_{11}VO_{40}$, that contains no acid sites at all, but still holds redox properties. Its activity is shown in

Fig. 18. The glycerol conversion was very high, despite the absence of strong acid sites, but the deactivation at intermediate temperature was less marked. Others differences between the acid and the salt form of the Keggin compound were:

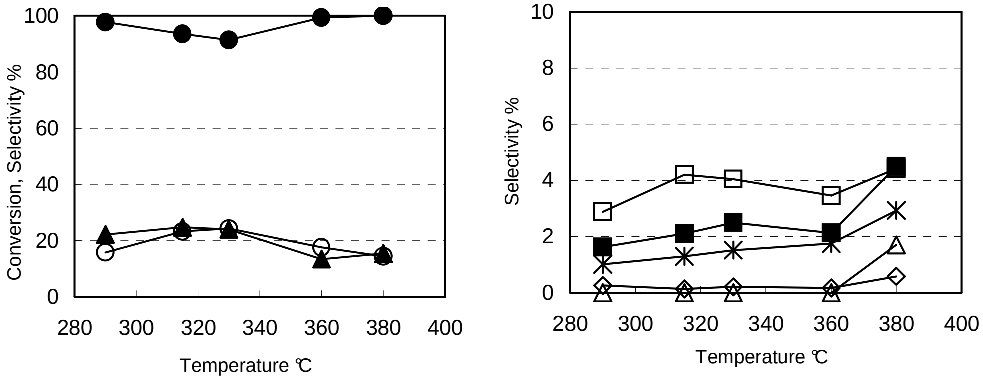

Fig. 18: Temperature effect on glycerol conversion and products selectivity with Cs4PMo11VO40 as catalyst; feeding mixture: glycerol/oxygen/water/helium=2/4/40/54 (molar ratio). Simbols: ●glycerol conversion; ■ acrolein selectivity; ✱ acetaldehyde selectivity; ○ CO2 selectivity; □ CO selectivity; ◆ acetic acid selectivity; ▲ "Others" selectivity; △ hydroxyacetone selectivity; ◇ allyl alcohol selectivity; × propionaldehyde selectivity

1. The carbon balance improved at low temperature, indicating a lower formation of heavy compounds. This also can be the reason why at 360°C the deactivation was not so marked as it was with the POM in the acid form. On the other hand, despite the absence of protons, the production of heavy compounds still was quite high. Actually, the etherification between alcohols can also be catalyzed by bases; therefore, we cannot exclude that the Cs ions can play a role in the formation of heavy compounds.
2. Acrolein selectivity was lower than with Keggin in the acid form; this confirms the fundamental role of acid sites in the dehydration reaction. It is important to observe that the acrolein selectivity, in function of temperature, was the same in both cases. This supports the hypothesis of two different mechanisms for aldehyde formation, that give a different contribution in function of temperature.
3. The catalyst keeps its oxidant features, producing a high amount of CO_x, but without acrylic acid formation.

The Brønsted acidity keeps a key role in the dehydration of glycerol to acrolein but, at the same time, it gives an important contribution to heavy compounds formation. Therefore, a control of the acid strength is a key tool for the control of the selectivity to acrolein.

Another important parameter is the ratio between the reagents in the feeding mixture. This could have different effects on the reaction:

The nature of the limiting reagent. In the oxidative reaction it is possible to use either an excess of oxygen (with respect to the stoichiometric amount) or a defect of it; in the first case the limiting reagent is the substrate, while in the latter case it is the oxygen. Usually, under oxygen-lean conditions, partial oxidation is favoured over combustion.

In redox mechanisms, the oxidized/reduced sites ratio, under steady conditions, is a function of the feeding mixture, in our case of the glycerol/oxygen feed ratio. In the specific case of the Keggin structure, a partially reduced state of the POM could influence the interaction with protons and modify the acidity.

In the presence of a great amount of heavy compounds, that deposit on the catalytic surface, an oxygen-rich gas phase can help in maintaining the active surface clean, transforming heavy compounds into carbon oxide or favouring their desorption.

Fig. 19 shows the results obtained under oxygen-rich conditions.

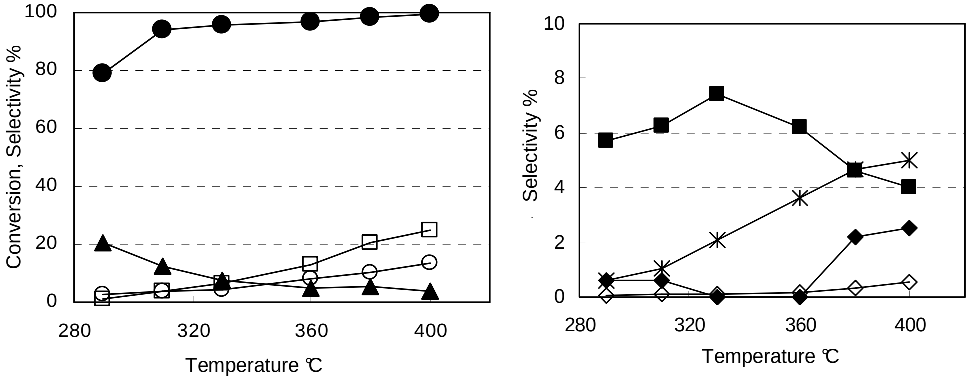

Fig. 19: Temperature effect on glycerol conversion and products selectivity with $H_4PMo_{11}VO_{40}$ as catalyst; feeding mixture: glycerol/oxygen/water/helium=2/13/40/45 (molar ratio). Symbols: ●glycerol conversion; ■ acrolein selectivity; ✱ acetaldehyde selectivity; ○ CO2 selectivity; □ CO selectivity; ◆ acetic acid selectivity; ▲ "Others" selectivity; △ hydroxyacetone selectivity; ◇ allyl alcohol selectivity; × propionaldehyde selectivity

Comparing the results obtained at different oxygen molar fraction (Fig. 17 and Fig. 19), it is possible to observe the following differences:

1. Under oxygen-rich conditions, glycerol conversion was high at all temperatures; this effect could be due either to the higher availability of oxygen or to the lower formation of heavy compounds. However, it is necessary to note that the production of "heavies" was still high also in the presence of a high amount of oxygen.
2. Under oxygen-rich conditions, acrolein selectivity was lower at high temperature. Also the selectivities to carbon oxides, and to "others" were lower.
3. The catalyst behaviour in oxygen-rich conditions suggests an increase of the catalyst acidity (higher formation of heavy compounds): this means that increasing the partial pressure of oxygen the catalyst surface is more oxidized, implying that an "oxidized" heteropolyacid also holds an higher acidity.

2.2.7 Catalytic systems: Main characteristics of supported Keggin-POMs

Keggin-type POMs are a class of molecular-type compounds with well-defined crystalline structure, and tuneable acidity properties. The proper choice of the addenda element allows controlling the redox properties. On the other hand, they lack thermal stability and usually have a low specific surface area. Therefore, it can be interesting to support the heteropolyacid on acidic or neutral carriers, such as SiO_2, ZrO_2 or ZrO_2/SO_4.

In literature, various papers describe the use of supported POMs as acid catalysts for the dehydration of glycerol:

$H_3PW_{12}O_{40}/ZrO_2$
$H_3PMo_{12}O_{40}/Al_2O_3$
$H_3PW_{12}O_{40}/Al_2O_3$
$H_4SiW_{12}O_{40}/Al_2O_3$
$H_3PMo_{12}O_{40}/SiO_2$
$H_3PW_{12}O_{40}/SiO_2$
$H_4SiW_{12}O_{40}/ SiO_2$

Zirconia turned out to be a good support for POMs, especially when the catalyst was obtained by impregnation of an alcool-derived $ZrO(OH)_2$. In this case, with a catalyst made of 30 wt% $H_3PW_{12}O_{40}$ loaded on zirconia, the acrolein yield was about 71%[121]. With silica support[122], the acrolein selectivity increased following this order: PMo<PW<SiW; the selectivity was greatly affected by operating conditions, but yields achieved were not as good as those obtained with either zirconia or alumina supports[123].

We prepared various catalysts made of supported POMs, ranging from acid to salified compounds, over supports having either weak acidity or strong acidic features (Table 4).

Table 4. Main characteristics of supported POMs prepared.

Samples labels	Description	Specific Surf. Area	Main features
HW30/S	$H_3PW_{12}O_{40}$(30%)/SiO_2	175 m^2/g	Strong acid POM + mild acid support
HW20/S	$H_3PW_{12}O_{40}$(20%)/SiO_2	187 m^2/g	Strong acid POM + mild acid support
CsHW20/S	$Cs_2HPW_{12}O_{40}$(20%)/ SiO_2	229 m^2/g	Non-acid POM + mild acid support (reference catalyst)
CsMo10/SZ	$Cs_4PVMo_{11}O_{40}$(10%)/ (ZrO_2/SO_4)	152 m^2/g	Redox POM + acid support

The POMs supported on silica were supplied by Johnson Matthey plc. They were prepared by impregnation of the support with an aqueous solution of heteropolyacid, having the appropriate concentration so as to achieve the desired loading on catalysts support. Thereafter, the impregnated material was dried in air.

The preparation of the CsMo10/ZS sample was more difficult, and a new synthetic strategy was necessary. In fact there were two problems to solve: (a) the deposition of an insoluble salt; it was necessary to generate *in situ* (over the

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[121] S.-H. Chai, H.-P. Wang, Y. Liang and B.-Q. Xu, *Appl Catal.A.Gen*, 2009, **353**, 213-22

[122] E.Tsukuda, S.Sato, R. Takahashi, T. Sodesawa; *Catal. Comm.*, 8 (2007) 1349-1353

[123] H. Atia, U. Armbruster and A. Martin, *J. Catal.*, 2008, **258**, 71–82

support) the desired Keggin structure with cesium as the counterion; (b) the procedure adopted had to leave the sulphate groups (on the zirconia support) untouched. We decided to develop the Cs salt of the POM by firstly impregnating the support with the cesium carbonate solution and then with the $H_3PMo_{12}O_{40}$; the reverse operation was also employed. By checking the IR spectra of the solids obtained (using zirconia as the support), it was possible to conclude that only when the first procedure was adopted (adding first the cesium source and then the POM solution), it was possible to preserve the Keggin structure. Afterwards, this procedure was applied to the sulphated zirconia support, using cesium carbonate and a solution of a Keggin compound containing also vanadium ($H_4PVMo_{11}O_{40}$).

The FT-IR spectra are shown in Fig. 20. The four IR bands characteristic of the Keggin unit at about 1062,963, 869, 784 cm^{-1} can be respectively assigned to P-O, M-O (M=Mo,W,V), inter-octahedral M-O-M and intra-octahedral M-O-M vibrations.

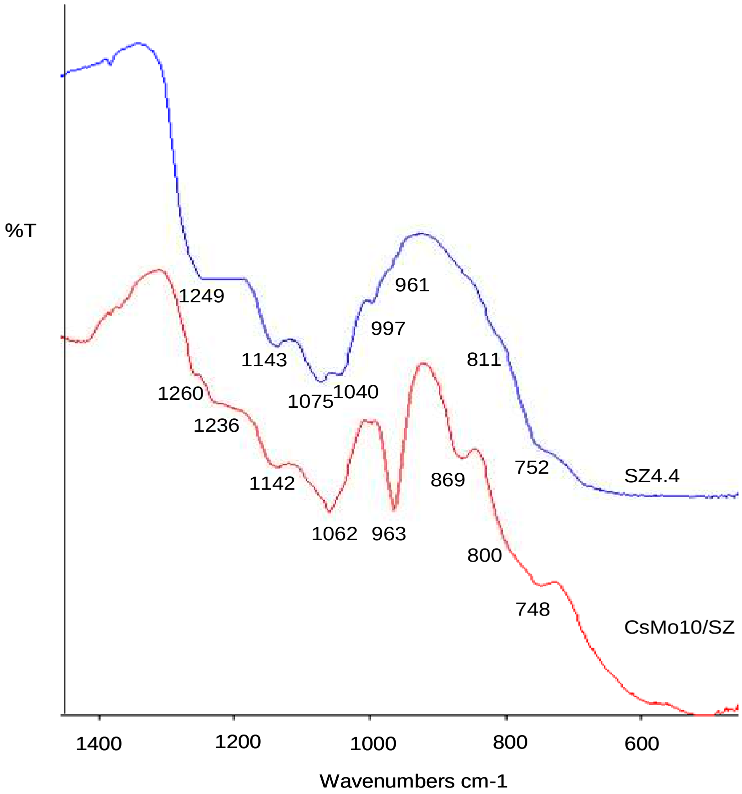

Fig. 20: FT-IR spectra of samples SZ4.4 and CsMo10/SZ.

2.2.8 Reactivity tests: supported Keggin POMs

Supported catalysts were tested in order to study the effect of the dispersion of the active phase on a support. In general, the results obtained with supported POMs are in good agreement with those obtained with bulk samples. In fact, the effects of oxygen on glycerol conversion and on products distribution, as well as the effect of the partial substitution of protons with cesium, experimentally observed with unsupported POMs, were confirmed even with the supported ones.

Fig. 21 shows the results obtained with the HW30/S catalyst in anaerobic conditions. At low temperature, glycerol conversion decreased, and reached a minimum value at 340°C. Since there was no oxygen in the feed, this effect was due the accumulation of heavy compounds. The selectivity to acrolein at low temperature was close to the 60%, but rapidly decreased when the temperature was increased. The temperature had an effect also on acetaldehyde formation, a product that even with these catalysts is likely obtained by acrolein decomposition. Selectivity to hydroxyacetone showed a maximum at 340°C, where the glycerol conversion was the lower.

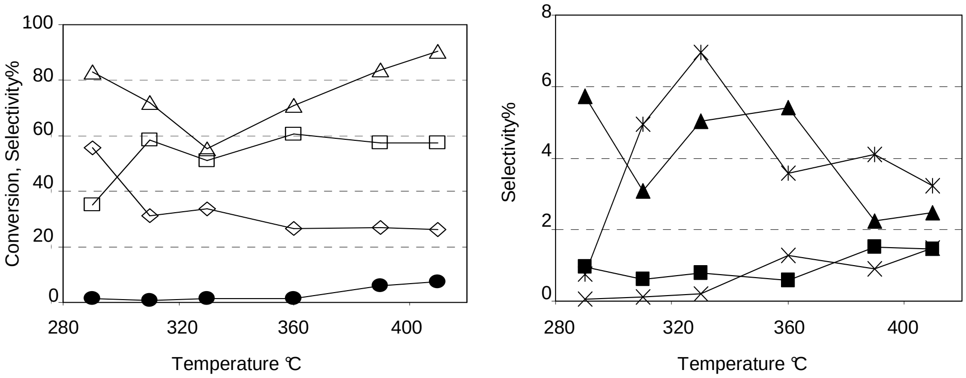

Fig. 21: Effect of temperature on catalytic behaviour of $H_3PW_{12}O_{40}$(30%)/SiO_2 (HW30/S) sample. Feed composition: glycerol / water / helium=2/40/58 (molar ratios). Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), to acetone (◆), acetaldehyde (●), propionaldehyde (■), CO_x (✕), hydroxyacetone (✱) and others (▲).

Fig. 22 shows the results obtained with the HW30/S sample under aerobic conditions, but with only a little amount of oxygen. The following considerations are possible:

1. The glycerol conversion increased in function of temperature without any deactivation effect; in this case the oxygen amount fed was high enough to avoid total conversion. At low temperature, the conversion was nearly 60%, while at 410°C it was 95%.
2. Selectivity to acrolein at low temperature, as well as at low conversion, was very high (40%) if compared with the results obtained with the bulk Keggin POM. The acidity of this sample was due to the presence of the Keggin units dispersed on silica. Acrolein selectivity decreased when the temperature was raised, and selectivity to CO_x, acetaldehyde and also acrylic acid increased. Selectivity to heavy compounds decreased, but remained nevertheless high over the whole temperature range.

3. The formation of acrylic acid is evidence that this kind of catalyst holds the right strength, number and nature of acid sites to produce acrolein from glycerol, and redox properties as well, suitable for the transformation of acrolein into acrylic acid (although with a low selectivity).

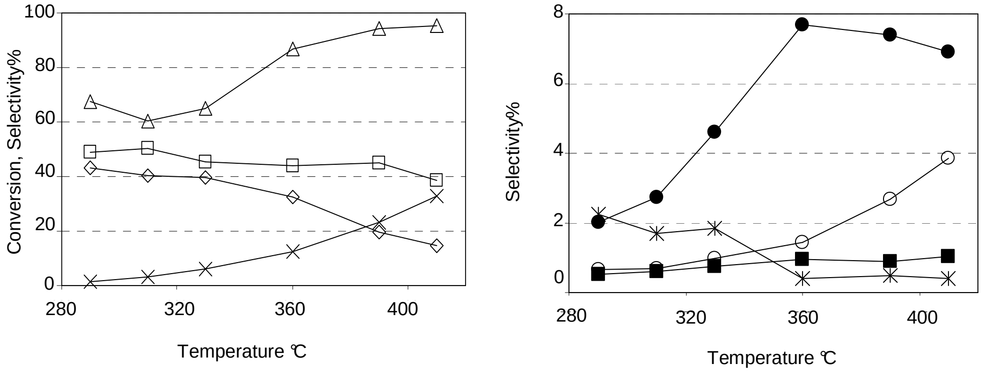

Fig. 22: Effect of temperature on catalytic behaviour of $H_3PW_{12}O_{40}$(30%)/SiO_2 (HW30/S) sample. Feed composition: glycerol / oxygen / water / helium=2/4/40/58 (molar ratios). Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to acrylic acid(○), to heavy compounds (☐), to acetaldehyde (●),propionaldehyde (■), CO_x (×), hydroxyacetone (✱), and others (▲).

Increasing the oxygen molar fraction in the feeding mixture (Figure 23) highlighted the role of the oxidant:

1. The glycerol conversion at low temperature was higher; oxygen helps in keeping the catalyst surface clean, but also contributes in the transformation of glycerol into products.
2. The selectivity to heavy compounds was quite high at low temperature but then slowly decreased, confirming the role of oxygen in the consumption of “heavies”. However, acrolein selectivity was lower, and was constant in function of temperature.
3. Acrylic acid and CO_x selectivity were not affected by oxygen.

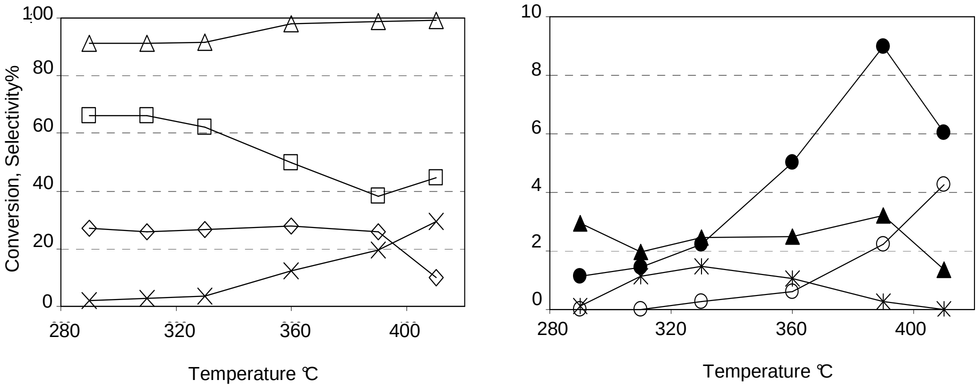

Fig. 23: Effect of temperature on catalytic behaviour of $H_3PW_{12}O_{40}$(30%)/SiO_2 (HW30/S) sample. Feed composition: glycerol / oxygen / water / helium=2/13/40/49 (molar ratios). Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), to acrylic acid(○), acetaldehyde (●),CO (✕), hydroxyacetone (✱) and others (▲).

Similar results were obtained with sample HW20/S (containing a lower amount of POM), under aerobic conditions (Fig not shown); neither glycerol conversion, nor selectivity to acrolein, to acrylic acid, to CO_x or to heavy compounds, were affected by the POM loading.

The partially Cs-salified catalyst (CsHW20/S) did not produce acrylic acid, and also the selectivity to acrolein and CO_x were lower (Fig 24). The acidity of the Keggin structure was decreased because of the replacement of protons with cesium cation. Moreover, more heavies were produced, probably because of the basic catalysis induced by the presence of Cs.

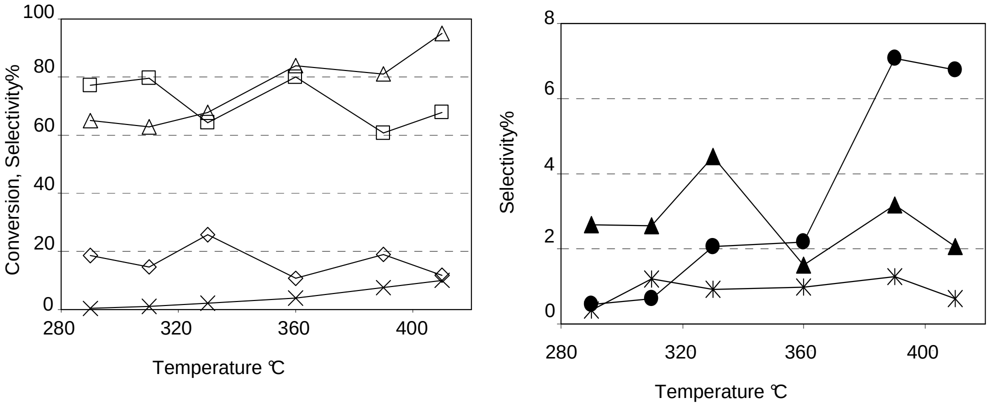

Fig. 24: Effect of temperature on catalytic behaviour of $Cs_2HPW_{12}O_{40}$(20%)/SiO_2 (CsHW20/S) sample. Feed composition: glycerol / oxygen / water / helium=2/4/40/58 (molar ratios). Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), acetaldehyde (●), CO (✕), hydroxyacetone (✱) and others (▲).

Finally, Fig 25 shows the performance of sample CsMo10/SZ.

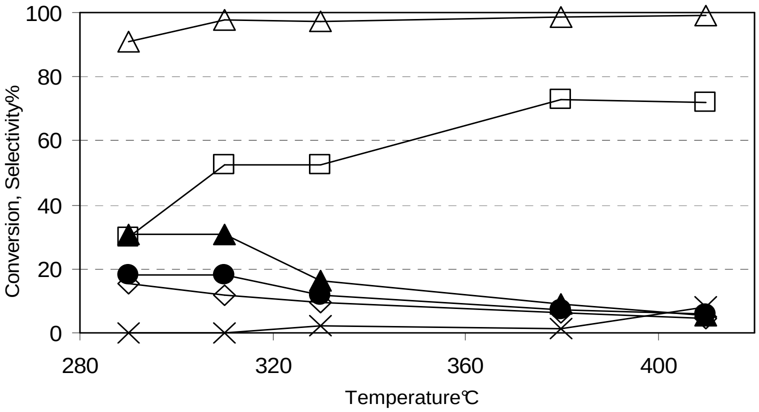

Fig. 25: Effect of temperature on catalytic behaviour of $Cs_4PMo_{11}VO_{40}$(10%) / ZrO_2/SO_4(4.4%) sample (CsHW20/S). Feed composition: glycerol / oxygen / water / helium=2/4/40/58 (molar ratios). Symbols: conversion of glycerol (△), selectivity to acrolein (◇), to heavy compounds (□), acetaldehyde (●), CO (✕), hydroxyacetone (✱) and others (▲).

Glycerol conversion was high at all temperatures, as it was with sulphated zirconia, but the activity of these latter catalysts was likely due to a different effect. The redox properties of Keggin units were profoundly modified by the interaction with the support (e.g., the CO_x selectivity was very low); the acid properties of sulphated zirconia were also decreased (acrolein selectivity was lower than that obtained with both the unsupported Keggin POM and the sulphated zirconia); therefore, new active species probably formed on the catalyst surface.

CHAPTER 3: CONCLUSIONS

Glycerol is a very reactive molecule, in fact it reacts in the gas-phase even in absence of catalyst. The homogeneous effect on the conversion is not irrelevant, and obviously it is influenced by the feed composition. These tests are fundamental to understand the heterogeneous catalytic reactivity; the intepretation of reactivity tests is meaningful only for tests carried out at below 360°C, that is, at conditions at which the homogeneous contribution is minimal.

The reactivity of sulphated zirconia in the gas-phase dehydration of glycerol into acrolein, a reaction aimed at the valorisation of glycerol surplus from biodiesel production, is greatly affected by the amount of sulphate loading. The conversion of glycerol suffers from an extensive deactivation phenomenon, especially when the reaction is carried out without oxygen co-feeding; however, this deactivation phenomenon is more relevant when the amount of sulphate loaded is as high as the 4.4 wt%.

Deactivation is due to three main reasons: (i) the accumulation of coke (that is limited but not completely avoided in the presence of co-fed oxygen), (ii) the self-reduction of sulphate into sulphite groups (that does not occur with co-fed oxygen, and does occur exclusively with high-loading of S), and (iii) the loss of S in the form of volatile organic esters (that does occur with all samples, regardless of the S content). These phenomena are of general interest for applications involving the use of sulphated zirconia as solid acid catalysts in high-temperature, gas-phase reactions.

The selectivity to acrolein is limited by the concomitant formation of several by-products, that form by both parallel and consecutive reactions upon acrolein. The principal by-products are heavy compounds, the selectivity of which however can be decreased and finally made nil through a careful control of the reaction conditions, in special mode the linear velocity of the inlet gas-vapours stream. This fact, and other experimental evidences as well, suggest that the formation of heavy compounds mainly occurs under mass- and heat-transfer limited conditions. These findings provide information on the most important reaction parameters affecting the reactivity behaviour during the acid-catalyzed dehydration of glycerol.

The attempt to directly transform glycerol into acrylic acid using bifunctional catalysts based on Keggin-type polyoxometalates was not been successful. Also in this case the acidity of the catalysts is too strong, and the selectivity to heavy compounds is high. Supporting the POM on a mildly acidic solid, such as silica, leads to an improvement of the catalytic performance; the selectivity to acrolein reaches the 40% at low temperature, and that to acrylic acid is 5% at high temperature. Therefore, these materiasl offer interesting opportunities; a proper design of the POM composition, of the type of support and of reaction conditions may be useful tools to improve the catalytic performance, and in special mode the selectivity to acrylic acid.

GENERAL CONCLUSIONS

During my PhD research, I have investigated some reactions of industrial interest, and tried to improve the catalytic performance by adopting strategies that belong to the "Green Chemistry" philosophy.

For example, I have investigated the use of hydrogen peroxide (HP) as a "green" oxidant for three different liquid-phase oxidations. Despite its higher cost, as compared to the cheaper oxygen (and air), the use of HP may offer some advantages, such as the possibility to use milder reaction conditions, and finally obtain higher selectivity to the desired, partially oxidized product. Moreover, the addition of a gaseous component (e.g., oxygen) may lead to mass-transfer limitation problems, which are not met when liquid aqueous solutions of HP are used. As compared to other oxidants for liquid-phase oxidations, HP also offers the advantage of the greater amount of active oxygen available; moreover, HP can be mixed with water in any proportion forming stable solutions, and the co-product of its reduction is water, which makes HP an environmentally friendly oxidant.

There are various heterogeneous catalytic systems that are able to activate HP, in particular those containing elements such as Nb^{5+}, Ti^{4+}, Zr^{4+}, W^{6+}, and V^{5+}, incorporated inside a silica or aluminosilica matrixes. These ions are able to form peroxo or hydroperoxo species with HP or other peroxidic agents. The most important property of these elements is that one of having an unsaturated coordination sphere that allows the activation of the reagents.

In Part A of my Thesis, I describe the use of catalytic systems made of Nb_2O_5-SiO_2 for the selective oxidation of 2-methyl-1-naphthol into menadione (vitamin K3) with HP. Results obtained suggest that this reaction is dominated by radical pathways, favoured by the nature of the substrate and the peculiar use of acetone as the solvent. This explains the large amount of undesired side products formed, and the observation that the uncatalyzed reaction is always significantly present and, in some cases, prevalent.

Radical reactions also occur in benzene hydroxylation with titanium silicalite TS-1 (described in Part B of my thesis), affecting the selectivity to phenol. Also in this case, the study of the reaction network allowed the identification of the key role of the solvent on reagents diffusivity, on the interaction with the Ti active sites, and on the diffusion rate of phenol from the TS-1 pores towards the bulk liquid phase.

The role of the solvent on the products distribution also was evident in phenol hydroxilation to diphenols (Part C of my thesis); using water solvent, it was possible to enhance the selectivity to the para-hydroxilated product (hydroquinone) instead of the ortho isomer (catechol). This made possible to reach the goal of finding a method to control the selectivity ratio between the two isomers, and finally to make the industrial process more flexible, in order to adapt the performance in function of fluctuations of the market requirements.

Finally, in Part D the target of transforming glycerol into chemicals was initially performed in the liquid-phase with HP and TS-1 catalyst. However, results achieved were not satisfactory, because the major product was acetic acid. Therefore, I decided to investigate the gas-phase transformation of glycerol into acrylic acid, focusing on the formation of acrolein, the first intermediate of the two-step process.

The reactivity of sulphated zirconia in the gas-phase dehydration of glycerol into acrolein was greatly affected by the amount of sulphate loading. An important deactivation phenomenon occurred, especially when the reaction was carried out without oxygen co-feeding; however, this deactivation phenomenon was more relevant with catalysts having the greater sulphate loading. The study of the reaction network allowed us to note that the selectivity to acrolein was limited by the concomitant production of several by-products, which form by both parallel and consecutive reactions. The principal by-products were heavy compounds, the selectivity of which however could be decreased and finally made nil through a careful control of the reaction conditions, in special mode the linear velocity of the inlet gas-vapours stream. The attempt to directly transform glycerol into acrylic acid using bifunctional catalysts based on Keggin-type polyoxometalates was not successful. Supporting the POM on a mildly acidic solid, such as silica, led to an improvement of the catalytic performance; the selectivity to acrolein was 40% at low temperature, but that to acrylic acid was no more than 5%, at high temperature.

In conclusion, by focusing our study on the reaction networks and mechanisms, and by paying attention to the target product without neglecting the formation of the other by-products, we could identify the most problematic steps, those limiting the selectivity to the desired product, for each one of the reactions investigated. The reactions studied are emblematic examples of how the application of the "green chemistry" strategies may also lead to improved performance (for instance, better selectivity or yield), and finally contribute to a more sustainable industrial chemistry, not only from the environmental but also from the economic point of view.

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