

Catalytic epoxidation of alkenes in the presence of a weakly acidic cation exchanger containing transition metal ions

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Abstract

Heterogeneous polymeric catalysts containing Mo, V and Ti for the epoxidation of alkenes by organic hydroperoxides were prepared by a simple modification of the weakly acidic cation exchanger Wofatit CA 20 (Germany) with aqueous solutions of the corresponding inorganic salts. The molybdenum-containing catalyst showed the highest activity for the epoxidation of cyclohexene in benzene solution of *t*-butylhydroperoxide (TBHP, 0.490–1.200 mol l⁻¹) at 79°C. The catalytic activity for alkenes with different structures was evaluated and compared to other catalysts under the similar conditions of cyclohexene epoxidation. Some data concerning the catalyst stability on heating and multiple recycling were also obtained. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous polymeric catalyst; Epoxidation; Epoxide yield; Molybdenum-containing cation exchanger

1. Introduction

The preparation of polymer-supported catalysts for the epoxidation of alkenes has received scientific attention since the late 1970s [1–3]. The attempts to immobilize molybdenum and vanadium complexes on polymers have initially included cation exchange resins [1,3–5], anion exchange resins [2], cross-linked poly(ethylene oxide), polyvinylalcohol, poly(vinylpyridine) [6,7], etc. The polymeric catalysts have been used for the epoxidation of alkenes, mostly cyclohexene and propene by organic hydroperoxides. More recently, a number of chelating

functional copolymers containing molybdenum and vanadium have been synthesized and employed as catalysts for the epoxidation of cyclohexene [8–14].

Catalysts preparation has frequently been associated with a multi-step procedure of synthesizing the polymeric support. In some cases, expensive starting materials have also been used [11,14]. In our opinion, commercially available ion exchange resins have not lost their potential as polymeric supports for the preparation of alkene epoxidation catalysts. Simple modification of the cross-linked copolymers in aqueous solution of inorganic salts results in the preparation of the corresponding catalysts [4,5]. We now describe our efforts to estimate the versatility of the cation exchanger containing molybde-

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num and other transition metals as a catalyst in the epoxidation reaction of alkenes of different structure using *t*-butylhydroperoxide as oxidant. We also report some data concerning the stability and the multiple use of the catalyst in the epoxidation reaction and compare its activity with other homogeneous and polymeric systems under similar reaction conditions.

2. Experimental

2.1. Starting materials

The weakly acidic cation exchanger Wofatit CA 20, a copolymer of methacrylic acid and divinylbenzene (DVB), (Germany) was employed as a polymeric support. The resin had macroporous (macroreticular) structure with particle diameter ~ 300 – $1200 \mu\text{m}$ and full ion exchange capacity in hydrogen form of 10 mmol g^{-1} . The commercial preparation of the cation exchanger is known to provide for formation of highly cross-linked colourless solid beads containing pores of relatively large dimensions (0.01 – $0.02 \mu\text{m}$), thus allowing an easy sorption of organic reactants even in a less polar medium [15]. The commercial availability and, also, the weak acidity which did not cause appreciable hydroperoxide decomposition were considered to be important advantages of Wofatit CA 20. The resin was initially treated by passing 200 ml 2% hydrochloric acid at a rate of 3 – 4 h^{-1} through 25 cm^3 Wofatit CA soaked preliminarily for 24 h in distilled water and placed into a glass column. The procedure was followed by washing with deionized water to pH 6–7 for the filtrate and drying for 24 h in air.

Cyclohexene (Fluka, $> 99.5\%$), 1-octene (Fluka, $> 98\%$), *t*-butyl hydroperoxide (Fluka, 80% in di-*t*-butylperoxide, purum), 2,4,4-trimethyl-1-pentene (Merck, $> 99.9\%$), 2,4,4-trimethyl-2-pentene (Merck, $> 98\%$), molybdenyl acetylacetonate $\text{MoO}_2(\text{acac})_2$ (Riedel de Haen),

ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck, p.a.), vanadyl sulfate $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (Fluka, $> 98\%$), titanyl sulfate TiOSO_4 (Riedel de Haen, 50% TiO_2) and ammonium metavanadate NH_4VO_3 (Fluka, p.a.) were used without further purification. Styrene (Petrochemical Plant, Bourgas, $\sim 99.8\%$) was subjected to vacuum distillation at 54 – $56^\circ\text{C}/30 \text{ mm Hg}$ to remove the inhibitor (*p*-*tert*-butylpyrocatechol) immediately before use. Benzene (Petrochemical Plant, Bourgas) was fractionally distilled and dried over sodium before use.

2.2. Catalysts preparation

A simple method for modification of Wofatit CA 20 was adopted, i.e., treatment of the resin in hydrogen form with diluted aqueous solutions of inorganic salts of the corresponding transition metals. In all cases the concentration of the inorganic salts was approximately the same (ca. 0.021 mol l^{-1}). The pH range was selected in order to achieve an optimum balance between the strong affinity of Wofatit CA 20 towards hydrogen ions and a reasonable concentration of cationic oxygen-containing species such as MoO_2^{2+} , VO^{2+} , $\text{VO}(\text{OH})^+$, TiO_2^{2+} or $(\text{TiO})_n^{2n+}$ etc. in the solutions [16–19]. The procedure for the preparation of molybdenum-containing Wofatit CA 20 catalyst (CA/Mo) was as follows: 6.5 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved into 200 ml deionized water. Equal volumes of the solution (50 ml each) were distributed into four 100 cm^3 Erlenmeyer flasks. Then, concentrated nitric acid was added dropwise to each solution until four different pH values were reached within the range of 1.5–3. Next, 1 g air-dried Wofatit CA 20 in hydrogen form was placed into each flask and this was followed by a vigorous shaking of the mixture for 5 h at room temperature. The cation exchanger so modified was filtered and washed with deionized water to neutral reaction. Finally, after consecutive washing with ethanol

and ether the polymer was dried in vacuo at 70°C to constant weight and stored in a desiccator.

Similarly, 1.35 g $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved into 200 ml deionized water. The solution of each salt was distributed into four Erlenmeyer flasks, and pH was adjusted within the range of 1.5–3 by adding concentrated H_2SO_4 . The final modified cation exchanger used as catalysts was labelled as CA/V. To prepare CA/Ti catalyst, 1.95 g TiOSO_4 containing 50% TiO_2 were dissolved into 250 ml deionized water followed by filtration. The resulting filtrate was distributed in the previous manner and concentrated H_2SO_4 was added dropwise to each of the four flasks until pH within the range of 0.8–1.8 was reached. The further treatment of the modified cation exchangers CA/V and CA/Ti after preparing the mixtures was the same as CA/Mo.

Colorimetric methods for metal analysis of the modified cation exchanger were adopted, based on the formation of coloured complexes with thiocyanate and hydrogen peroxide respectively [20,21].

2.3. Catalytic epoxidation

Certain amount of dry modified cation exchanger used as catalyst, corresponding to 0.09 mmol transition metal sorbed, alkene and benzene as a solvent were placed into a three-necked 50 cm³ thermostated glass reactor fitted with a reflux condenser, thermometer and a septum cap. The mixture was stirred for 5 min at 79°C and then 1.5–3.8 ml (12–30 mmol) *t*-butylhydroperoxide were added. In all cases the total volume of the reaction mixture was 30 ml and the molar ratio of alkene to *t*-butylhydroperoxide (TBHP) was kept within 4.5–5. Thus, the ‘concentration’ of the catalyst was ca. 3×10^{-3} mol l⁻¹. The reaction was monitored at certain time intervals to determine the concentration of alkene oxide and commonly proceeded for 7 h.

In a modified experimental procedure the catalyst, TBHP and benzene were first placed into the reactor and the mixture was stirred continuously at 79°C for 1 h (catalyst activation). Then alkene was introduced and the reaction monitoring started accordingly.

2.4. Catalyst recycling

0.05 g (0.032 mmol) molybdenum-containing polymeric catalyst and 10 ml (0.098 mol) cyclohexene were placed into the thermostated glass reactor and stirred for 5 min at 79°C. Then 1.5 ml (0.012 mol) TBHP were added and the reaction was allowed to proceed for 5 h. Finally, the catalyst was removed from the reaction solution, evacuated and placed in the reactor with fresh reactants. This process was repeated up to nine times with the same catalyst sample. The cyclohexene oxide yield was evaluated for each consecutive run. The molybdenum content in the catalyst was determined after the first and the ninth reaction cycle.

2.5. Analyses

Gas–liquid chromatographic (GLC) analyses of the reaction products were performed on a SIGMA 2000 instrument (Perkin-Elmer, Norwalk, CT, USA) equipped with a flame ionization detector. Data handling was provided by Chromatographics 2 Data System (Perkin-Elmer). The chromatograph was fitted with Permaphase DMS (polydimethylsiloxane) fused-silica capillary column (50 m × 0.25 mm). The oven temperature was 70°C and nitrogen (30 psi) was the carrier gas. GLC analysis was combined with both the titrimetric determination of alkene oxide in non-aqueous medium [22] and standard hydroperoxide iodometric method.

Differential infrared (IR) spectra of the polymeric catalysts were recorded as KBr pellets on a Specord 75 IR spectrometer (Germany) with Wofatit CA 20 in hydrogen form as a reference

sample. The thermal stability of both the molybdenum-containing catalyst CA/Mo and Wofatit CA 20 in hydrogen form was assessed by thermal gravimetric analysis (TGA) using OD-102 instrument (MOM, Budapest, Hungary). A heating rate of 10°C/min over the temperature range 20–900°C in both the air and nitrogen static atmosphere was employed.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

The carboxylic acid functionality has been known to promote the predominant formation of coordination bond with molybdenum. Hence, weakly acidic cation exchangers have served as useful polymeric ligands forming the corresponding heterogeneous catalysts for epoxidation of alkenes [3–5]. Table 1 summarizes the results concerning the metal content of the potential polymeric catalysts CA/Mo, CA/V and CA/Ti prepared at different pH. The highest content of metal sorbed by Wofatit CA 20 was associated with the molybdenum-containing cations (most probably, MoO_2^{2+}) at pH = 2. In this case, the most pronounced influence of pH on the degree of sorption was also found. At higher pH the equilibrium in the aqueous solution is shifted towards the formation of molybdenum-containing anionic species whereas at pH < 2 the strong affinity of the carboxylate groups with respect to hydroxonium ions pre-

dominates [16]. The content of vanadium sorbed (presumably, as VO^{2+} mainly) was found to be several times lower than Mo. No clear influence of pH on Ti content was observed and the selectivity of the cation exchanger with respect to the corresponding cationic species was very poor. Most likely, a radical change of the conditions for modification of Wofatit CA 20 with salts and complexes of V and, especially, Ti is required in order to achieve higher content of these transition metals in the polymer.

The differential IR spectrum of CA/Mo showed a strong band at 905–940 cm^{-1} which can be assigned to the stretching vibrations of MoO_2 fragment including Mo(V)=O and Mo(VI)=O bonds [23,24]. The probable presence of mixed valence species (Mo (V–VI)) was also supported by the colour of the polymeric beads which varied from dark-green to dark-blue predominantly [25,26]. No band at 710–740 cm^{-1} characteristic of bridged Mo–O–Mo species [10,11] was detected. On the other hand, the absorption observed at 1550–1570 cm^{-1} indicated the existence of Mo–O bond derived from the interaction of the ligand carboxylic groups with Mo [27].

The course of TGA scans for both the molybdenum-containing Wofatit CA 20 and the metal-free cation exchanger in air and in nitrogen atmosphere was similar. The onset of relatively rapid decomposition was observed at 220–230°C. The differential thermogravimetric (DTG) curves, however, showed some peculiarities within the 300–450°C temperature region. Two maximums in the rate of thermal decomposition at 310–320 and 410–420°C respectively were observed for Wofatit CA 20 in hydrogen form, whereas the molybdenum-loaded catalyst indicated clearly the maximum at 410–420°C only. This effect was even more pronounced in nitrogen atmosphere. It is very likely, that some thermal and thermooxidative changes of the carboxylic group functionality occur to a significant degree within 300–450°C, perhaps including formation of anhydrides, decarboxylation, etc. Some transformations probably take place

Table 1
Influence of pH on the metal content of the weakly acidic cation exchanger Wofatit CA 20 modified in aqueous medium

pH	Mo (mmol g ⁻¹)	pH	V (mmol g ⁻¹)	pH	Ti (mmol g ⁻¹)
1.50	0.297	1.54	0.142	0.88	0.068
2.01	0.651	1.86	0.212	1.10	0.067
2.50	0.615	2.11	0.213	1.30	0.067
3.02	0.613	2.55	0.239	1.74	0.070

'in full speed' with the metal-free cation-exchanger as early as 310–320°C. This was proved by the full ion exchange capacity (IEC) determined by back titration. Wofatit CA 20 in hydrogen form treated thermally under vacuum at 310–320°C for 6 h had IEC of 0.6 meq/g, as compared to 10.4 meq/g for the 'fresh' polymer. For the CA/Mo catalyst, the effects of rapid weight loss at 310–320°C are probably, to some extent, suppressed by the presence of molybdenum coordinated to part of the carboxylic ligand groups.

TGA of CA/Mo catalysis in air indicated an inorganic residue at 900°C of ca. 9.5% with respect to the initial weight of the sample which, calculated as MoO₃ was very close to the results from the colorimetric analysis.

3.2. Catalytic epoxidations

The yields in the reactions were expressed as $Y = (C_{\text{ox}}/C_0) \times 100$ where C_{ox} and C_0 (mol l⁻¹) are the concentration of epoxide formed and the initial concentration of TBHP respectively. Usually, the kinetic curves illustrating the experimental results represented the dependence of alkene oxide yield on the reaction time. In some cases, as an induction period was observed, the 'rate' of reaction was defined as the gradient of the steady part of the kinetic curve. In the absence of induction period, the initial reaction rate was taken into consideration. These parameters indicating the catalytic activity were expressed in appropriate units (e.g., mol alkene oxide mol⁻¹ Mo min⁻¹).

The first series of experiments were conducted in the presence of different catalysts consisting of Wofatit CA 20 with Mo, V and Ti sorbed. The reactants and the catalyst were introduced into the reactor simultaneously, i.e., no preliminary activation of the catalyst by TBHP was employed. The molybdenum-containing catalyst CA/Mo was found to be the most active one, whereas cyclohexene oxide yield in the presence of CA/V and, particularly, CA/Ti was much lower. The kinetic curve for the

catalyst CA/Mo showed a long induction period which was followed by a steady rate of acceleration and, finally, almost constant cyclohexene oxide yield was reached. No induction period for the catalysts CA/V and CA/Ti was observed which was combined with very low catalytic activity (Fig. 1).

The following experiments were designed to study the effect of the catalyst activation conducted by stirring at 79°C for 1 h in the presence of benzene solution of TBHP *before* the introduction of alkene. The hydroperoxide decomposition during the period of activation was found to be negligible. The preliminary treatment of CA/Mo with TBHP of concentration 0.490–0.500 mol l⁻¹ resulted in a significant reduction of the induction period and an increase of the yield for the epoxidation of cyclohexene (Fig. 2). Still, these induction periods did exist for cyclohexene and styrene, thus implying that longer periods of activation would be necessary. However, no induction period was detected at higher TBHP concentrations (1.04–1.20 mol l⁻¹) and this was accompanied by sharp increase of the reaction rates and the yields in the epoxidation of cyclohexene (Fig. 2) and styrene (Fig. 3). In this case, no preliminary activation of the catalyst was necessary. A common explanation of these phenomena is the formation of a complex involving the CA/Mo catalyst and TBHP and conversion of Mo (V) to the catalytically efficient Mo (VI) species. Such an oxidation was confirmed in earlier studies by ESR [4] but the oxidation state of all the molybdenum active centres remains unclear. Also, the greenish-blue polymer beads turned into yellow ones after the activation which is indicative for the oxidation of Mo(V) to Mo(VI). The same changes in colour were observed in the experiments with both the non-activated and activated CA/Mo *after* the epoxidation reaction.

The preliminary treatment of catalysts CA/V and CA/Ti with TBHP, however, did not result in any favourable changes of their activity in the epoxidation of cyclohexene. Consequently, the further experiments at lower TBHP initial con-

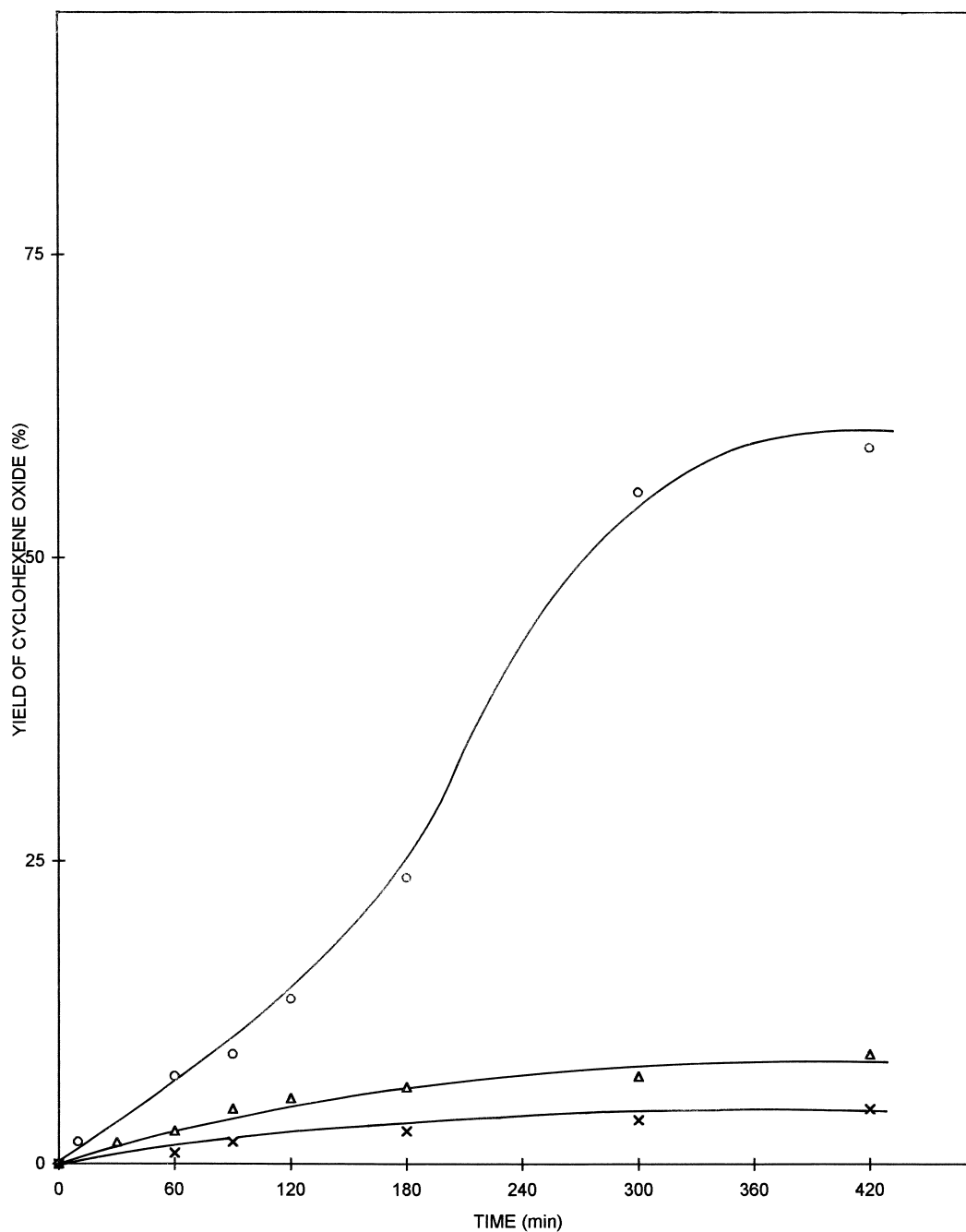


Fig. 1. Kinetic curves for the epoxidation of cyclohexene by TBHP in the presence of modified cation exchanger Wofatit CA 20 as catalyst (non-activated). Initial TBHP concentration $C_0 = 0.496 \text{ mol l}^{-1}$; molar ratio of cyclohexene to TBHP = 4.5; catalyst concentration $3 \times 10^{-3} \text{ mol l}^{-1}$; 30 ml total volume with benzene as a solvent; temperature 79°C . \times CA/Ti; \triangle CA/V; \circ CA/Mo.

concentrations were carried out in the presence of activated CA/Mo as catalyst only which showed the most reliable results.

The apparent lack of an induction period for 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene and 1-octene even at low TBHP initial

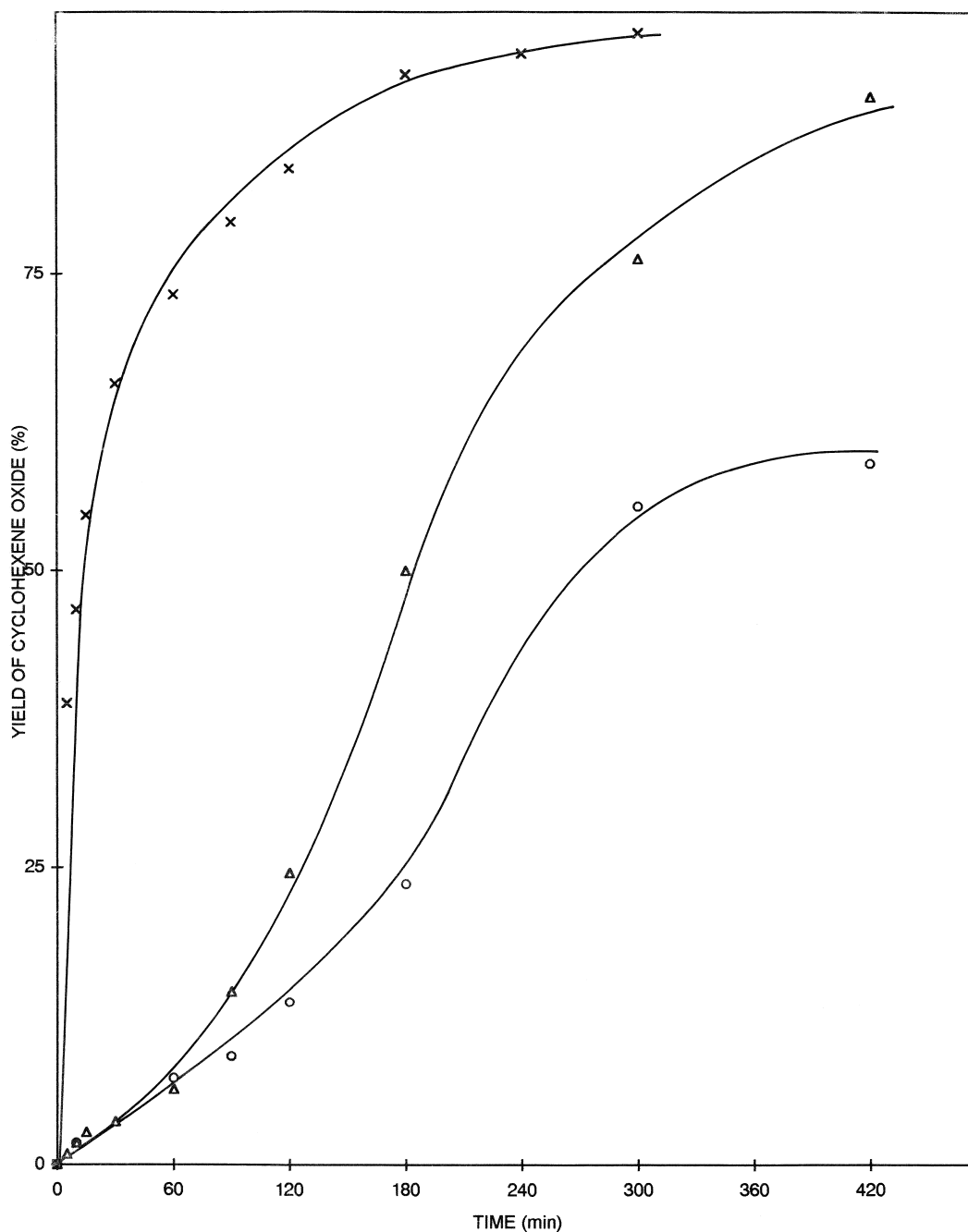


Fig. 2. Kinetic curves for the epoxidation of cyclohexene by TBHP in the presence of molybdenum-containing Wofatit CA 20 (CA/Mo) as catalyst. ○ Reaction conditions as in Fig. 1, non-activated catalyst; Δ CA/Mo activated by stirring in benzene solution of TBHP ($C_0 = 0.496 \text{ mol l}^{-1}$) at 79°C for 1 h before adding cyclohexene; × non-activated CA/Mo, $C_0 = 1.189 \text{ mol l}^{-1}$. The rest of reaction conditions as in Fig. 1.

concentration (Fig. 4) may well be misleading since the catalytic activity was very low for these substrates as compared with styrene and

cyclohexene. The latter, being the most reactive and compatible with the polymeric matrix, probably becomes coordinated rapidly at the

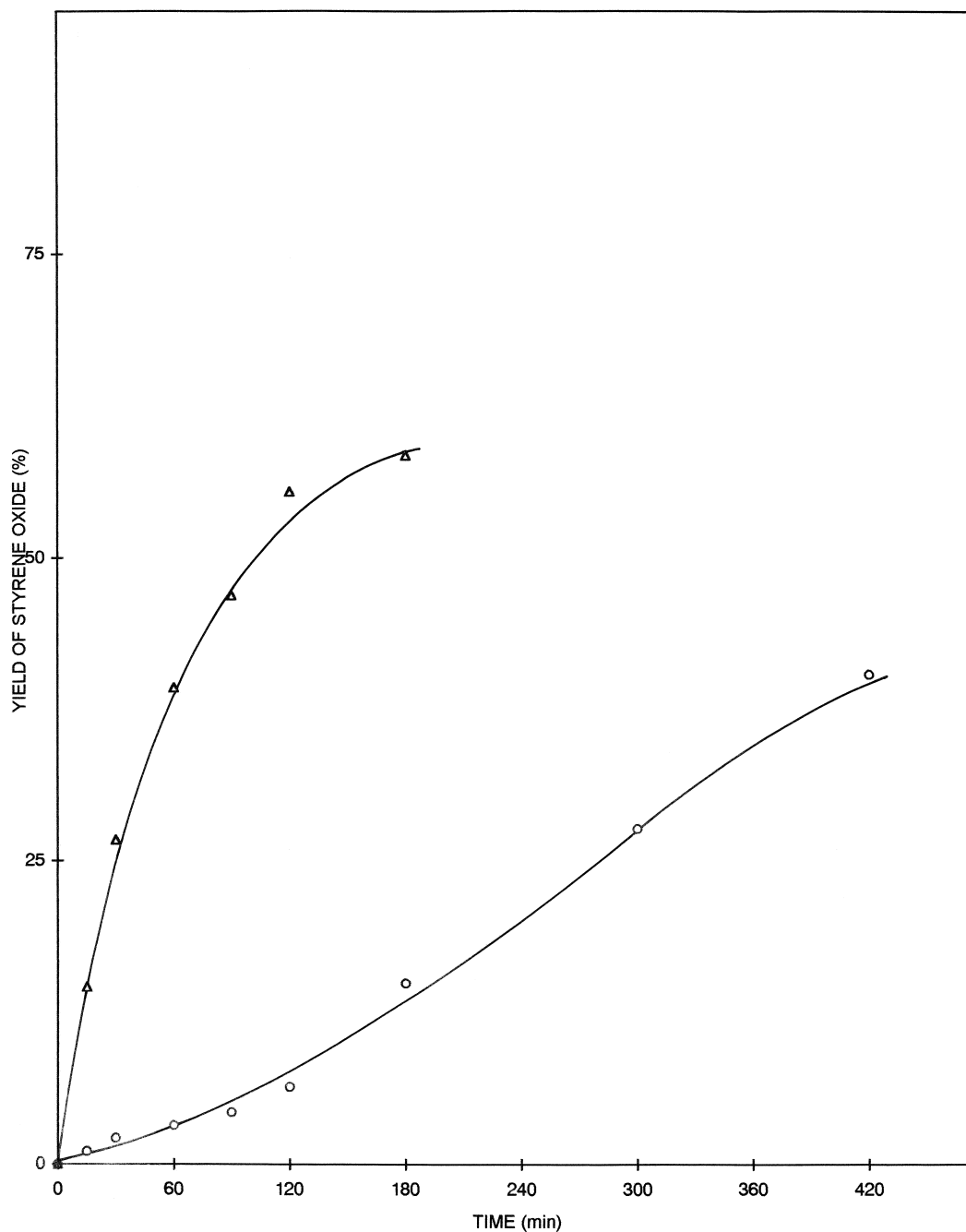


Fig. 3. Kinetic curves for the epoxidation of styrene by TBHP in the presence of CA/Mo catalyst activated under the conditions of Fig. 2. \circ $C_o = 0.493 \text{ mol l}^{-1}$; Δ $C_o = 1.140 \text{ mol l}^{-1}$.

molybdenum centres, thus partially competing with TBHP in the formation of the 'heterogenized' active complex. As a result, a slower oxidation of Mo(V) to Mo(VI) occurs and the

induction period is observed with both cyclohexene and styrene. To overcome this effect, higher TBHP initial concentrations corresponding to higher TBHP/Mo ratio in the presence of

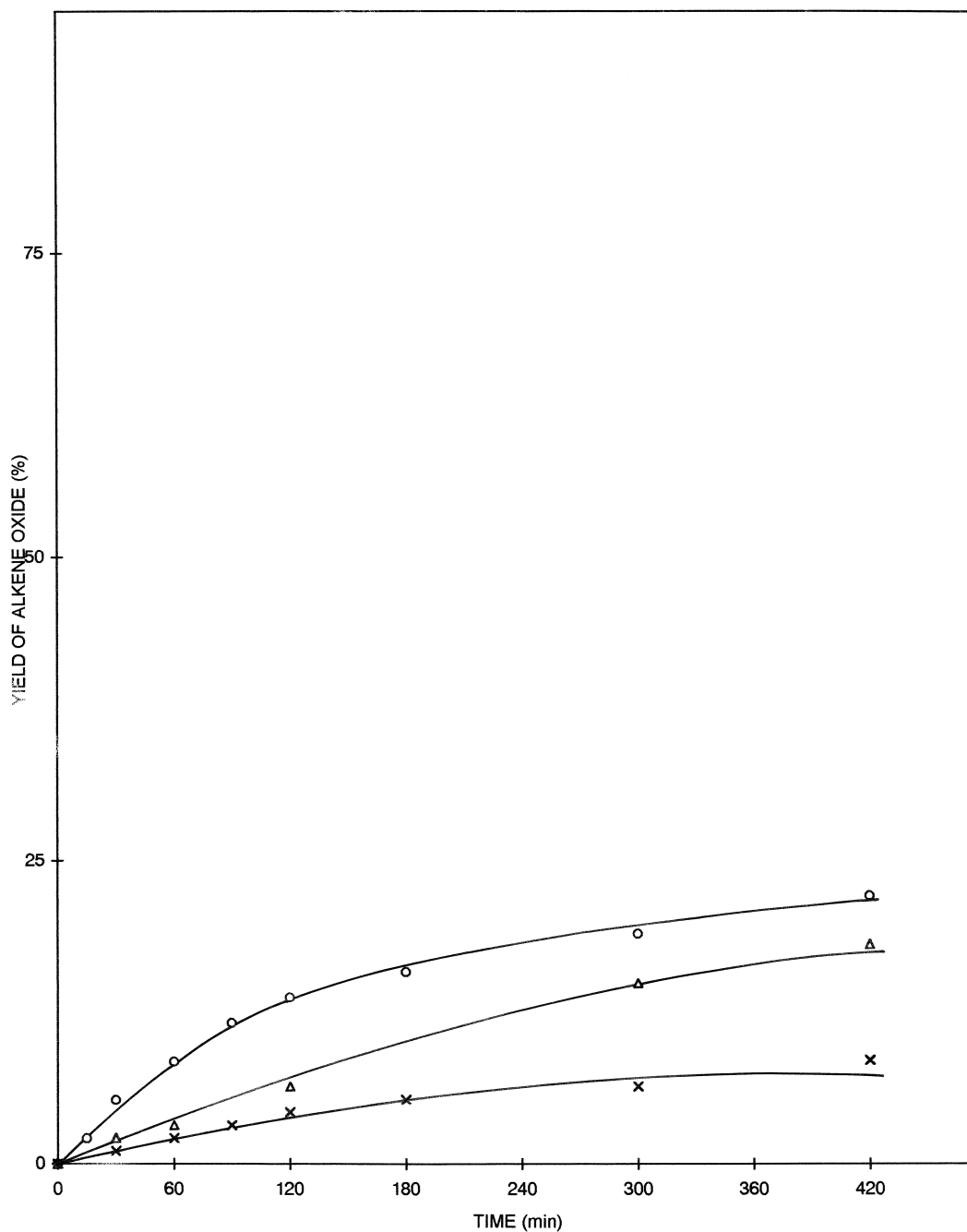


Fig. 4. Kinetic curves for the epoxidation of some alkenes by TBHP in the presence of CA/Mo catalyst (activated). $C_0 = 0.493\text{--}0.498 \text{ mol l}^{-1}$; the rest of reaction conditions as in Figs. 2 and 3. \times 1-octene; Δ 2,4,4-trimethyl-2-pentene; \circ 2,4,4-trimethyl-1-pentene.

proportionally reduced amount of solvent are necessary (Figs. 2 and 3).

Table 2 summarizes the results obtained in the epoxidation of the various alkenes by TBHP

with two different initial concentrations. The highest reactivity of cyclohexene followed by styrene is not surprising, taking into account the electron-donor substituents and the degree of

Table 2

Epoxidation of some alkenes using TBHP of different initial concentration catalyzed by molybdenum-containing Wofatit CA 20

Alkene	TBHP initial concentration C_o (mol l ⁻¹)	TBHP conversion and yield of alkene oxide ^d (%)				Rate of epoxidation (mol epoxide min ⁻¹ mol Mo ⁻¹)
		30 min	180 min	300 min	420 min	
Cyclohexene	0.493–0.498	3.6	52.5	77.4	95.1	0.75
		3.6	50.0	76.3	89.9	
Styrene		2.1	19.3	36.5	50.1	0.24
		2.1	14.9	27.7	40.4	
2,4,4-Trimethyl-1-pentene		8.0	20.5	25.5	31.5	0.20
		5.3	15.8	19.0	22.1	
2,4,4-Trimethyl-2-pentene		7.7	30.4	34.5	37.9	0.13
		2.1	11.7	14.9	18.1	
1-Octene		1.6	5.6	6.6	8.8	0.08
		1.1	5.3	6.4	8.5	
Cyclohexene	1.040–1.190	72.0	94.8	96.9	–	20.00
		65.8	91.8	95.3	–	
Styrene ^a		31.6	70.1	–	–	3.73
		26.7	58.5	–	–	
2,4,4-Trimethyl-1-pentene ^b		–	–	–	–	–
		–	–	–	–	
2,4,4-Trimethyl-2-pentene ^c		5.5	8.7	–	–	–
		5.4	6.9	–	–	
1-Octene		4.0	13.4	15.6	17.6	0.17
		2.4	5.6	6.6	8.0	

^aSignificant formation of polymer observed at reaction times above 120–180 min.^bNo data obtained.^cNo further increase in the yield at reaction times above 180 min.^dThe upper value corresponds to TBHP conversion and the lower one is alkene oxide yield.

substitution at the double bonds. Also, the compact carbocyclic molecules perhaps are structurally more compatible with the polymeric matrix of the catalyst. The abrupt increase in both the yield of epoxides and reaction rate at higher initial concentration of the reactants resulted from the complete disappearance of the induction period for these alkenes. The lowest reactivity of 1-octene should also be expected by analogy with the results obtained in the presence of homogeneous catalysts [24]. The surprisingly low reactivity of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene could be explained by slower coordination and nucleophilic attack of their relatively bulky, branched molecules on the 'heterogenized' catalyst-TBHP complex. It is quite tempting to explain the somewhat higher reactivity of 2,4,4-trimethyl-1-pentene as compared with its position isomer by steric reasons concerning the location of the methyl groups with respect to the double bond.

In the case of the less reactive alkenes, the higher initial concentration of the reactants had even negative effect on the epoxide yield. Clearly, a much more pronounced difference in the reactivity of alkenes studied was observed at higher initial concentration of TBHP as no induction periods were detected under these conditions.

During the epoxidation of styrene, a formation of significant amount of poly(styrene) was observed, especially at reaction times above 120 min and at higher TBHP concentration. Further studies on the possibility of decreasing the polymer formation are deemed necessary. The reaction mixture in the epoxidation of 2,4,4-trimethyl-2-pentene by TBHP of initial concentration 1.04–1.06 mol l⁻¹ became turbid as the reaction proceeded for more than 120–150 min and no further increase of the epoxide yield was observed. Therefore, no reliable data concerning the reaction rate were obtained and future inves-

tigations on the versatility of the polymeric catalyst for epoxidation of branched alkenes would be helpful.

To compare the efficiency of the heterogeneous polymeric catalyst CA/Mo with a homogeneous one, epoxidation reactions of both cyclohexene and 2,4,4-trimethyl-1-pentene were conducted in the presence of $\text{MoO}_2(\text{acac})_2$ of the same molar concentration in the reaction mixture (Table 3). No preliminary activation of the homogeneous catalyst was carried out and no induction period was detected in this case. A certain epoxide yield was reached rapidly in the presence of $\text{MoO}_2(\text{acac})_2$ but then it remained almost constant implying that perhaps some secondary reactions occurred involving the product. Direct comparison of the homogeneous and the polymeric catalyst should be made cautiously because of the different structure of the ligands. Still, the homogeneous catalyst showed a higher activity, as expected. The higher ratio between the observed rates of the homogeneously (r_{hom}) and heterogeneously (r_{het}) catalyzed formation of epoxide for 2,4,4-trimethyl-1-pentene compared to cyclohexene probably reflected the stronger influence of steric factors in the heterogeneous system.

Both the catalytic activity and stability after multiple recycling of the CA/Mo catalyst were compared with a molybdenum-containing polymeric catalyst reported previously in the literature [10] for the epoxidation of cyclohexene

with TBHP (Table 4). Although two important parameters of the experiment (initial TBHP concentration and temperature) were almost the same, the difference in the catalytic activity is believed to result from both the different ligand structure and reaction conditions such as the reactants ratio and the solvent employed. More significant Mo leaching with the CA/Mo catalyst (up to 6–7% with respect to the initial Mo content) was observed after the first recycling experiment. The average ‘rate of leaching’ for the next runs was ca. 0.5% Mo per cycle but it is not clear whether, at some point during these experiments, the leaching would become negligible. A relatively slight drop in the epoxide yield was observed which remained essentially constant over the last few recycling runs. Experiments in a column fixed-bed catalytic reactor would only clarify the real catalyst performance.

The solution collected after several consecutive runs was evaporated under vacuum. The oily, somewhat sticky residue was dried, dissolved in 10 ml cyclohexene and consequently introduced into the reactor. Then the epoxidation reaction was conducted under the conditions of the recycling test (Table 4). After a long induction period (180–200 min), epoxide yield was found to reach 14.5% for the reaction time of 300 min. The comparison with the corresponding results from the experiment carried out in the absence of any catalyst (6.6%)

Table 3

Epoxidation of cyclohexene and 2,4,4-trimethyl-1-pentene in the presence of homogeneous $\text{MoO}_2(\text{acac})_2$ and heterogeneous CA/Mo polymeric catalysts

Alkene	Catalyst	TBHP conversion and yield of alkene oxide ^a (%)					Epoxidation rate ratio $r_{\text{hom}}/r_{\text{het}}$
		15 min	30 min	180 min	300 min	420 min	
Cyclohexene	$\text{MoO}_2(\text{acac})_2$	69.8	83.8	88.8	–	–	11.3
		67.7	76.2	79.2	–	–	
	CA/Mo	3.0	3.6	52.1	77.4	95.1	
		2.7	3.6	50.0	76.3	89.9	
2,4,4-trimethyl-1-pentene	$\text{MoO}_2(\text{acac})_2$	40.4	59.6	85.4	90.9	–	18.4
		33.7	48.4	59.0	59.0	–	
	CA/Mo	3.6	8.0	20.5	25.5	31.5	
		2.1	5.3	15.8	19.0	22.1	

Initial TBHP concentration $C_0 = 0.493\text{--}0.496 \text{ mol l}^{-1}$.

^aThe upper value corresponds to TBHP conversion and the lower one is alkene oxide yield.

Table 4

Catalytic activity and stability after multiple recycling of Wofatit CA/Mo catalyst vs. molybdenum-containing polymeric catalyst reported previously [10]

Type of polymeric catalyst	Epoxidation reaction Rate of epoxidation (mol epoxide min ⁻¹ mol Mo ⁻¹)	Catalyst recycling (multiple use)			
		Run no.	Mo leaching (%) ^c	Epoxide yield (%)	Rate of epoxidation (mol epoxide min ⁻¹ mol Mo ⁻¹)
Copolymer of DVB and methacrylic acid treated with aqueous solution of (NH ₄) ₆ MoO ₇ O ₂₄ at pH 2 (catalyst CA/Mo) ^a	0.75	1	6.5	100.0	– ^d
		2	– ^d	94.6	–
		3	–	– ^d	–
		4	–	99.5	–
		5	–	98.1	–
		6	–	97.0	–
		7	–	96.8	–
		8	–	94.0	–
		9	10.3 ^e	95.1	–
Chelating resin derived from chemical modification of chloromethylated copolymer of styrene and DVB with <i>N</i> -(2-hydroxypropyl)aminomethyl-2-pyridine, treated by ligand exchange with MoO ₂ (acac) ₂ in toluene solution (catalyst PsMo) [10] ^b .	1.25	1	0.35	– ^{d,f}	1.25
		2	– ^d	–	– ^d
		3	0.22	–	0.98
		4	–	–	–
		5	0.17	–	0.97
		6	–	–	–
		7	0.11	–	1.08
		8	–	–	–
		9	0.90 ^e	–	0.96

^aReaction conditions for the epoxidation reaction: $C_o = 0.496 \text{ mol l}^{-1}$; temperature 79°C; cyclohexene/TBHP molar ratio = 5 in benzene as a solvent. Reaction conditions for the recycling test: $C_o = 1.043 \text{ mol l}^{-1}$; temperature 79°C; cyclohexene/TBHP molar ratio = 8.2; no solvent; time 5 h.

^bReaction conditions for both the epoxidation reaction and recycling test [10]: $C_o = 0.476 \text{ mol l}^{-1}$; temperature 80°C; cyclohexene/TBHP molar ratio = 16.6; bromobenzene and 1,2-dichloroethane as solvents; time 4 h.

^cRelative to the initial Mo content in the polymeric catalyst.

^dThe reactions were run but the corresponding parameters indicated in the column were not monitored.

^eTotal (accumulated) Mo loss with respect to the initial Mo content.

^fNo data concerning TBHP consumption published.

suggested that the homogeneous molybdenum-containing species, possibly generated by leaching, did not significantly contribute to the catalysis observed.

The better stability on repeated use of Ps/Mo catalyst reported previously reflected the multi-dentate nature of the ligand functional group attached to the polymeric matrix [10].

4. Conclusion

The modification of the weakly acidic cation exchanger Wofatit CA 20 of macroreticular structure with an aqueous solution of ammonium hexamolybdate at pH 2 renders polymeric catalyst for epoxidation of alkenes of much higher activity than vanadium and titanium-con-

taining catalysts prepared under similar conditions. The catalytic activity for alkenes of different structure decreases in the order: cyclohexene > styrene > 2,4,4-trimethyl-1-pentene > 2,4,4-trimethyl-2-pentene > 1-octene. This difference in the activity is much stronger at higher initial *t*-butylhydroperoxide concentrations as no induction periods are observed under these conditions. The catalytic activity does not change significantly on multiple recycling in the epoxidation reaction.

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