

Some molybdenum-containing chelating ion-exchange resins (polyampholites) as catalysts for the epoxidation of alkenes by organic hydroperoxides

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Abstract

Heterogeneous molybdenum-containing polymeric catalysts for the epoxidation of alkenes by organic hydroperoxides were prepared by a simple treatment of the chelating ion exchange resins (polyampholites) Amberlite IRC718, Amberlite IRC748 and Duolite C467 (Rohm & Haas, USA) with both the aqueous solution of sodium molybdate at pH 3.5 and solution of molybdenyl acetylacetonate in toluene. The formation of the catalytically active centres by the interaction of the oxomolybdenum species from the reaction solution with ligand functional groups of the ion exchangers was proved. The stability of these polymeric complexes on multiple use with the epoxidation of cyclohexene by *tert*-butylhydroperoxide (TBHP) in the absence of an inert solvent at temperature 79°C and initial TBHP concentration of 1.2–1.3 mol l⁻¹ was studied. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chelating ion exchange resins; Cyclohexene; Epoxidation; Cyclohexene oxide 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. More recently, a number of chelating functional molybdenum-containing copolymers

have been synthesized and employed as catalysts for the epoxidation of cyclohexene and other alkenes [8–15].

In our previous work [16], we reported on the catalytic epoxidation of various alkenes in the presence of a weakly acidic molybdenum-containing cation exchanger. The multiple use of the monofunctional cation exchanger as the polymer, carrying the ligand functional (carboxylic) groups in the epoxidation reaction of the highly reactive cyclohexene was accompanied by some molybdenum leaching. The latter, after nine-fold recycling, amounted to ca. 10% with respect to the initial Mo content, but the cat-

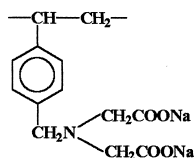
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alytic activity in these repeated experiments remained almost unchanged [16]. In general, however, polymer-supported metal complexes tend to become even more stable as the dentate number of the immobilizing ligand increases [10]. Therefore, we now describe our efforts to estimate the versatility of some commercially available bifunctional chelating cation exchange resins (polyampholites) containing molybdenum as catalysts with the multiple use in the epoxidation reaction of cyclohexene by *tert*-butylhydroperoxide (TBHP).

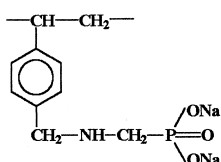
2. Experimental

2.1. Starting materials

The industrial grade chelating ion exchange resins Amberlite IRC718, Amberlite IRC748 and Duolite C467 (Room&Haas, USA), which are chemically modified copolymers of styrene and divinylbenzene of macroporous (macroreticular) structure and particle diameter ~ 300 to $1200 \mu\text{m}$ were employed as polymeric supports. The commercial preparation of these cation exchangers is known to provide for formation of highly cross-linked colourless solid beads containing pores of relatively large dimensions ($0.01\text{--}0.02 \mu\text{m}$), thus allowing an easy sorption of organic reactants even in a less polar medium. On the basis of the relatively poor information available [17], the structures of the principal polymer segments containing the ligand functional groups in the “commercial” (sodium) form can be expressed as follows:



Amberlite IRC 718 и IRC 748



Duolite C 467

The resins were initially treated by passing 500 ml 1.5 N HCl at a rate of $3\text{--}4 \text{ h}^{-1}$ through

$25\text{--}30 \text{ cm}^3$ of the polymers 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, $> 99.5\%$), TBHP (Fluka, 80% in di-*t*-butylhydroperoxide, purum), sodium molybdate $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Fluka), molybdenyl acetylacetonate $\text{MoO}_2(\text{acac})_2$ (Riedel de Haen, Germany) and 1,2-dichloroethane (99%, Merck–Schuchardt) were used without further purification. Toluene (The Oil Chemical Plant, Bourgas, Bulgaria) was initially distilled and the corresponding fraction (bp. $110\text{--}111^\circ\text{C}$) was collected and refluxed over sodium for several hours. This was finally followed by the second distillation within the same temperature range. The gas chromatography analysis (GLC) showed the purity of the final product over 99.9%.

2.2. Catalysts preparation

2.2.1. Catalysts prepared in the organic medium

3.35 g molybdenyl acetylacetonate $\text{MoO}_2(\text{acac})_2$ were added to 120 cm^3 toluene in a round-bottomed flask equipped with reflux condenser. The suspension was heated with stirring under reflux for 30 min and then 1.5 g ion exchanger in hydrogen form, preliminary dried under vacuum at 70°C to constant mass, were added. The mixture was refluxed with stirring for another 24 h. Finally, the modified cation exchanger was filtered, washed with acetone until dissolved molybdenum was absent from the filtrate and dried under vacuum at 70°C to constant mass. The catalysts thus obtained were further labelled as IRC718/Mo/org, IRC748/Mo/org and C467/Mo/org, respectively, and were stored in a desiccator.

2.2.2. Catalysts prepared in the aqueous solution

The most pronounced amphoteric properties of the chelating ion exchange resins, associated

with both the ion exchange and formation of strong coordination complexes with transition metals, are known to be manifested at a weakly acidic to neutral medium [18,19]. Therefore, the procedure for the preparation of molybdenum-containing catalysts in aqueous solution was as follows: 18.2 g (0.075 mol) $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved into 400 ml deionized water. Then, concentrated nitric acid was added dropwise to the solution until pH value of ca. 3.5 was reached. Next, 2.8 g air-dried ion exchange resin in hydrogen form was introduced and this was followed by a vigorous shaking of the mixture for 24 h at room temperature. The ion 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 mass and stored in a desiccator. The catalyst samples were further labelled as IRC718/Mo/aq, IRC748/Mo/aq and C467/Mo/aq, respectively.

2.3. Catalytic epoxidation

For the typical experimental procedure, 0.03 g of dry molybdenum-containing cation exchanger used as catalyst and 5 ml (0.049 mol) cyclohexene were placed into a three-necked 15 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, 0.75 ml (0.006 mol) TBHP was 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 five times with the same catalyst sample. The cyclohexene oxide yield was evaluated for each consecutive run and the molybdenum content in the catalyst was determined after some of the reaction cycles, including the last one.

In a modified experimental procedure, 0.1 g molybdenum-containing ion exchanger were introduced into the reactor together with the solu-

tion of 1.5 cm³ TBHP in 10 cm³ 1,2-dichloroethane. The mixture was kept under stirring at 79°C for 5 h and samples for the determination of both the initial and final TBHP concentrations were collected.

2.4. 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 [20] and standard hydroperoxide iodometric method.

The concentration of the functional groups in the initial (i.e., non-modified) ion exchange resins was determined by back titration in accordance with the method described elsewhere [19]. This was combined with the elemental microanalysis of the corresponding samples in hydrogen form on the Carlo Erba instrument (Italy). Colorimetric methods for molybdenum analysis of the modified cation exchangers were adopted, based on the formation of coloured complexes with thiocyanate [21].

The standard infrared (IR) spectra of the polymeric catalysts were recorded as KBr pellets on a Specord 75 IR spectrometer (Germany). The experiments for the catalysts characterization in the far-infrared region were performed on the Bruker IFS 113 FT–IR instrument in the 400–100 cm⁻¹ interval using CsI pellets (6 mg polymer/200 mg CsI) and the scans were compared with those for the starting non-modified ion exchange resins.

The thermal stability of both the molybdenum-containing catalysts and non-modified resins in hydrogen form was assessed by ther-

mal 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

Table 1 summarizes the results concerning the basic characteristics of the starting chelating ion exchange resins in hydrogen form and the molybdenum-containing polymeric catalysts prepared therefrom. The content of the ligand functional groups, i.e., the ligand loading was calculated as follows:

$$LL = 10 \frac{\%N}{14n}$$

where LL represented the ligand loading of the starting ion exchange resin in hydrogen form (mmol g⁻¹); %N was the nitrogen content determined by elemental microanalysis, and *n* represented the number of nitrogen atoms in the ligand functional group.

The data from Table 1 showed the highest functional groups content for Amberlite IRC718

resin, which probably caused the low mechanical strength of the latter. The full ion exchange capacity with respect to 0.1 N NaOH did not exactly correspond to the ligand loading, probably because of some non-uniformity in the polymer chemical structure. The treatment of the ion exchangers in aqueous medium led to significantly higher molybdenum content, as compared to the catalysts prepared in toluene solution of MoO₂(acac)₂. On the other hand, the polyampholites containing carboxylic functional groups (Amberlite IRC718, Amberlite IRC748) were found to be more susceptible towards the sorption of molybdenum-containing species from the solutions than Duolite C467 with the phosphonic acid groups. The calculated “superficial” immobilized ligand/metal ion ratio LL/[Mo] > 1 probably means that at least one ligand group of the polymer support was coordinated to a given molybdenum-containing ion but the diffusion and local conformational limitations should also be considered.

The standard IR spectra of all molybdenum-containing catalysts showed two distinct absorption bands at 900–910 cm⁻¹ and 930–940 cm⁻¹, which could be assigned to both the symmetric and asymmetric stretching vibrations of terminal MoO₂ *cis*-dioxofragment [2,10]. The presence of specific (“iminodiacetic”) ligand functional groups and the higher molybdenum

Table 1

Some basic characteristics of the chelating ion exchange resins (polyampholites) and the catalysts prepared therefrom

Type of catalyst	Ligand functional group of the starting ion exchanger	Nitrogen content in the starting ion exchanger, %N	Ligand loading LL, mmol.g ⁻¹	Ion exchange capacity towards 0.1N NaOH (IEC), mequiv.g ⁻¹	Molybdenum content in the catalyst [Mo], mmol.g ⁻¹	LL/[Mo] ratio
IRC 718/Mo/org IRC 718/Mo/aq		5.58	3.98	6.5	0.47 1.89	8.5 2.1
IRC 748/Mo/org IRC 748/Mo/aq		4.92	3.51	4.8	0.68 1.55	5.2 2.3
C 467/Mo/org C 467/Mo/aq		2.88	2.06	2.9	0.11 1.18	18.7 1.7



Fig. 1. Infrared spectra of Amberlite IRC748 (—) and IRC748/Mo/aq catalyst (.....).

content for the catalysts prepared in aqueous solution and based on the Amberlite IRC718 and Amberlite IRC748 chelating resins caused

the most pronounced changes in this respect. For example, the IRC748/Mo/aq catalyst, apart from the strong bands at 900–910 and 930–940 cm^{-1} showed reduced intensity at 1710–1720 cm^{-1} ($\nu(\text{C}=\text{O})$) and enhanced one at 1650–1550 cm^{-1} ($\nu(\text{COO}^-)$) as well as some shift of the latter towards the higher wave numbers, when compared with the starting, non-treated ion exchange resin (Fig. 1). This was probably due to the formation of ionic and, possibly, coordination bonds of the carboxylic functional groups with the oxomolybdenum species from the solution [19].

For the catalysts prepared in the organic medium no bands at 1585–1595, 1515–1535 and 1260–1270 cm^{-1} attributable to the bonding of the acetylacetonate ligand in $\text{MoO}_2(\text{acac})_2$ [11,14,22] were present. Therefore, the modification in organic medium was probably accompanied by the complete ligand exchange.

The presence of absorption bands in the region of the lower wave numbers (400–100 cm^{-1}) is known to serve as an evidence for the coordination between the molybdenum and the electron donor atoms (N and O) in the ligand functional groups. The appearance of a number of bands in the corresponding FT-IR spectra of

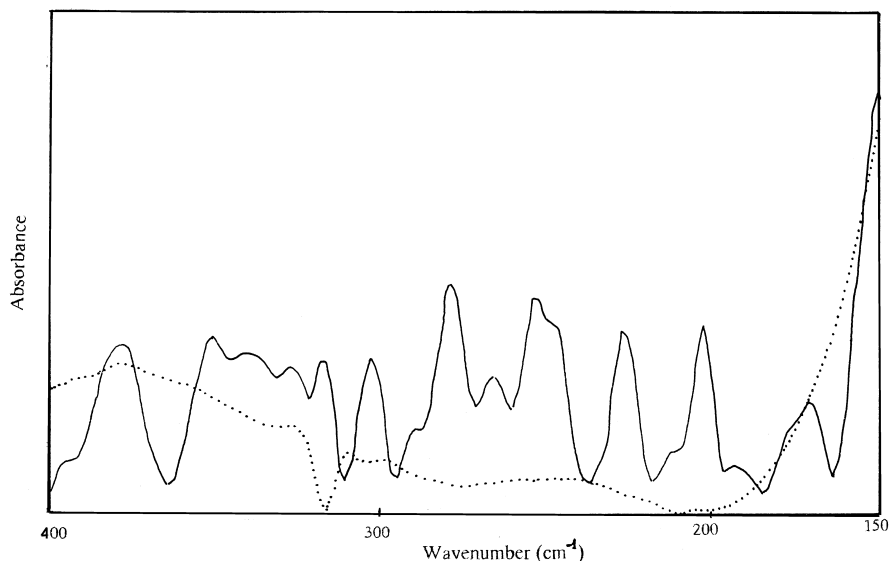
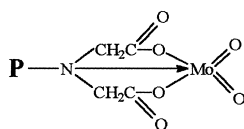


Fig. 2. FT-IR spectra in the region of the low wave numbers of Amberlite IRC748 (.....) and IRC748/Mo/aq catalyst (—).

the catalysts as compared to the almost “blank” spectra of the starting ion exchange resins (Fig. 2) proved the formation of N–Mo coordination bonds [19,23].

Therefore, although a detailed structural picture of the coordination centres is hardly possible, it is believed that the formation of structural units of the following type:



e.g., Amberlite IRC748 occurs where **P** represents the polymeric matrix of the chelating ion exchange resin.

The course of TGA scans for both the molybdenum-containing chelating ion exchange resins and the metal-free starting polymers in air and in nitrogen atmosphere was similar. Apart from the mass loss due to some water sorbed, the

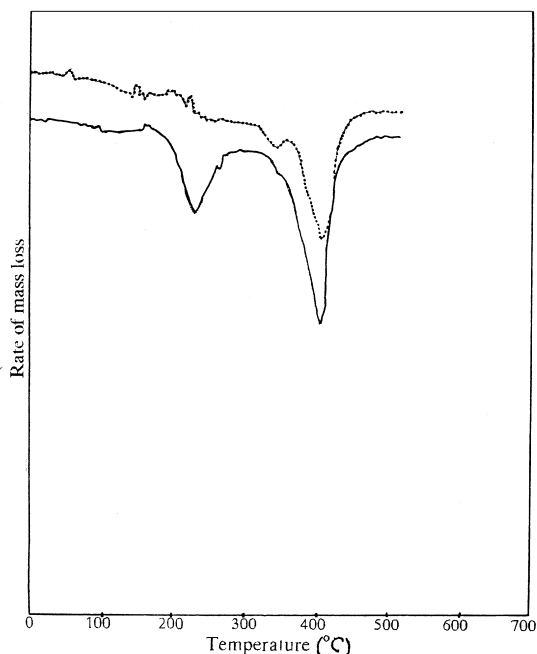


Fig. 3. DTG curves in nitrogen atmosphere of Amberlite IRC748 (—) and IRC748/Mo/aq catalyst (.....).

Table 2

Epoxidation of cyclohexene with TBHP in the presence of the IRC718/Mo/org^a and IRC748/Mo/org catalysts

Run No.	Molybdenum content in both the fresh and recycled catalyst	TBHP conversion, %	Cyclohexene oxide yield, %
<i>IRC718/Mo/org catalyst^a</i>			
1	0.470	62.0	67.9
2		79.3	84.8
3	0.475	92.6	99.0
4		94.5	106.4
<i>IRC748/Mo/org catalyst</i>			
1	0.680	100.0	105.2
2		98.3	94.7
3		99.1	92.6
4		97.6	105.3
5	0.646	100.0	98.2

^aSignificant crumbling and mass loss of the catalyst were observed during the recycling experiments.

onset of the relatively rapid thermal decomposition was observed, in most cases, at 150–170°C with the Amberlite IRC748 resin and the corresponding catalyst, whereas, with the Duolite C467 series, the decomposition over 150°C occurred more gradually. The differential thermogravimetric (DTG) curves for Amberlite IRC748 and the IRC748/Mo/aq catalyst showed some peculiarities within the 170–500°C temperature region in nitrogen medium. It is believed that in the temperature interval between 170°C and 500°C, the complete decomposition of the ligand functional groups took place. This process was probably accelerated and shifted towards the lower temperatures for the starting non-mod-

Table 3

Epoxidation of cyclohexene with TBHP in the presence of the IRC748/Mo/aq catalyst

Run No.	Molybdenum content in both the fresh and recycled catalyst	TBHP conversion, %	Cyclohexene oxide yield, %
1	1.55	100.0	105.8
2		100.0	116.3
3		100.0	116.4
4		100.0	116.4
5	1.54	100.0	116.4

Table 4
Epoxidation of cyclohexene with TBHP in the presence of C467/Mo/aq catalyst

Run No.	Molybdenum content in both the fresh and recycled catalyst	TBHP conversion, %	Cyclohexene oxide yield, %
1	1.18	100.0	100.4
2		96.7	100.4
3		96.0	107.0
4		96.7	116.3
5	1.22	98.2	107.0

ified chelating resin, as compared to the corresponding polymeric catalyst (Fig. 3). The presence of chemically bound molybdenum is likely to retard, to some degree the thermal decomposition processes such as decarboxylation, dehydration, fission of the C–N bonds, etc., affecting the functional groups of the polymer support in inert medium. Unfortunately, the thermooxidative processes in air suppressed these differences.

3.2. Catalytic epoxidations

The yields in the reactions were expressed as $Y = (C_{ox}/C_o) \times 100$ where C_{ox} and C_o (mol l^{-1}) are the concentration of epoxide formed and the initial concentration of TBHP, respectively. The selectivity with respect to the TBHP reacted and expressed by the ratio $S = 100C_{ox}/(C_o - C)$, where C is the final TBHP concentration, was found to be, in most cases, close to 100%. This was proved by the treatment of the polymeric molybdenum-containing

catalysts under stirring at 79°C for 5 h with the solution of 1.5 ml TBHP in 10 ml 1,2-dichloroethane in the absence of cyclohexene. In this case, the degree of TBHP decomposition did not exceed 3–4%. After the treatment by TBHP and/or use in the epoxidation reaction, the greenish–blue polymer beads turned into yellow ones, which is indicative for the oxidation of Mo(V) to Mo(VI) [24,25].

All consecutive runs for the epoxidation of cyclohexene by TBHP with the same catalyst sample were conducted under the same conditions, indicated in Section 2. The results concerning the catalysts prepared in organic medium are shown in Table 2. No significant leaching of the sorbed molybdenum under the conditions of recycling was observed. The mechanical strength of the IRC718/Mo/org catalyst was, however, much lower than that of IRC748/Mo/org. This probably led to the fluctuation of the results for each consecutive run concerning both the TBHP conversion and cyclohexene oxide yield, particularly, in the presence of the IRC718/Mo/org catalyst.

Unfortunately, the use of Duolite C467 as the polymer carrier subjected to modification with $\text{MoO}_2(\text{acac})_2$ in organic medium was not rewarding. Low mechanical strength combined with poor activity in the epoxidation reaction were observed with the C467/Mo/org catalyst. No clear explanation for this can be found for the time being. It is believed, however, that the low molybdenum content (Table 1) combined with the limited chemical stability of Duolite C467 under the conditions of the modification

Table 5
Composition of the reaction products obtained in the epoxidation of cyclohexene with TBHP in the presence of IRC748/Mo/aq as catalyst

Run No.	Composition of the reaction products, %					
	TBA ^a	Cyclohexene	Cyclohexene oxide	2-Cyclohexene-1-ol	2-Cyclohexene-1-one	Other
1	7.8	64.7	18.1	0.4	4.0	5.0
2	7.9	66.2	18.3	0.3	4.0	3.3
3	7.8	63.3	19.9	0.4	4.5	4.1
4 ^b	6.6	45.1	22.6	1.4	17.3	7.0
5	7.2	57.6	22.6	0.8	7.6	4.2

^aTBA — *tert*-butyl alcohol.

^bThe temperature of thermostat reached spontaneously 95–98°C for 20–25 min during the experiment, due to technical failure.

Table 6

Composition of the reaction products obtained in the epoxidation of cyclohexene with TBHP in the presence of C467/Mo/aq as catalyst

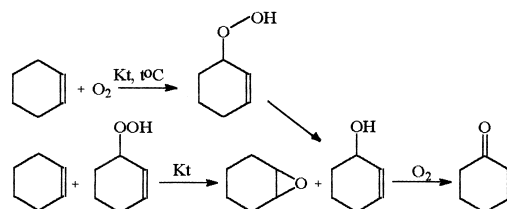
Run No.	Composition of the reaction products, %						
	TBA	Cyclohexene	TBHP	Cyclohexene oxide	2-Cyclohexene-1-ol	2-Cyclohexene-1-one	Other
1	7.1	62.4	–	20.6	0.3	5.5	4.4
2	7.4	61.5	0.4	21.2	0.4	4.4	4.7
3	8.5	66.2	0.5	17.2	0.5	4.2	2.9
4	7.8	65.8	0.4	19.2	0.2	3.5	3.1

with toluene solution of $\text{MoO}_2(\text{acac})_2$ might cause these effects.

The low mechanical strength of Amberlite IRC718 which was established as early as at the time of its treatment with the aqueous solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ at room temperature prompted us to concentrate further mainly on the IRC748/Mo/aq and C467/Mo/aq catalysts. The corresponding results are shown in Tables 3 and 4. Unlike the catalysts prepared in the organic medium, the modification of the polyampholites Amberlite IRC748 and Duolite C467 in aqueous solution of sodium molybdate at room temperature produced catalysts, which showed more stable results on recycling in the epoxidation reaction and, as a matter of fact, no molybdenum leaching was observed.

The experimental fact that, in most cases cyclohexene oxide yield exceeded TBHP conversion and was over 100% could mean that molecular oxygen was intervening as an oxidant in the reaction. As a result, 2-cyclohexene-1-ol and 2-cyclohexene-1-one side products were formed (Tables 5 and 6). The formation of these products is believed to be caused by the catalytic oxidation at the carbon atom in the “allylic” position with respect to the cyclohexene

double bond thus leading to 2-cyclohexenyl hydroperoxide. The degree of this oxidation increased significantly at higher temperature (Table 5, run No. 4). The following processes are believed to take place in the presence of the corresponding catalysts (Kt) [15,26]:



In support of the above assumptions are the data from Table 7, which showed that a small amount of cyclohexene oxide was formed even in the absence of TBHP, and the formation of 2-cyclohexenyl hydroperoxide by the oxidation of cyclohexene with molecular oxygen was facilitated at higher temperature. The decomposition of the latter resulted in the formation of 2-cyclohexene-1-ol and 2-cyclohexene-1-one at concentrations close to those obtained under “normal” conditions (epoxidation with TBHP at 79°C) but significantly increased at elevated

Table 7

Composition of the reaction products obtained in the treatment of cyclohexene under aerobic conditions with IRC748/Mo/aq and C467/Mo/aq catalysts at 79°C for 5 h in the absence of TBHP

Run No.	Catalyst	Composition of the reaction products, %				
		Cyclohexene	Cyclohexene oxide	2-Cyclohexene-1-ol	2-Cyclohexene-1-one	Other
1	IRC 748/Mo/aq ^a	34.9	4.0	26.0	32.4	2.7
2	C 467/Mo/aq	89.5	2.5	3.5	3.9	0.6

^aThe temperature of thermostat reached spontaneously 90–95°C for 30–40 min during the experiment, due to technical failure.

temperatures (Table 7, run No. 1). Apparently, the non-selective decomposition of 2-cyclohexenyl hydroperoxide was predominant, rather than the epoxidation of cyclohexene by the latter.

4. Conclusion

The treatment of the chelating ion-exchange resins Amberlite IRC718, Amberlite IRC748 and Duolite C467 of macroreticular structure with molybdenum salts and complexes in both the organic and aqueous medium renders polymeric catalysts for the epoxidation of alkenes. The formation of the coordination centres involving the polydentate ligands of the ion exchange resins and the oxomolybdenum species from the solution is proved by using IR spectroscopy, including the far-infrared one. The molybdenum content is much higher with the catalysts prepared in the aqueous solutions. The catalysts based on the Amberlite IRC748 and Duolite C467 chelating resins, obtained in aqueous medium are active and stable on multiple recycling in the epoxidation reaction. The epoxidation of cyclohexene with TBHP to cyclohexene oxide under aerobic conditions is accompanied by the formation of 2-cyclohexene-1-ol and 2-cyclohexene-1-one as side products, due to the catalytic oxidation of cyclohexene by molecular oxygen.

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