Effect of tetralol and tetralone in the tetralin oxidation with copper and chromium heterogeneous catalysts
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Effect of tetralol and tetralone in the tetralin oxidation with copper and chromium heterogeneous catalysts

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Abstract

The oxidation of tetralin in air was studied as a probe molecule on two type catalyst, Cu/PVP and Cr/PVP, to characterize their active sites and optimize their selectivity. The kinetics of the reaction was studied in a semi continuous stirred tank reactor in presence of different concentration of products (tetralone and tetralol) and time on stream. The products were analyzed by GC-MS and the solid characterized by chemical analysis, FTIR, CNMR, and ESR measurements. This work shows that the activity and selectivity of the Cu/PVP catalysts is affected by tetralol, one of the products of the reaction. When Cr^{+3} is used instead of Cu^{+2}, the effect is lower. The FTIR characterization of both fresh and used catalysts revealed that the C-N stretching band shifts towards higher wavenumber due to changes in metal coordination. The preferential adsorption of tetralol results in gradual loss of activity since no metal leaching was detected. The potential mechanism of deactivation is discussed based on catalyst characterization and activity test.

Keywords: tetralin oxidation, Cu/PVP, Cr/PVP, tetralol, tetralone

1. Introduction

The oxidation of naphtheno-aromatic molecules is important in the production of oxygenated diesel to reduce emissions [1], as well as for the fine chemistry industry to produce ketone type derivatives. In particular the development of a selective catalyst able to perform oxidations with high stability is an important area of research [2]. Polymer-bound-metal catalysts in the form of Cu^{2+} poly(4-vinylpyridine) (Cu/PVP) have been deeply surveyed from the point of view of their physical and redox properties and also their catalytic behaviour in a large number of organic reactions [3-13]. As a result of these examples, crosslinked polymers have largely been used to immobilize transition metal catalysts. A review of its potential was provided by Goe et. al [14-15]. This supports can be functionalized to provide ligands for attaching transition metals (or metal complexes) through coordination bonds. The objective of all those approaches was the preparation of active and selective catalysts typical of homogeneous catalysts combined with the easy separation and recovery, characteristic of heterogeneous catalysts. Other remarkable applications of PVP-metal complexes in chemistry are found in the literature [16-26].

The oxidation of tetralin with copper has mainly been studied using homogeneous catalysts sometimes with the aid of radical initiators or peroxides, and using organic solvents [27-29]. This makes difficult that industrial processes meet environmental regulations in the short term. On the other hand, homogeneous cobalt [30] and cobalt-pyridine supported catalysts have also been reported for this reaction [31-33]. In the latter case, it was suggested that pyridine-like ligands may reduce the oxidation potential for conversion of Co(II) to Co(III) if compared with other ligands, which is a beneficial factor when oxidative reaction are performed.

The objective of this work is to study the catalytic conversion of tetralin into tetralol and tetralone using Cu/PVP, complementing our previous work [34] in the area, and Cr/PVP catalyst. After surveying both activity and selectivity of these catalysts, the solids used for the reaction were characterized via FTIR, chemical analysis and ESR to elucidate the effect of main products on the active sites. For that both, tetralol and tetralone were added into the reaction system under different conditions to find out whether they may affect the catalytic behaviour. The results are used to propose a mechanism for the product effects on activity and selectivity that certainly will contribute in future improvements in this research area.

2. Experimental
2.1. Synthesis of Cu/PVP

5 g of 33% divinylbenzene crosslinked poly(4-vinylpyridine (Reillex 425^{TM}, Aldrich) were added to a vigorously stirring solution of 0.7020 g of $CuCl_2 \cdot H_2O$ in 100 mL of absolute ethanol at 90ºC. After contact time the solids were filtered off and washed with ethanol and then vacuum dried overnight before use under reaction conditions. The resulting liquid solution was analyzed by atomic absorption in order to determine the amount of non-coordinated copper to the initial support as a difference with the initially loaded amount of the salt. Owing to the fact that the spherical particles of the resin contain a non-negligible fraction of swelling agent in order to allow access of reactants into the resin matrix, such amount had to be taken into account when it comes to determining the composition. In order to remove the swelling agent 5.086 g of resin were treated with boiling ethanol (90ºC for 90 minutes). Afterwards, filtration and drying of the material as indicated above followed, yielding 2.74 g of dry solids. This latter datum was taken into account in further calculations.

2.2. Synthesis of Cr/PVP

10 g of 33% divinylbenzene crosslinked poly(4-vinylpyridine (Reillex 425^{TM}, Aldrich.) were added to a vigorously stirring solution of 6.4323 g of $Cr(NO_3)_3 \cdot 9H_2O$ in 100 mL of methanol at 80ºC. After contact time the solids were filtered off and washed with methanol and then vacuum dried overnight before use under reaction conditions. The resulting liquid solution was analyzed by atomic absorption in order to determine the amount of non-coordinated chromium(III) to the initial support as a difference with the initially loaded amount of the salt. For the same reasons as indicated above, the swelling agent removal was carried out by contacting 10,0036 g of resin with boiling methanol (90ºC for 90 minutes). Afterwards, filtration and drying of the material as indicated above followed, yielding 5.49 g of solids.

2.3. Catalytic tests: bubbled-air semicontinuous oxidations

7.0 g of tetralin (0.052 mol) were loaded in a two-necked flask with the corresponding amount of catalyst. The system was heated at 90ºC and then the reaction started by feeding air into the reaction mixture. The oxidant flowrate was kept constant at 0.6 mL/s throughout the reaction by means of an adjustable valve. A reflux system with PEG at 0ºC was installed, so that vapors were condensed down into the liquid phase, hence total mass balance was around 99% wt. After 24 hours reaction time, the reactor cooled down at room temperature. Samples intake was done after 1.5, 3, 5, 7 and 24 hours running reaction.

2.4 Products analysis

Tetralin, tetralol (TOH) and tetralone (TO) concentrations were determined by GC analysis of the samples using n-hexadecane as external standard. The reaction intermediate tetralin-hydroperoxide (TOOH) was quantitatively determined by means of an indirect method with triphenyl-phosphine (TPP) [35]. The sample from the reactor at a given contact time was immediately poured into a 250 μL of a 0.2 g TPP and 2.0 g acetone solution placed into a vial. When the sample of reaction contacted an excess TPP, THP quantitatively decomposed into triphenyl-phosphine oxide (TPPO) and tetralol. Therefore, the number of moles of TPPO formed in the vial equals those moles of THP present in the sample which was representative of the reaction mixture.

2.5. Analytical instrumentation

The IR characterization of the fresh and used catalysts was performed using a Nicolet 750 spectrophotometer. The spectra were obtained in KBr pellets in the region 3800-400 cm^{-1} with a resolution of 4 cm^{-1} by accumulating 40 scans. The absorbance signal intensities were adjusted to have a quasi constant signal in a known band in the spectra to be able to compare the values.

The content of organic matter was measured by chemical analysis of C, H, N and S using a EA-1108 CHNS Fisons analyzer and sulphanil-amide as standard. Metal loading was determined by atomic absorption spectrophotometry, prior sample desegregation with mixture of HF/HNO$_3$. Dilution of the resulting solution with Milli Q water followed and then the corresponding measurements were performed with SPECTRAA-10 plus Varian equipment.

EPR, Q band spectra (υ=34 GHz were recorded using a Bruker E500 ELEXSYS from 300 to 4 K range of temperature. The spectra were measured in the 9500–13500 Gauss range with a microwave powers in the range of 0.06–60 MW and with modulation amplitudes of 1–3 gauss. The sweep times were 80 or 160 s.

Gas chromatography (GC) analysis was performed using a Varian 3300 chromatograph equipped with a flame ionization detector and the capillary column was TRB-5 (sizes 30-0.25-0.25) as purchased from Teknokroma. A mass spectrometer Agilent 5973 equipped with a selective mass detector was used to verify the type of compounds present in the sample.

3. Results and discussion
3.1.Catalytic tests with Cu/PVP

Autooxidation of tetralin (blank test) was performed bubbling air at 90ºC at atmospheric pressure for 24 hours. As a result of this 7.8% mol conversion was achieved with selectivity towards tetralin-hydroperoxide (TOOH) of 85% by mol. This result indicated that thermal autoxidation of tetralin occurred producing mainly tetralin-peroxide without significant generation of ketones, the desired product. Nevertheless, when the same reaction was carried out in presence of PVP support, without any metal attached to it, a negligible conversion was observed at the same reaction time and temperature. This result brings about that pyridine clearly inhibited the conversion via peroxide adsorption, thus suppressed any thermal reaction.

Tetralin was oxidized with Cu/PVP without any added tetralol or tetralone. The results of tetralin conversion are shown in *Table 1* for different successive tests carried out with the same catalyst but using fresh feed for a period of 24 hours. There it can be seen that fresh and used up to three times catalysts (fresh, reused 1, reused 2 in *Table* 1) converts near 24% mol of tetralin with over 95% selectivity towards tetralone plus tetralol, and with 7 tetralone to tetralol mol ratio. Yields as a function of contact time are presented in *Figure* 1 for fresh and reused catalyst. For fresh catalyst, after 13.5 hours of reaction and beyond this time no increase in conversion was observed, and there is no noticeable conversion of tetralol into tetralone. The used catalyst after one cycle required nearly 24 hours to reach the same result. The instant at which tetralin conversion started to be significant with the reused batches of catalyst was completely different from that with fresh catalyst. This induction period is around 8 hours for all reused samples of catalyst while at that contact time fresh one had reached 17.5% mol tetralin conversion. The analysis detected a low concentration of tetralin hydroperoxide present in the product of reaction obtained at different contact time that confirms the role of PVP. Furthermore, no Cu leaching occurred during the catalytic tests as it is shown by the high catalytic activity kept by the catalyst along the three cycle length. Due to the fact that in both -fresh and used catalyst- the peroxide generation is quite similar and that the time required to reach the same value of conversion differed considerably between the first and subsequent reactions, it might be suggested that Cu^{2+} sites were going through a process which severely affected their initial activity. After a certain period of time such properties were recovered to accomplish its catalytic function.

Table 1. Catalytic activity of Cu/PVP [1]

Cu/PVP		USES			
		Blank	Fresh	Reuse 1	Reuse 2
Conversion (%mol)		7.8	23.21	23.53	23.40
Yield (%mol)	TOOH	6.59	0.14	0.15	0.14
	Tetralol	0.01	2.90	3.19	3.09
	Tetralone	1.20	19.90	20.03	20.02
	By-products	0	0.27	0.16	0.15

(1) Reaction conditions: Bubbled reactor, 0.052 mol tetralin, 0.560 g catalyst, 90ºC, 1 bar air, flowrate 0.6 mL/s, 24 hours. Yield: 100*mol product/mol initial tetralin

In order to ascertain what kind of phenomenon was taking place on the catalytic site which could justify the delay in catalytic activity, several experiments were carried out using tetralol. It might be possible that products could be adsorbed onto the surface of the catalyst where copper was located, causing severe hindrance to access the catalytic site or it could form adduct within its sphere of coordination. If any of this happened, tetralin would have little chance to reach copper sites and the oxidation reaction would be limited. Moreover, not even peroxides would be formed through the reaction in the presence of tetralol as unoccupied pyridyl are capable of preventing the generation of intermediates, as observed in blank tests. To verify these hypotheses, a solution of tetralin and tetralol (10% wt tetralol) was prepared and the same amount of Cu/PVP catalysts was used as in tetralin lone experiments. *Table* 2 shows the results on the effect of tetralol at the beginning, and after it is reused, and after three hours of contact times at the same other operating conditions as in previous experiments. Adding tetralol at the beginning of the reaction, no tetralin conversion was obtained and only 1% tetralol reoxidation into tetralone was detected. This result confirmed that tetralol had an inhibiting effect over the catalytic sites; therefore, a recycle of the catalyst, once the reaction mixture was disposed of, could be interesting to verify if there is an irreversible passivation of the active site by tetralol. That is the case and the reused catalyst (*Table 2* second column) shows a negligible conversion in the second cycle with pure tetralin. Then, if the same amount of tetralol was added into the reaction mixture once the reaction with pure tetralin was started (*Table* 2-third column), 6%mol conversion was obtained at the same operating conditions. This procedure produced an inhibition of the tetralin oxidation by the tetralol hence the final conversion after 24 hours of contact time remained the same as that at the time (3hr) when tetralol was added. As a consequence, no reuse of the catalyst was possible.

Table 3 shows the results of the tetralone effect and *Figure* 1 the yield as a function of contact time. Tetralone did not have such a negative effect on the oxidation of tetralin; in fact conversion and product distribution, when 10% wt of tetralone in tetralin was used, were almost the same and once again reusability of first test catalyst was entirely feasible.

Table 2. Effect of tetralol on the catalytic activity of Cu/PVP [1]

Cu/PVP		TOH 0hr[2]	Reuse[3]	TOH 3hr[4]
Conversion (%mol)		2.20	2.14	6.55
Yield (%mol)	TOOH	0.38	0.02	0.03
	Tetralol	0	0.13	0.30
	Tetralone	1.82	1.99	6.10
	By-products	0	0	0.12

(1) Reaction conditions: Bubbled reactor, 0.052 mol tetralin (and tetralol), 0.560 g catalyst, 90ºC, 1 bar air, flowrate 0.6 mL/s, 24 hours. Yield: 100*mol product/mol initial tetralin
(2) 10% wt Tetralol was added from the beginning of the reaction.
(3) Catalytic test with used catalyst from (2) and pure tetralin
(4) 10% wt Tetralol was added after 3 hours of running reaction.

Table 3. Effect of tetralone on the catalytic activity of Cu/PVP [1]

Cu/PVP		TH [1]	TO 0hr [2]	Reuse
Conversion (%mol)		23.21	20.27	25.01
Yield (%mol)	THP	0.14	0.04	0.07
	Tetralol	2.90	2.88	3.23
	Tetralone	19.90	17.19	21.6
	By-products	0.27	0.16	0.11

(1) Reaction conditions: Bubbled reactor, 0,052 mol tetralin, 0.560 g catalyst, 90ºC, 1 bar air, flowrate 0.6 mL/s, 24 hours. Yield: 100*mol product/mol initial tetralin
(2) 10% wt Tetralone was added from the beginning of the reaction.
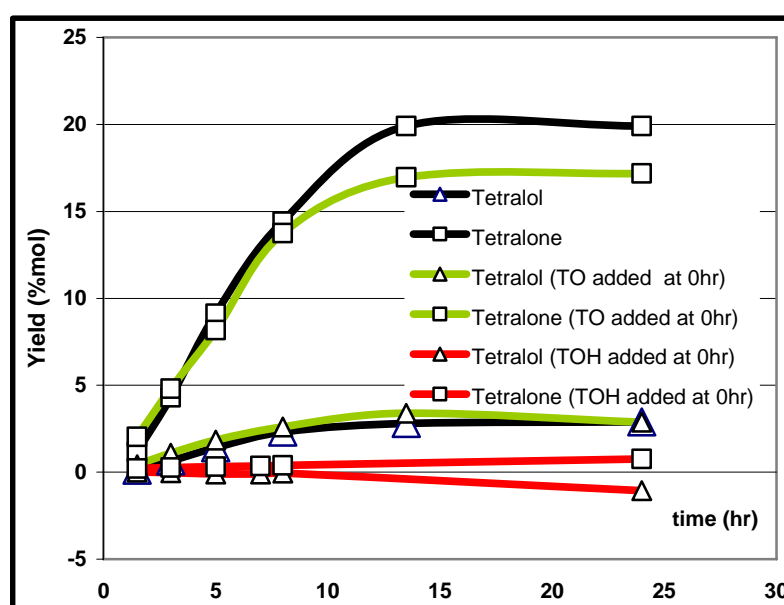
Figure 1. Kinetics of the effect of TOH and TO onto tetralin oxidation with Cu/PVP

3.2.Catalytic tests with Cr/PVP

When Cr replaced Cu in the catalyst different results were obtained for the oxidation of tetralin. *Table* 4 presents the results of fresh, reused 1, and reused 2 catalysts. Cr/PVP was able to oxidize tetralin into tetralol and tetralone at a similar conversion (24 %mol), but with different selectivity than Cu/PVP catalyst. The ratio TO/TOH was slightly higher (nearly 8) than that observed in the former one. *Figure* 2 shows the yields as a function of contact time for the different feeds. Successive reuses of the catalyst were also successfully carried out with only a small loss of activity and selectivity after 24 hours. Nevertheless, the induction period was also present in Cr/PVP reused catalysts. So no conversion was detected after 8 hours of starting up the oxidation with used catalyst, while at this contact time fresh ones yielded nearly 10%mol of tetralin conversion. It is important to highlight that reaction conversion progressed at a constant rate in fresh catalysts contrarily to what happened in the case of copper, without displaying asymptotic conversion.

Table 5 shows the effect of tetralol in the catalytic activity and selectivity for adding tetralol at the beginning and reusing the catalyst, and after 3 hours of running the reaction. The results must be compared with those of *Table* 3. Cr/PVP catalytic activity is different from Cu/PVP because Cr-catalyst was able to yield tetralone either by direct tetralin oxidation or by the corresponding alcohol reoxidation, but the activity was half of the fresh catalyst. Besides, when the catalyst was reused conversion was higher than in the presence of tetralol but lower than this observed in the experiments with fresh catalysts. On the other hand, similar activity and selectivity was observed - as it was expected - when tetralol was added after 3 hours the reaction was started with pure tetralin, if it is compared with the experiments where tetralol was added at the beginning of the test (*Table* 5 third column). Therefore, the passivation effect of tetralol on Cr-catalyst was lower than Cu-catalyst.

Table 6 shows the conversion and yields with pure tetralin (fresh catalyst), with 10% of tetralone (fresh catalyst), and with pure tetralin when the catalyst that had worked with tetralone was reused. It can be observed that tetralone, as occurred with Cu/PVP, did not influence negatively in the oxidation of the tetralin. *Figure* 2 summarizes the effect of tetralone on the products of tetralin oxidation.

Table 4. Catalytic activity of Cr/PVP [1]

Cr/PVP		USES		
		Fresh	Reuse 1	Reuse 2
Conversion (%mol)		24.53	19.58	18.68
Yield (%mol)	TOOH	1.60	3.25	2.38
	Tetralol	2.60	1.49	1.52
	Tetralone	20.33	14.84	14.78
	By-products	0	0	0

(1) Reaction conditions: Bubbled reactor, 0.052 mol tetralin, 0.560 g catalyst, 90ºC, 1 bar air, flowrate 0.6 mL/s, 24 hours. Yield: 100*mol product/mol initial tetralin

Table 5. Effect of tetralol on the catalytic activity of Cr/PVP [1]

Cr/PVP		TOH 0hr [2]	Reuse	TOH 3hr [3]
Conversion (%mol)		10.01	17.26	13.2
Yield (%mol)	TOOH	0.31	3.36	1.05
	Tetralol	-0.29 [4]	1.33	-0.52 [4]
	Tetralone	9.41	12.57	11.63
	By-products	0	0	0

(1) Reaction conditions: Bubbled reactor, 0.052 mol tetralin (and tetralol), 0.560 g catalyst, 90ºC, 1 bar air, flowrate 0.6 mL/s, 24 hours. Yield: 100*mol product/mol initial tetralin
(2) 10% wt Tetralol was added from the beginning of the reaction.
(3) 10% wt Tetralol was added after 3 hours of running reaction.
(4) Negative signs stand for the %mol of added tetralol reoxidized into tetralone.

Table 6. Effect of tetralone on the catalytic activity of Cr/PVP

Cr/PVP		TH[(1)]	TO 0hr [(2)]	Reuse
Conversion (%mol)		24.53	22.3	22.25
Yield (%mol)	THP	1.60	1.14	5.35
	Tetralol	2.60	2.39	1.56
	Tetralone	20.33	18.87	15.34
	By-products	0	0	0

(1) Reaction conditions: Bubbled reactor, 0.052 mol tetralin, 0.560 g catalyst, 90ºC, 1 bar air, flowrate 0.6 mL/s, 24 hours. Yield: 100*mol product/mol initial tetralin
(2) 10% wt Tetralone was added from the beginning of the reaction.
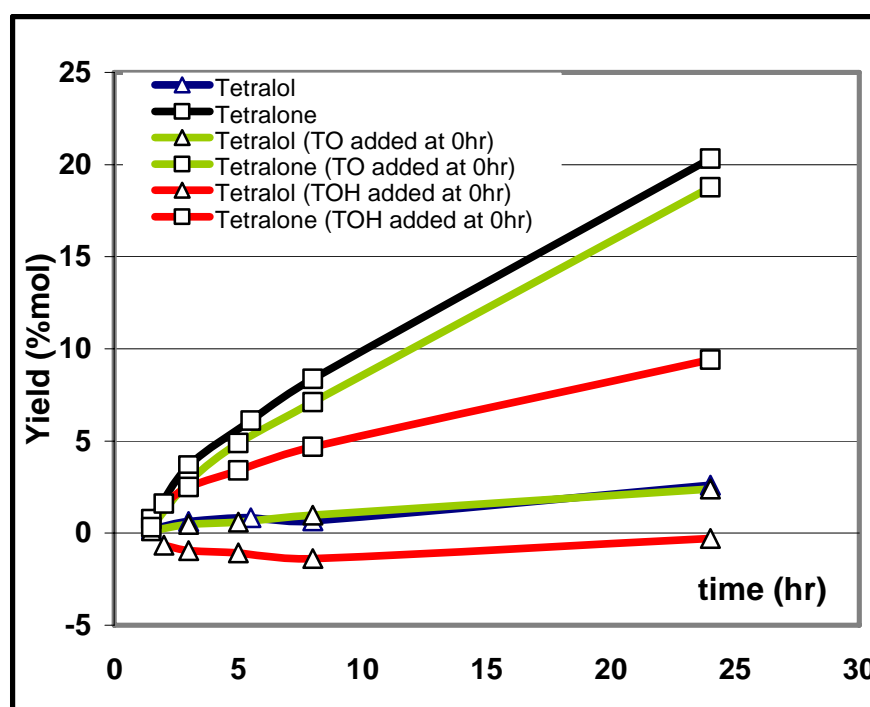
Figure 2. Kinetics of the effect of TOH and TO onto tetralin oxidation with Cr/PVP

3.3.Characterization of Cu /PVP catalysts.

To determine and assess the changes in the catalyst structure during the reactions, different techniques were used for both, fresh and used catalysts employed to oxidize tetralin and/or its oxidation products.

Figure 3 shows the FTIR spectra of PVP, fresh and used catalyst and tetralin-hydroperoxide (TOOH). *Figure* 4 presents the deconvolution of two characteristic bands on Cu/PVP fresh and used. First of all, it is observed the characteristic bands of pyridine C-N in Cu/PVP catalyst at 1599 cm^{-1} that appears together with its corresponding shifted metal-coordinated one at 1615 cm^{-1} (lines *a* and *d*). According to the literature [4-5], this shift evidences that there is a metal coordination to the nitrogen, as it was indicated previously. *Figure* 3-line c shows the spectra of the

TOOH and line b that of the support contacted with TOOH produced by thermal reaction. There, a new band appears at 742 cm^{-1} ascribed to adsorbed tetralin peroxide on PVP. The same band is present on used catalyst which has shown good activity to convert tetralin (lines e and f). Nevertheless, inactive used-catalyst (Cu/PVP + TOH) did not display such peroxide-like band (line f). The fact that peroxide bands are also present on used catalysts might indicate that on-surface peroxide is generated during the reaction to further decompose into reaction products. In addition, after its use under reaction conditions, it appears at 1681 cm^{-1} the band associated to carbonyl group of tetralone (lines e and f), except on those catalysts where tetralol was added during the reaction (line g).

The chemical and spectroscopic analysis of Cu/PVP catalyst was performed to determine the Cu and N content that were 8.53 and 6.87% weight respectively. The percentage of coordinated pyridyl nitrogen was determined by deconvolution of FTIR bands, as it is shown in *Figure 4 a* and *4 b*. In this way it was determined that 62.1 % of pyridine groups were coordinated to copper in fresh catalyst. Thus, the degree of coordination (DC) on fresh Cu/PVP was estimated to be around 2.34 as shown in *Table 7* fourth column.
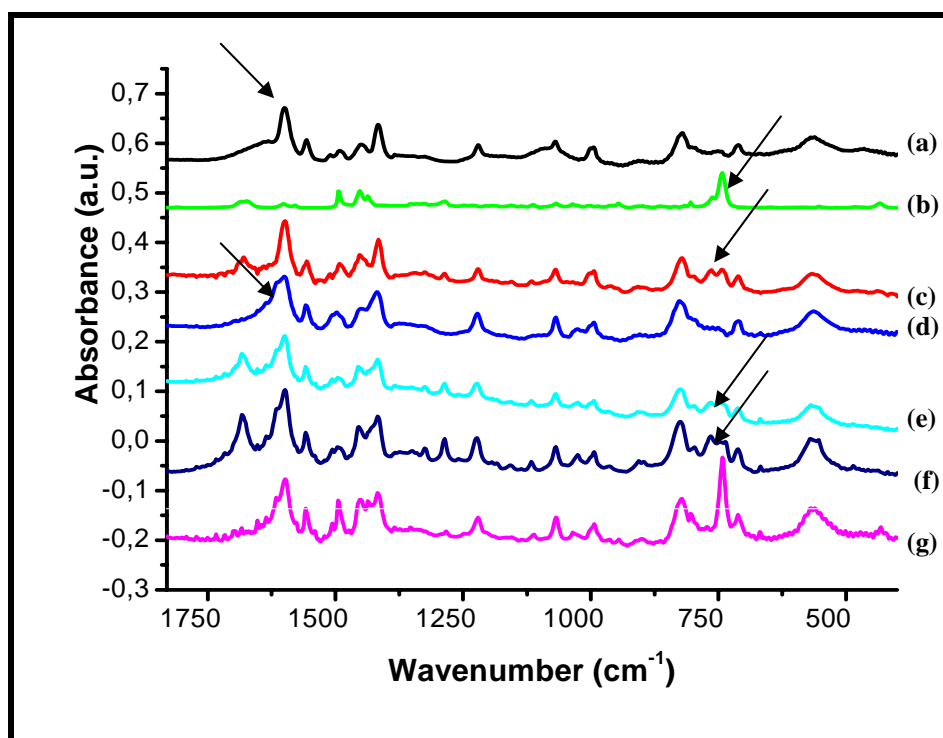
Figure 3. FTIR spectra of (a) PVP (b) TOOH (c) PVP+TOOH (d) Cu/PVP (e) Used Cu/PVP (f) Used Cu/PVP (TO added at 0hr) (g) Used Cu/PVP (TOH added at 0hr).
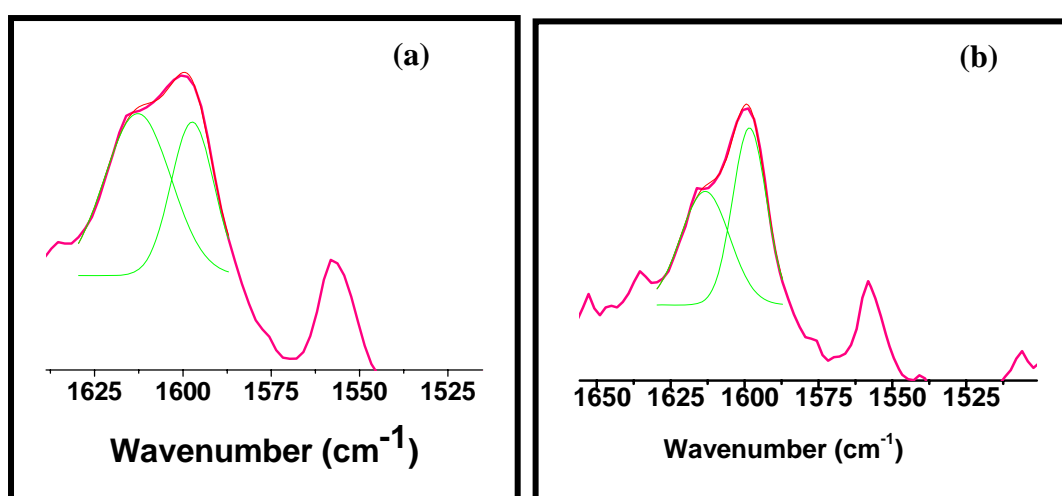
Figure 4. Deconvolution of the C-N bands on (a) fresh (b) used Cu/PVP catalyst

For used catalyst the pyridine coordination (DC) was decreased by 48.15% respect to the fresh catalyst, without trace of Cu (leaching) in solution. This result might be explained by the changes in the coordination of several copper atoms, which had evolved into peroxo-like species (Cu-O-O·) within its sphere of coordination, according to previous discussions about FTIR results.

***Table* 7**. Coordination on Cu/ PVP and Cr/PVP catalysts

Material	%N_{TOTAL}[1]	%N_{Coord}[2]	%Cu or % Cr [3]	DC[4]
Fresh Cu/PVP	0.49	62.1	0.13	2.34
Used Cu/PVP	0.49	48.15	0.13	1.81
Fresh Cr/PVP	0.52	83.7	0.07	-
Used Cr/PVP	0.52	65.1	0.05	-

(1) Stands for total moles N from chemical analysis per 100 g of solid.
(2) Mol percentage of coordinated pyridyl N as yielded in FTIR deconvolution.
(3) Moles of Cu or Cr from atomic absorption measurements per 100 g of solid.
(4) Degree of coordination defined here as the ratio N/Cu by mol.

In previous studies [34] it had been demonstrated by XPS analysis that some Cu forms a dimmer species Cu^+-Cu^{++} that is linked with two pyridyl group. The XPS signal change before and after reaction (*Table 8* resumed from ref [34]). The XPS band at 933.8 eV, attributed to Cu^{2+} species, is sharper in fresh than in used catalyst and it appears in the latter a new band at 932.1 eV, assigned to Cu^+. Fresh catalyst presents asymmetric well-defined N_{1s} bands around 398–400.4 eV, while the spent one shows an enlarged signal. Both peaks are shifted to 932.1 and 911 eV, respectively. The Cl_{1s} and O_{1s} signal also shows an important modification before and after reaction. Clearly the square planar copper coordination with Cl is also modified during the catalyst activation by the peroxide that replaced a Cl by oxygen modifying

the square planar structure. The fact that other oxidized species might be adsorbed (FTIR, CNMR, and HNMR results) in spent catalyst makes the interpretation difficult because the presence of any adduct TOH-metal can be masked by other signals.

***Table* 8.** XPS data for the catalyst before and after reaction (from ref [34]).

Binding E eV	Fresh Cu/PVP	Used Cu/PVP
N_{1s}	399.1 and 400.3	398.2 and 400.0
Cu $_{2p3/2}$	933.8	932.1 and 933.8-934.0 shake up
N/Cu	2.1	1.66

The ^{13}CNMR spectroscopy spectrum of Cu/PVP fresh and used, resumed from ref [34], are depicted in *Figure 5*-left side. The fresh catalyst presents a weak signal of methylene carbon, C_1-C_3 and C_8-C_{11} in the range of 110–150 ppm, whereas the methyl carbon C_4-C_7 and C_{12} -C_{14} appears in the range of 20–60 ppm. These signals - that are deeply attenuated by the presence of an important magnetism- gives a low signal/noise ratio in the spectrum obtained with polarization. In any case, by qualitatively comparing fresh and used catalyst, an important modification in the bands of carbon signal can be observed due to the presence of aromatics adsorbed hydrocarbons on the latter used catalyst. The ^{1}HNMR spectrum of fresh catalyst, *Figure 5*- right side, present a broad signal from -5 to 8 ppm that may contain unresolved the typical signal of the PVP at 6.3 and 8.4 ppm ascribed to the ortho and metha-proton of the pyridine ring, and the peaks at 7, 4.3 and 0.9 attributed to aromatics, methylene, and methyl-protons. The spent catalyst spectrum presents an enlargement of the shoulder and a particular modification in the pyridine protons. That is ascribed to the interaction of adsorbed species with the metal that modified the Metal nitrogen bonds of the pyridil-groups, thus the signal at 3.7 ppm.
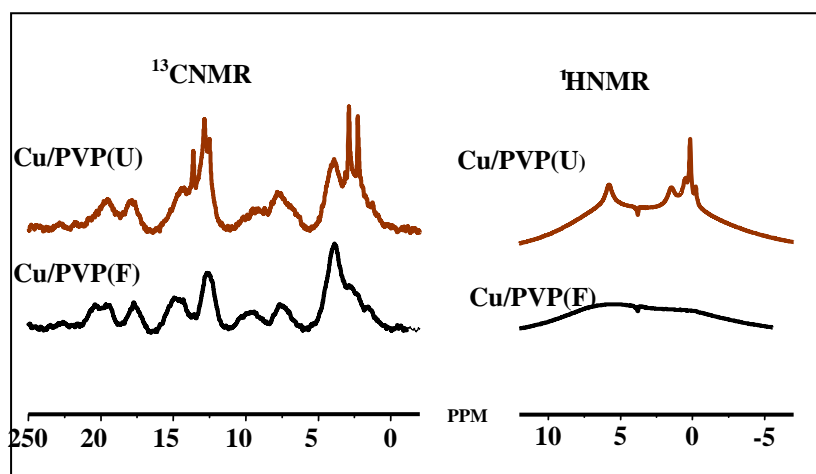

***Figure* 5.** Left side: ^{13}CNMR: CuPVP(F) and Cu/PVP (U), right side: ^{1}HNMR: Cu/PVP (F), Cu/PVP(U) (resume from ref [34])

ESR spectra [34] of fresh Cu/PVP, at room temperature, presents the axial signal with $g_\parallel > g_\perp > 2.03$, typical of tetragonal Cu^{2+} d^9 environment. The $G = (g_\parallel\text{-}2)/(g_\perp\text{-}2) = 2.9$ is lower than 4 that reflects the exchange interaction between the Cu^{2+} centers in the solid polymer complexes. A value of 250 cm measured in the $g_\parallel/A_\parallel$ ratio indicates an average tetrahedral distortion of the square planar configuration of the Cu^{2+}. Used catalyst shown shows a narrowing of the Cu^{++} signal probably due to the partial reduction of Cu^{2+} into Cu^+, in agreement with observation done by XPS. The effect of temperature indicated and higher dipole interaction for used catalyst than for fresh catalyst, but no additional information about the effect of TOH adduction was detected; magnetic susceptibility studies are underway to try to clarify the point.

3.4. Characterization of Cr /PVP catalysts.

Figure 6 shows the FTIR spectra of Cr/PVP. This catalyst present similar bands to Cu/PVP; For instance, it presents both metal-coordinated and free pyridyl C-N bands, as indicated in line c. These bands are clearly differentiated in its deconvolution shown in *Figure 7a* and *7b*. However, in Cr/PVP signal of the nitrate ligand is clearly present at 1380 cm^{-1} in both fresh and used catalysts. As it can be observed no noticeable peroxide band at 743 cm^{-1} was found in any of the used catalysts which evidenced the low concentration, if any, of the on-surface peroxide
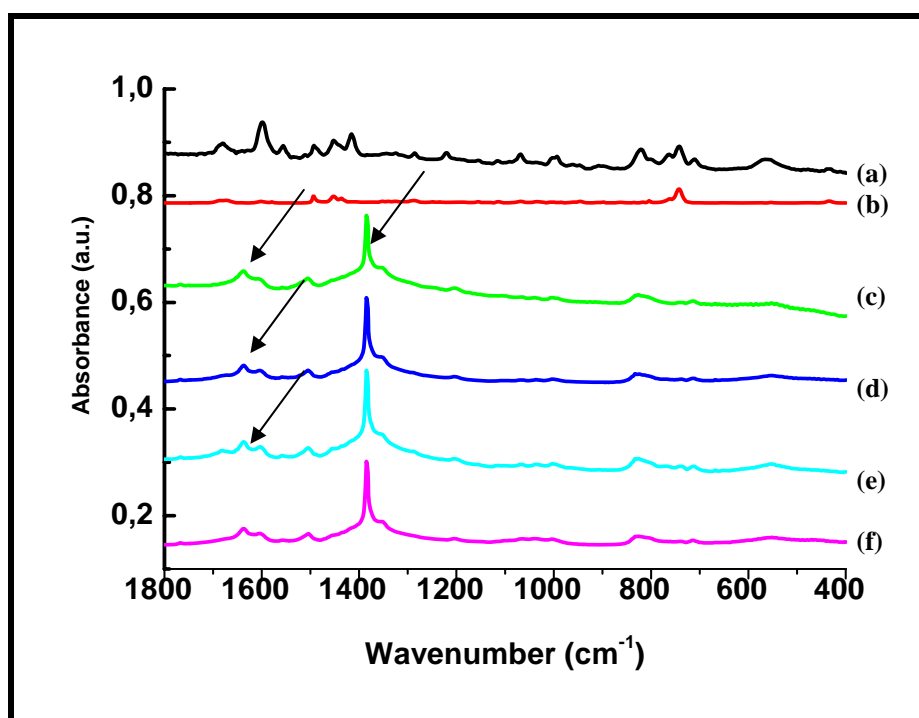
Figure 6. FTIR spectra of (a) PVP (b) TOOH (c) Cr/PVP (d) Used Cu/PVP (e) Used Cr/PVP (TO added at 0hr) (f) Used Cr/PVP (TOH added at 0hr)

The chemical and the spectroscopic analysis were done on fresh and used Cr/PVP catalyst. For them the content of Cr and N were 7.28 and 3.66% weight respectively. The pyridyl-Cr coordination, obtained from the FTIR bands deconvolution of fresh catalyst (*Figure* 7a), is 83.75 % (*Table 7*). In used catalyst this coordination is around 65.1% (*Figure* 7b, and *Table* 7), a much higher values than those observed on used Cu/PVP; In this case the analysis of metal content on used Cr/PVP indicates a 25% leaching of the metal during the reaction for this catalyst preparation. That can be associated to the decomposition on the nitrate ligand to produce a weaker Cr-N bond, or the formation of a stronger adduct between TOH or TOOH with the $-Cr(O)_yNO_x-$ site, than those between nitrogen and $-Cr(O)_yNO_x$ ligands, and for that some Cr might be leached out of the surface. Nevertheless the remaining Cr on-surface looks stable and the activity seems to be less sensitive to the TOH than Cu-catalyst. In particular it was reported [36] that Cr(CO)/PVP is able to convert alcohol into ketone type molecules. That might explain why the effect of tetralol on Cr/PVP is low. Some of the Cr sites might be able to convert the tetralol adduct into tetralone and be reoxidized, that is not the case on the Cu sites, as it is shown in the activity test.
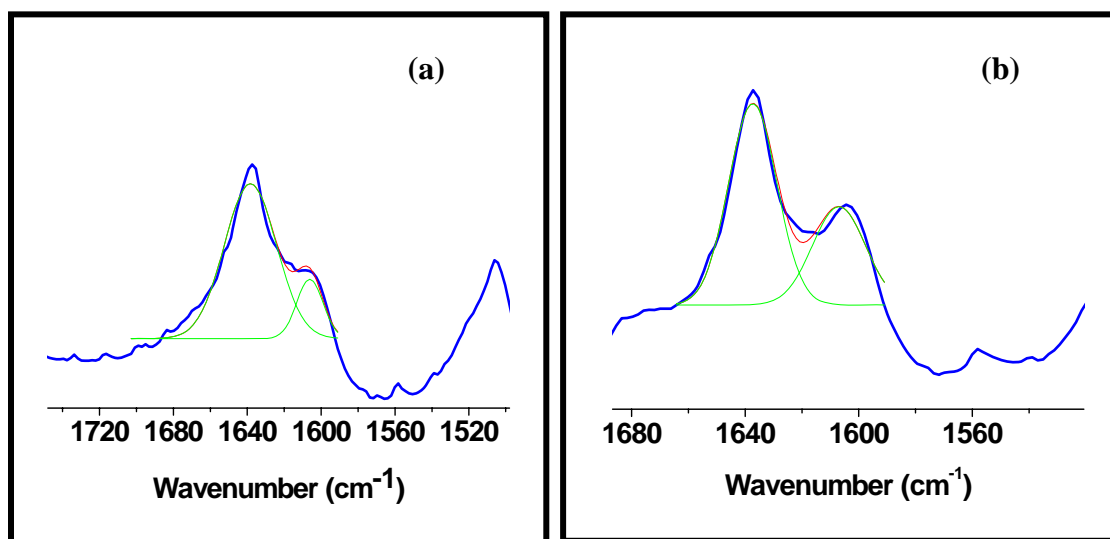

Figure **7**. Deconvolution of the C-N bands on (a) fresh (b) used Cr/PVP catalyst

3.4.   Proposed mechanism for the TOH effect on Cu/PVP passivation

In a previous paper [34], we proposed that the oxidation of tetralin is initiated by the formation of OCuCl - CuCl active sites by interaction of thermal hydroperoxide with the original ClCuCl -linked to pyridyl group- located on the plane by losing one of the Cl and replacing it by oxygen and hydroxyl. Then, it starts the propagation cycle that proceeds through the adsorption of another molecule of tetralin by hydrogen bonding to the oxygen on the OCuCl site. There, the adduct tetralin-

active site suffers an intramolecular isomerization that transfers oxygen into the nuclei of the cycloparaffin -in alpha position- to produce tetralol, and "reduces" the site to –CuCl (Cu$^+$). This site is then reoxidized by the molecular oxygen to generate –OOCuCl site. This structure might adsorb another tetralin molecule by a hydrogen bridge. Again, after the intramolecular isomerization, oxygen transfer, and tetralone desorption is produced a HOCuCl site, which restarts the catalytic cycle by adsorbing another molecule of tetralol generating tetralone plus water product and reduced catalyst site to -CuCl. The latter is then reoxidized to OO-CuCl and so on. At the same time, the OCuCl- site could convert the TOH into TO and dioxygenated molecules. See proposed reaction mechanism in *F*igure 8 where the main on-surface intermediary is indicated in blue.
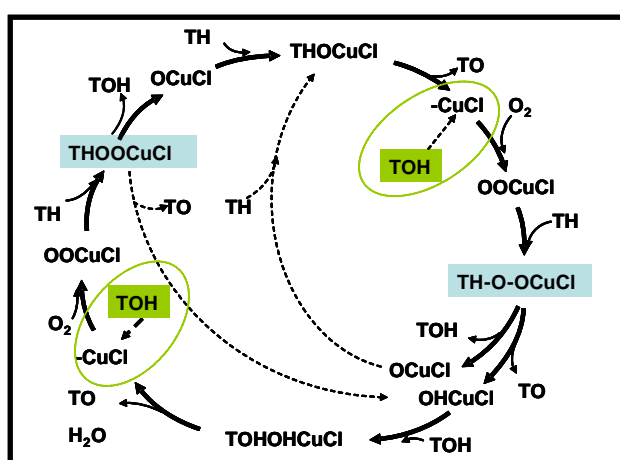

Figure **8** Mechanism of catalyst passivation by Tetralol

From the experimental results of catalytic tests, it can be observed that tetralol had a clearly inhibiting effect on substrate oxidation onto copper sites, either before or after catalyst activation. This effect may be ascribed to the strong adsorption on TOH in some active sites to form an stable adduct TOH-CuCl that could not be accessible to molecular oxygen, nor reoxidized to Cu^{+2}. That is indicated in green in *Figure* 8. If the concentration of tetralol is too high (poor selectivity to ketone formation) the reaction is stopped by the TOH adsorption, regardless that the reaction was in progress (100% of tetralin at the beginning followed by the addition of 10% tetralol after 3 hours of reaction) or starting up (10% of tetralol on tetralin at the beginning of the reaction). However, if tetralol concentration is too high either at the beginning or during the reaction, it constrains the catalyst reoxidation, as it is proposed in the mechanism of reaction. Presumably, when tetralol concentration reaches a given equilibrium value, within the concentration of accessible copper active sites, no further activity may be yielded, because the driving force that should impel the process, i.e. Cu$^+$ centers, depends directly upon the concentration of this product.

4. Conclusion

The selective oxidation of tetralin into ketone was studied using a Cu/PVP catalyst to understand the effect of intermediaries on activity and selectivity.

The results indicated that

- The tetralol inhibits the tetralin oxidation while the tetralone does not affect the activity or the selectivity to ketone production. By operating the Cu/PVP catalyst at high selectivity the catalyst can be reused without loss of activity or selectivity.

- The used catalyst has different Cu species on surface than fresh catalyst. The characterization of the former shows the presence of oxygen and Cu^+ in a on- the-plane distorted tetragonal structure (XPS, ESR) that are not present on the fresh catalyst. The ratio N-Cu ligants changed during the tetralin oxidation in accordance with redox mechanism

- It is proposed the formation of a stable adduct between tetralol and -CuCl species that passivates the active site for further oxidation

The use of a Cr/PVP catalyst instead of Cu/PVP shows that the former catalyst is able to transform the TOH into tetralone with minor effect on tetralin oxidation Therefore the effect of TOH on Cr is not as important as in Cu catalyst.

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References

[1] Tian, G., Xia, D., Zhan, F. (2004) *Energy and Fuels*, 18, 49-53.
[2] Corma, A., García, H. (2002) *Chemical Reviews*, 102, 3837-3892.
[3] Lyons, A.M., Vasile, M.J., Pearce, E.M., Waszczak, J.V. (1988) *Macromolecules*, 21, 3125-3133.
[4] Kirsh, Y. E., Kovner, V.Y., Kokorin, A.I., Zamaraev, K.I., Chernyak, V.Y., Kabanov, V.A. (1974) *European Polymer Journal*, 10, 671-678.
[5] Nishikawa, H., Tsuchida, E. (1975) *The Journal of Physical Chemistry*, 79, 2072-2076.
[6] Tadokoro, H., Nishiyama, S., Tsuruya, S., Masai, M. (1992) *Journal of Catalysis,* 138, 24-37.
[7] Sato, Y., Souma, Y. (2000) *Catalysis Surveys from Japan,* 4, 65-74.
[8] Nishide, H., Minikata, T., Tsuchida, E. (1982) *Journal of Molecular Catalysis,* 15, 327-335.
[9] Pardey, A.J., Rojas, A.D. ; Yánez, J.E. ; Betancourt, P. ; Scott, C. ; Chinea, C. ; Urbina, C. ; Moronta, D. ; Longo, C. (2005) *Polyhedron* 24, 511-519

[10] Wu, K.H.; Wang, Y.R.; Hwu, W.H. (2003) *Polymer Degradation and Stability*, 79, 195-200.

[11] Santana, A.L.; Noda, L.K.; Pires, A.T.N.; Bertolino, J.R. (2004) *Polymer Testing*, 23, 839-845.

[12] Nishide, H., Tsuchida, E. (1981) *Journal of Polymer Science*, 19, 835-837.

[13] Kokorin, A.I.; Zamaraev, K.I., Kovner, V.Y., Kirsh, Y.E., Kabanov, V.A. (1975) *European Polymer Journal,* 11, 719-722.

[14] Goe, G., Marston, C., Scriven, E.; Showers, E. (1990) "Application of pyridine containing polymers in organic chemistry" Chap 17 (Prentice Hall), 275-285.

[15] Goe, G., Bailey, T.D., Beadle, J.R. (1988) US Patent 4,753,911.

[16] Baricelli, P. J.; Sanchez, V. J.; Pardey, A. J.; Moya, S. A. (2000) *Journal of Molecular Catalysis A: Chemical,* 164, 225-234.

[17] Yarapathi, R.V. ; Kurva, S. ; Tammishetti, S. (2004) *Catalysis Communications,* 5, 511-513.

[18] Saladino, R., Neri, V., Pelliccia, A.R., Caminiti, R., Sadun, C. (2002) *Journal of Organic Chemistry.* 67, 1323-1332.

[19] Kim, H.S., Kim, J.J., Kwon, H.N., Chung, M.J., Lee, B.G., Jang, H.G. (2002) *Journal of Catalysis,* 205, 226-229.

[20] Pardey, A. Fernandez, M., Alvarez, J., Urbina, C., Moronta, D., Leon, V., Haukka, M., Pakkanen, T. A. (2000) *Applied Catalysis A: General,* 199, 275-283.
[21] Drelinkiewicza, A., Waksmundzka, A., Makowski, W., Sobczak, J.W., Krol, A., Zieba, A. (2004) *Catalysis Letters,* 94, 143-156.

[22] Moghadam, M., Tangestaininejad, S., Habibi, M.H., Mirkhani, V. (2004) *Journal of Molecular Catalysis,* 217, 9-12.

[23] Gniewek, A., Trzeciak, A.M., Ziolkowski, J.J., Kepinski, L., Wrzyszcz, J. Tylus, W. (2005) *Journal of Catalysis,* 229, 332-343.

[24] Tsuchida, E., Kaneko, M., Nishide, H. (1973) *Die Makromolekulare Chemie,* 164, 203-213.

[25] Chanda, M., O'Driscoll, K.F., Rempel, G.L. (1981) *Journal of Molecular Catalysis,* 12, 197-211.

[26] Kumar, S.S., Govindarao, V.M.H., Chanda, M. (1997) *Journal of Chem. Tech. Biotechnology,* 69, 209-225.

[27] Imamura, S., Teramoto, M., Sumi, T., Aomi, H., Teranishi, H., Takegami, Y. (1976) *Bulletin of the Chemical Society of Japan*, 49, 1659-1665.

[28] Velusamy, S., Punniyamurthy, T. (2003) *Tetrahedron Letters*, 44, 8955-8957.

[29] Feldberg, L., Sasson, Y., (1996) *Tetrahedron Letters*, 37, 2063-2066.

[30] Lunak, S., Vaskova, M., Lederer, P., Vepreksiska, J. (1986) *Journal of Molecular Catalysis*, 34, 321-324.

[31] Chandran, R.S., Srinivasan, S., Ford, W.T. (1989) *Langmuir*, 5, 1061-1071.

[32] Chandran, R.S., Ford, W.T. (1988) *Journal of the Chemical Society, Chemical Communications*, 104-105.

[33] Galiasso, R.E., Gomez (2007) *Journal of Catalysis*, in press.

[34] West, Z., Zabarnick, S., Striebich, R.C. (2005) *Industrial & Engineering Chemistry Research*, 44, 3377-3383.

[35] Fares M.M., El-Khateeb M, Asali K.J. (2003) *Journal of Inorganic and Organometallic Polymers*, 13, 3, 143-155.