

# MoO<sub>2</sub>(acac)<sub>2</sub> Immobilized on Polymers as Catalysts for Cyclohexene Epoxidation: Effect of the Degree of Crosslinking.

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**ABSTRACT:** Crosslinked poly(4-vinylpyridine-co-styrene) used as support for a immobilized oxomolybdenum complex was synthesized by radical polymerization. As crosslinking agent, 1,4-divinylbenzene (DVB) was incorporated at 2, 4, and 6 mol %. Catalysts having similar MoO<sub>2</sub>(acac)<sub>2</sub> loading on different resins were obtained by refluxing a solution of the complex with the polymeric supports at 70°C. FTIR, specific surface area, and XPS techniques were used for characterization. It was found that a significant increase in the surface area occurs as the degree of crosslinking increases, presumably due to the development of branched polymers having higher porosity. XPS showed that the complex is anchored to the pyridinic nitrogen on the resin and that Mo was present essentially as Mo(VI) species. The Mo/C atomic surface ratio exhibits a

maximum for the catalyst with medium crosslinking degree. The epoxidation of cyclohexene was studied in the temperature range 40–60°C by using *tert*-butyl hydroperoxide as oxidant agent. The catalysts were active and selective to the corresponding epoxide and almost no leaching of the active phase was observed. The highest catalytic activity of the studied solids was displayed by the one supported on the resin with intermedium degree of crosslinking. The results are explained in terms of the access to the active sites and surface composition. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1602–1608, 2004

**Key words:** immobilized complex; crosslinking resin; cyclohexene epoxidation; supports; catalysts; XPS

## INTRODUCTION

Successful applications of the homogeneous catalysis in the production of fine chemicals were achieved in the recent past, in terms of both activity and selectivity to the desired product. However, problems related to separation and reuse of the usually expensive catalysts have pointed to immobilization of homogeneous complexes as one of the more relevant challenges. To face this task, different attempts were made in which the active site is bound to a heterogeneous surface.<sup>1–7</sup> Linear, noncrosslinked polymers and also better defined dendrimers<sup>8</sup> soluble in appropriate solvents were employed as supports that can produce catalysts with high mobility and good mass transport properties. However, separation of the homogeneous systems becomes difficult, requiring precipitation or ultrafiltration. Swellable, slightly crosslinked polymers such as polystyrene crosslinked with 1,4-divinylben-

zene can be easily separated; if the used solvents are suitable for swelling, they allow good mass transport. Highly crosslinked polymers (e.g., macromolecular polystyrenes) and inorganic supports (alumina or silica) hardly swell and can be efficiently used in different solvents without changes of texture or mass transport properties.<sup>9,10</sup> Immobilization via entrapment or intercalation in materials having well-defined pores and cavities such as zeolites or clays can also be used to produce reliable confinement of the metal complex. Whatever the used procedure, it is necessary to provide an appropriate anchorage of the active phase to the carrier surface to avoid leaching during catalytic reaction.

Polymers offer a great opportunity to immobilize complexes by bounding to a given site in the main chain or by anchoring the complex in functionalized lateral chain. Thus, recovery of the catalysts from a reaction based on a solid/liquid filtration may be achieved. The most common method for using a polymer uses a crosslinked insoluble polymer as support. Such polymers are generally insoluble, with divinylbenzene crosslinked polystyrene as typical support. Bayston et al.<sup>9</sup> prepared a bis(diphenylphosphino)-1,1'-binaphthyl (BINAP)-based diphosphine containing a functional group in the 6-position of the naphthalene ring. This diphosphine was then attached to

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an aminomethyl derivative of polystyrene (1 mol % DVB crosslinking) via this carboxylic acid group. The resulting diphosphine, when attached to the polymer, was converted into a ruthenium catalyst and this catalyst was effectively used in asymmetric alkene hydrogenation. Thus, 56% ee in reducing itaconic acid, 64% ee in reducing 2-acetamidoacrylic acid, and 97% ee during reduction of methyl propionylacetate was observed. After reuse, almost no leaching was detected. Another interesting example of development of polymer-bound catalysts was described by Sigman and Jacobsen<sup>10</sup> for the asymmetric Strecker reaction. They used combinatorial chemistry and polymer-supported catalysts to identify the best catalyst for this chemistry. The aim was to design a tridentate polymer-bound Schiff-base catalyst by using various tethering groups, various amino acid groups, various chiral 1,2-diamines, and various salicylaldehyde derivatives. Sherrington et al.<sup>11</sup> reported a polymer-supported version of Sharpless allylic alcohol epoxidation catalyst by using the tartrate chiral auxiliary as part of the polymer main chain.

Different organometallic complexes were assayed as catalysts in homogenous phase. Thus, Mn(III) porphyrin or Fe(III) porphyrin was successfully used in epoxidation reactions.<sup>12,13</sup> Chatterjee and Mitra<sup>14</sup> studied the epoxidation of 1-hexene by using Mn(III) (salen) and Ni(III) (salen complexes). Ni(II)-Schiff-base complexes have also been employed in epoxidation of various olefins; however, rather limited yields of the epoxide were obtained. Kureshy et al.<sup>15</sup> reported the use of disymmetric Mn(III) and Ru(III) chiral Schiff-base complexes in asymmetric epoxidation of styrene. Mn (salen) complexes were also used since 1990 in the catalytic asymmetric epoxidation of olefins, mainly conjugated with an aromatic ring.<sup>16-19</sup> Several tungstic anions in the free form, complexed or polycondensed, were also used as catalysts for epoxidation of alkenes with hydrogen peroxide as oxidant.<sup>20-22</sup> However, the most active catalysts in epoxidation of olefins by hydroperoxides seem to be those of molybdenum complexes, particularly, molybdenum naphthenate, molybdenum resinate, Mo(CO)<sub>6</sub>, and MoO<sub>2</sub>(acac)<sub>2</sub>,<sup>23-30</sup> among others.

The aim of the present article was to study the effect of the crosslinking degree of copolymers poly(4-vinylpyridine-*co*-styrene) as support of MoO<sub>2</sub>(acac)<sub>2</sub> catalysts on the cyclohexene epoxidation. The catalysts were characterized by FTIR, chemical analyses, surface area determination, and XPS to understand the observed catalytic behavior.

## EXPERIMENTAL

### Reagents

4-Vinylpyridine (Aldrich, Milwaukee, WI) and styrene were purified by distillation. 2,2'-Azobisisobutyroni-

trile (AIBN) (Merck, Darmstadt, Germany) was recrystallized from methanol. 1-4-Divinylbenzene (DVB) (Aldrich) was used without further purification.

### Syntheses of the polymeric support

The polymeric matrices used as support were synthesized by radical polymerization, using 4-vinylpyridine and styrene as monomers in a mole ratio of 1 : 9, and toluene as solvent. DVB (2, 4, or 6 mol %) and AIBN (0.5 mol %) as crosslinking agent and initiator were used, respectively. The polymerization reaction was carried out at 343 K for 24 h, and a higher yield of 93% of the poly(4-vinylpyridine-*co*-styrene) was obtained. The polymer was completely insoluble in water and in common organic solvents, including methanol, acetone, *N,N*-dimethylformamide, and dichloromethane.

### Synthesis of dioxobis(acetylacetonate) molybdenum(VI), MoO<sub>2</sub>(acac)<sub>2</sub><sup>31,32</sup>

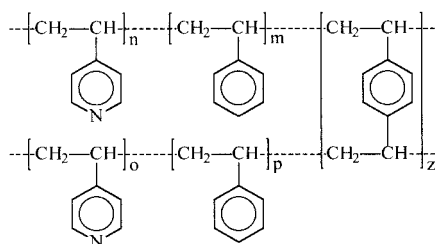
Ammonium heptamolybdate was dissolved in warm water. The solution was cooled and 2M HNO<sub>3</sub> was added until pH = 3. Then, acetylacetonate was added and the system was stirred for 3 h. The yellow solid obtained was filtered, washed with water, ethanol, and ether, and dried by suction. The product was recrystallized from a warm solution of 10% acetyl acetone in ethanol.

Chemical analysis (wt %) Calcd. for MoC<sub>10</sub>H<sub>14</sub>O<sub>6</sub>: C = 36.82, H = 4.32, Mo = 29.52. Found: C = 36.16, H = 4.18, Mo = 30.40. Melting point (mp): 184-186°C.

### Catalysts preparation

#### Characterizations

Chemical analyses of Mo were carried out by atomic absorption spectrometry by using a Perkin-Elmer model 3100. DTA experiments were performed in a Polymer Lab STA-625 electrobalance. They were carried out under nitrogen flow by using a heating rate of 10°/min. The CO<sub>2</sub> adsorption isotherms at 273 K were performed in a Micromeritics ASAP 2010 apparatus. FTIR spectra were collected in a Magna Nicolet 550 spectrometer. For these studies, the samples were ground to a fine powder and then made up into KBr disks by using the normal procedures. Photoelectron spectra were recorded by using an Escalab 200 R spectrometer provided with a hemispherical analyzer and by using nonmonochromatic MgK $\alpha$  X-ray radiation ( $h\nu = 1253.6$  eV). The surface Mo/C atomic ratio was estimated from integrated intensities of Mo 3d and C 1s lines after background subtraction and corrected by the atomic sensitivity factors.<sup>33</sup> The spectra of Mo 3d, N 1s, and C 1s were fitted to a combination of Gaussian-Lorentzian lines of variable proportion. The



poly[4-vinylpyridine-*co*-styrene], PVPS

**Figure 1** Structure of the resin poly(4-vinylpyridine-*co*-styrene) PVPS.

binding energy of the C 1s at 284.9 eV was taken as an internal standard.

### Catalytic measurements

Catalytic experiments were carried out in a glass batch reactor in flowing He ( $20 \text{ cm}^3 \text{ min}^{-1}$ ). In all the studies, 100 mg of catalysts was used. The epoxidation reactions were performed in a three-necked reactor with a condenser, a mechanical stirrer, and an airtight rubber septum, using a thermostatic water bath. Cyclohexene, dichloromethane, and a *tert*-butyl hydroperoxide (TBHP) solution were kept at the desired temperature of the previous reaction. Then, the required amount to total 60 mL of solution having initial concentration of cyclohexene and TBHP of 0.83 and 0.55M, respectively, were taken and injected into the reactor. Samples were taken periodically by using a syringe with a 20-cm needle.

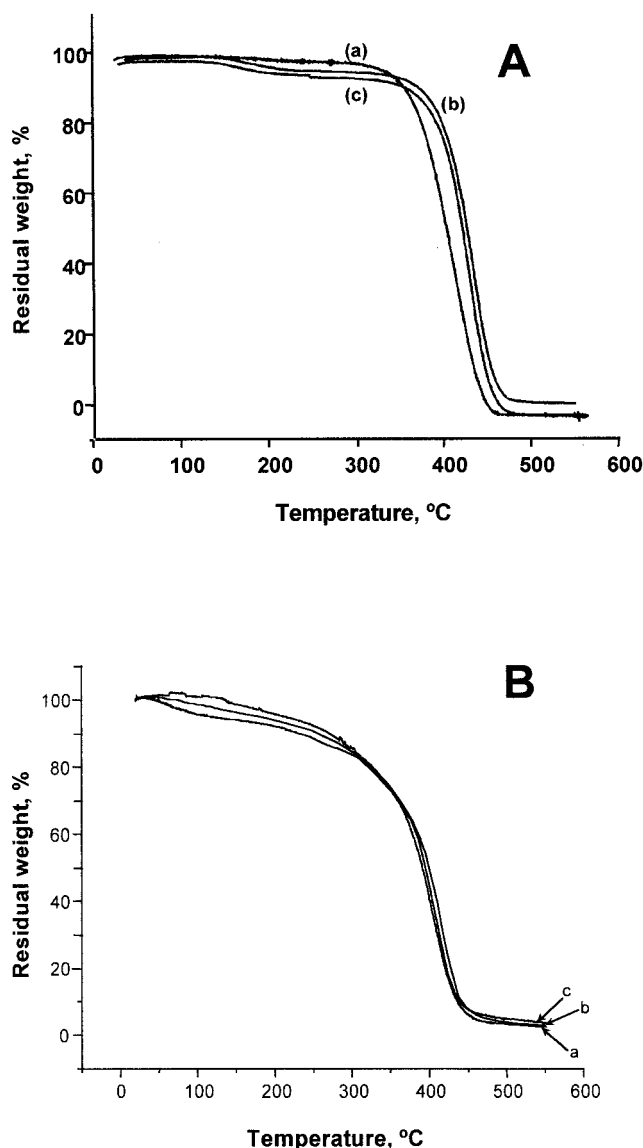
Aliquots were removed at intervals from 0 to 210 min and the analyses were carried out by gas chromatography. Nonane (the solvent of TBHP) was used as internal standard. GC analyses were carried out on a Gow-Mac series 550 gas chromatograph with a Cromosorb P 90/120 column.

## RESULTS AND DISCUSSION

To obtain polymer matrices as a potential carrier for epoxidation catalyst, the crosslinked poly(4-vinylpyridine-*co*-styrene) copolymers were obtained by radical polymerization, with a yield ranging from 93 to 95%. The copolymers were completely insoluble in water, toluene, and dichloroethane among other solvents, and a scheme of the synthesis of the resins is shown in Figure 1.

Thermogravimetric (TG) studies of the resins and catalysts were performed under nitrogen flow; the thermograms obtained for the crosslinked resins are given in Figure 2(A). The three resins show similar behaviors: a first weight loss of approximately 3.3 wt %, presumably corresponding to water evolution in the temperature range 150–200°C, and a second step

due to degradation of the polymer, which takes place at temperatures higher than 350°C and is completed at 460°C. A slight shift to higher temperatures as the crosslinking degree increases can be observed, in agreement with the higher thermal stability expected for the more crosslinked solids. The TG for the  $\text{MoO}_2(\text{acac})_2$  anchored catalysts are shown in Figure 2(B). The observed trends are similar. In the first step, in the temperature range 200–280°C, the weight loss is approximately 6 to 10%, being mainly attributed to evolution of water, whereas the degradation step shifts to lower temperatures compared with the pure resins. Polymer degradation begins at 330°C and finishes at temperatures close to 430°C. For these solids, the weight lost is not complete (5.5–6.2 wt %) due to the presence of residue of the organometallic complex.



**Figure 2** Thermogram (A) resins and (B) catalysts. (a) PVPS-2, (b) PVPS-4, (c) PVPS-6.

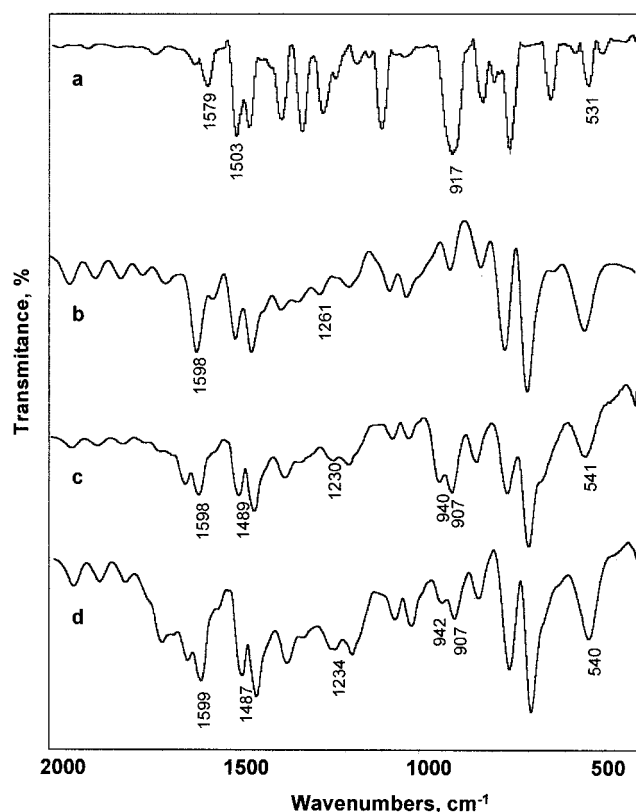


Figure 3 IR spectra (a) MoO<sub>2</sub>(acac)<sub>2</sub>, (b) PVPS-4 resin, (c) MoAC/PVPS-4 fresh, (d) used catalyst.

These values are in close agreement with those expected weight loss, considering the extent of anchored Mo, equivalent to  $\sim 1.6$  wt % of Mo.

The FTIR spectra of the MoO<sub>2</sub>(acac)<sub>2</sub> complex, one of the crosslinked resin, the anchored complex, and the catalyst after reaction are shown in Figure 3. Figure 3(a) corresponds to the MoO<sub>2</sub>(acac)<sub>2</sub> complex. The most relevant bands of this compound are the one centered at 1579 cm<sup>-1</sup> assigned to stretching of C=O bonds and that at 1503 cm<sup>-1</sup> attributed to C=C bonds. In the region close to 916 cm<sup>-1</sup> appears a band (or doublet) due to stretching modes of terminal Mo=O bonds, indicative of Mo centers. In the spectral region of 500–650 cm<sup>-1</sup>, absorption bands due to the deformation of the ring and stretching of Mo—O also appear. The spectrum of the resin PVPS shows several absorption bands in the region. Among them, those attributed to C—H and C—N centered at 1598 and 1230 cm<sup>-1</sup> can be mentioned. In the fresh and used catalysts, the bands due to the complex and resin may be expected with slight shifts due to the interaction produced during the anchorage—this is indeed observed. Additionally, a band attributed to the linkage of the complex to the resins, such as N—O band, should appear in the region 1200–1300 cm<sup>-1</sup>; unfortunately, this band cannot be clearly seen. The absence of a band at 720 cm<sup>-1</sup> associated with stretching of

Mo—O—Mo bridges seems to rule out a structure similar to that reported by Sherrington et al.,<sup>34</sup> in which the complex is immobilized on a polybenzimidazole resin, by coordination of Mo centered to N atoms of the resin.

Specific surface areas of the different resins and catalysts as well as the Mo loading are compiled in Table I. A significant increase in the surface area, from 86 to 238 m<sup>2</sup>/g, as the crosslinking degree increases from 2 to 6 wt %, can be observed. This fact can be understood taking into account that an increase in the proportion of divinylbenzene (crosslinking agent) leads to more branched solids and consequently the porosity and surface areas should also increase. Upon the anchoring of the oxomolybdenum complex, a slight decrease in the surface area is observed, accounting for the partial blockage of the porous structure by the Mo species.

Table I also summarizes Mo loading of the studied catalysts. A 4 : 1 ligand : Mo ratio was used (1.63 wt % Mo) to obtain the desired fixed metal loading on the polymer. That value corresponds to 1.63 Mo wt %. The molybdenum content of all samples tested were close to the theoretical value, indicating that metal was successfully anchored. Additionally, chemical analyses of the solids after their use in catalytic reactions at 60°C revealed that practically no leaching occurred during reaction. The lower Mo loading in the resin with higher degree of crosslinking seemed to be associated with the access of the complex to small pores of the resin, as surface area results suggest.

XPS analysis of the samples provided interesting insights into metal–polymer bindings. Thus, N 1s core level spectra of the catalysts displayed rather complex profiles, indicating the presence of different species, as can be seen in Figure 4(A). After spectral deconvolution, the signal at 397.8 eV was attributed to pyridinic N=C bond; 399.2 eV corresponding to N—C bond and at 402.1 eV assigned to N—O bond were observed. This latter is of special relevance because it suggests that the anchorage of the Mo complex takes place for coordination of one of the O with a N atom

TABLE I  
Specific Surface Areas and Mo Loading of the Resins and MoO<sub>2</sub>(acac)<sub>2</sub> Catalysts

Solid	S <sub>BET</sub> (m <sup>2</sup> /g)	Mo (wt %)		
		Theoretical	Fresh	Used
PVPS-2	86	—	—	—
PVPS-4	126	—	—	—
PVPS-6	236	—	—	—
MoAC/PVPS-2	72	1.63	1.54	1.50
MoAC/PVPS-4	103	1.63	1.62	1.60
MoAC/PVPS-6	224	1.63	1.25	1.19

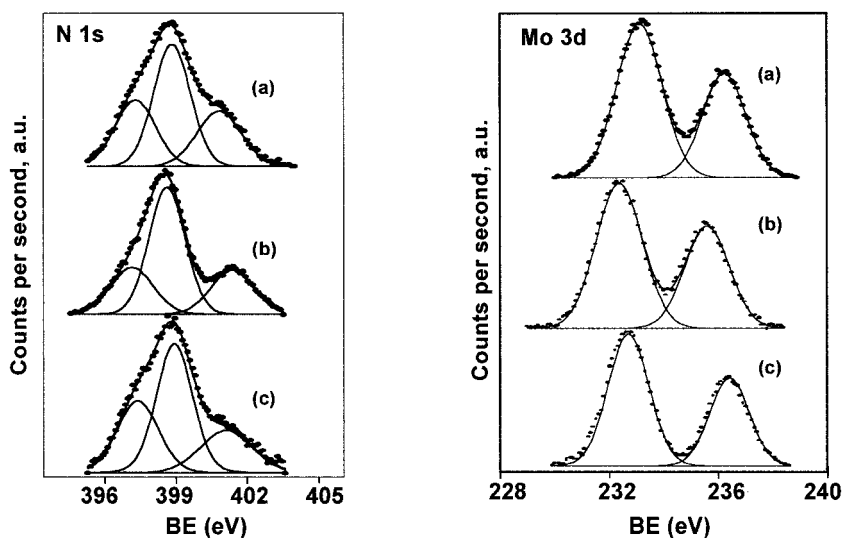


Figure 4 XP spectra of (A) N 1s and (B) Mo 3  $d_{5/2}$  core level: (a) MoAC/PVPS-2, (b) MoAC/PVPS-4, (c) MoAC/PVPS-6.

of the pyridinic ring. Figure 4(B) shows the Mo 3  $d$  core level spectra of the different catalysts used in this work. All samples tested displayed essentially the same spectrum. The binding energy close to 232.2 eV corresponding to Mo(VI)<sup>35</sup> was observed for all the samples. The presence of Mo(VI) is extremely important for epoxidation reactions because the Lewis acidity of the catalysts was pointed out as the key function of the catalyst.<sup>29</sup> The major role of the Mo(VI) ion is to withdraw electrons from the peroxidic oxygens, making them more susceptible to attack by nucleophiles such as olefins.

Table II compiles the binding energies of N 1s and Mo 3  $d_{5/2}$  obtained for the studied samples. It also includes the Mo/C surface atomic ratio obtained from the integrated signal of both elements after correction with their photoelectron cross-sectional factor.

Catalytic evaluation in the epoxidation of cyclohexene was performed in the temperature range 40–60°C by using TBHP as oxidant agent. Under the studied conditions, only *tert*-butanol and the corresponding epoxide were the obtained products and the decom-

position of the TBHP does not occur in a measurable extent, due to this lateral reaction taking place essentially at temperatures higher than 70°C. As comparison, the homogeneous reaction using the same amount of Mo complex that was used in the heterogeneous catalysts was also studied. Figure 5 displays the evolution of the molecules of cyclohexene converted per site, turnover number (TON), with time on stream for the different studied systems at 60°C. It can be seen that the highest reaction rates are obtained during the first reaction period, and the trends followed by the catalysts are different. In those heterogenized catalysts MoAC/PVPS-2 and MoAC/PVPS-6, after a fast increase in the TON, it reached almost constant values after ~ 2 h, with low conversion levels, being lower in the catalysts MoAC/PVPS-6, which exhibits the highest access limitation. The MoAC/PVPS-2 displays similar trends but shows higher TON. The support of this catalysts possesses lower

TABLE II  
XPS Binding Energies of Mo 3 $d_{5/2}$  and N 1s, Core Levels, Mo/C Surface Atomic Ratios of MoO<sub>2</sub>(acac)<sub>2</sub> Anchored on PVPS Resins

Catalyst	B. E.(eV) Mo 3 $d_{5/2}$	B. E. (eV) N 1S	(Mo/C) <sub>s</sub> × 10 <sup>3</sup>
MoAC/PVPS 2	232.9	397.8 (21)	2.03
		399.2 (61)	
MoAC/PVPS4	233.0	397.8 (26)	4.65
		399.3 (50)	
MoAC/PVPE6	232.6	397.9 (25)	1.03
		399.5 (63)	

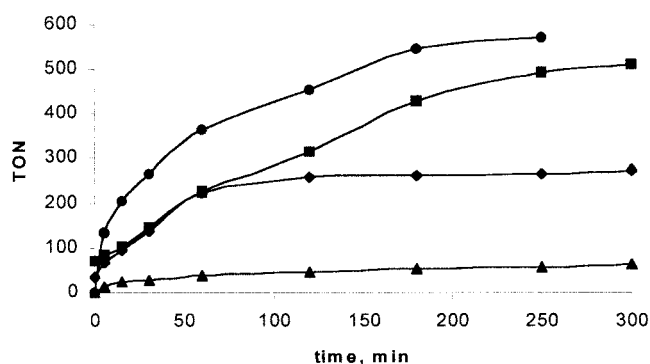
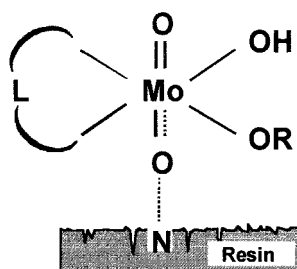


Figure 5 Evolution of TON with time on stream during cyclohexene epoxidation at 60°C. (●) MoO<sub>2</sub>(acac)<sub>2</sub>, (◆) MoAC/PVPS-2, (■) MoAC/PVPS-4, (▲) MoAC/PVPS-6.

surface area with essentially mesopores and an important flexibility of the chain. It is likely that this later factor negatively affects the catalytic behavior, as it has been mentioned in previous reports. In both catalysts, the observed results suggest the occurrence of a deactivation process. The generation of Mo diols during the reaction,<sup>36</sup> which is not an active species, may account for this behavior. The formation of these species is favored in the case of complexes anchored in close sites of the resin, which allow the condensation of intermediates type



On the other hand, the MoAC/PVPS-4 displays a behavior similar to that exhibited by the homogeneous system, but showing lower activity. After 4 h on stream, the heterogenized catalyst shows ~ 90% of the activity of the homogeneous counterpart and the same product distribution pattern. This result suggests that most of the complexes anchored in this resin are available for catalytic reaction and they are not affected by access limitation, in line with the appropriate surface area and porosity of the carrier. Similar features were observed at the other reaction temperatures, but obviously showing different activities. A comparison of the TON at the same reaction time, 180 min, is given in Figure 6. The highest activity was displayed by the MoAC/PVPS-4, whatever the reaction temperature. It is interesting to note that these results are in good agreement with surface composition obtained by XPS, indicating that the accessibility to the active species plays an important role in the catalytic reaction.

## CONCLUSION

Crosslinked poly(4-vinylpyridine-co-styrene) may be used as support to immobilized MoO<sub>2</sub>(acac)<sub>2</sub>, without significant leaching during epoxidation reaction when dichloroethane was used as solvent. The specific surface area of the resins and catalysts increases as the crosslinking degree increases, due to a development of branched polymers having higher porosity. XPS showed that the complex is anchored to the pyridinic nitrogen on the resin. Additionally, it showed that Mo was present essentially as Mo(VI) species and the Mo/C atomic surface ratio exhibits a maximum for the catalyst with medium crosslinking degree (4%). The highest catalytic activity of the studied solids was

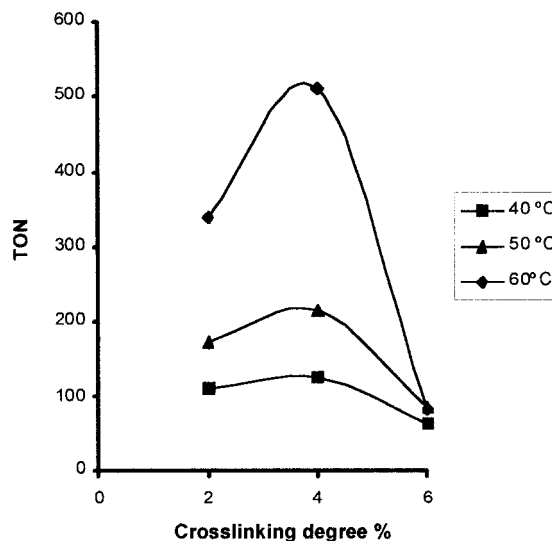


Figure 6 TON versus crosslinking degree of PVPS supported MoO<sub>2</sub>(acac)<sub>2</sub> catalysts. Epoxidation of cyclohexene at 180 min at different temperatures.

displayed by the one supported on the resin with medium crosslinking degree.

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