Catalyst recycling in the epoxidation of alkenes catalyzed by MoO$_2$(acac)$_2$ through precipitation with poly(ethylene oxide)

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Abstract

Addition of poly(ethylene oxide) (PEO) to the catalytic system MoO$_2$(acac)$_2$/TBHP/*t*-butanol used for epoxidation of olefins allowed an easy strategy for catalyst recycling and product recovery. This procedure is based upon catalyst removal by precipitation of a complex with the polymer, being advantageous over other similar recycling methodologies in that there is no requirement for specially prepared catalysts or solvents. Although some catalyst leaching is detected, the epoxidation of *cis*-cyclooctene was achieved with global turnover numbers close to 650. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Soluble Mo(VI) compounds are amongst the most versatile catalysts for epoxidation of olefins [1]. Homogeneous catalysis, however, presents several drawbacks, in particular the difficult recovering of the catalyst at the end of the process, warranting a search for supported molybdenum catalysts. Research done so far has focused on the use of organic polymers as supports. Preparation of such polymer-supported catalysts has usually been based on anion exchange [2], cation exchange [3,4] and chelating ion exchange resins [5–7]. Among these systems, the ones based on polybenzoimidazol [8,9] and on functional polyimide beads [10] showed the best performance and stability. Other strategy to be considered is the use of thermoregulated phase transfer ligands, allowing the reaction to be carried out in a homogeneous solution [11,12]. Recently, one of us [13] has described an organic biphasic system containing poly(ethylene oxide) (PEO), CH$_2$Cl$_2$ and heptane which shows a strong segregation between the polar polymer and the hydrocarbon solvent, the polymer being concentrated in the bottom phase. Further studies showed that such a system could be applied in hydrogenation reactions using Rh complexes allowing the easy recovery of the catalyst without any apparent leaching of the complex to the non-polar phase [14]. We wish to report here some results of our attempts to use this approach to recover the catalyst in the epoxidation of alkenes with MoO$_2$(acac)$_2$.

2. Experimental

2.1. Materials

PEO 3350 (Sigma), *cis*-cyclooctene (95%, Aldrich), *t*-butylhydroperoxide (88% (v/v) in cyclohexane,

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Nitrocarbono S.A.), $MoO_2(acac)_2$ (Aldrich), *t*-butanol (Merck) and heptane (Synth) were used as received.

2.2. Catalytic experiments

The catalytic experiments were carried out at 70 °C in a Schlenk flask equipped with a condenser. In a typical experiment, the appropriate amount of PEO 3350, 20.0 mg (0.0613 mmol) of $MoO_2(acac)_2$, 0.1 ml of *n*-decane (internal standard), 1.29 ml (9.41 mmol) of *cis*-cyclooctene (95%), 5 ml of *t*-butanol and 1.41 ml of TBHP/cyclohexane (9.41 mmol of TBHP) were employed. Precipitation of the polymer along with the molybdenum complex was observed within half-an-hour. After the reaction, 40 ml of heptane were added to the reaction solution, which was then allowed to stand in a freezer overnight to precipitate the remaining PEO. The solution was removed via cannula (to be analyzed on molybdenum by ICP-EAS) and the precipitated PEO–Mo complex (a green or green-yellowish solid) was dried under vacuum, suspended in 5 ml of *t*-butanol and tested in another run (with addition of only *cis*-cyclooctene and TBHP/cyclohexane). The PEO–Mo complex remained in suspension upon heating.

Reactions were monitored through GC analyses of the liquid phase (HP 5890 gas chromatograph, equipped with an HP 5 capillary column and a gas flame ionization detector) using *n*-decane as internal standard.

Infrared spectra were recorded from KBr-pellets on a Bomem FT-IR spectrometer model MB-100 (16 scans) with a resolution of $4.0 \, cm^{-1}$.

3. Results and discussion

The catalytic epoxidation of alkenes may be carried out in different solvents, e.g. toluene or dichloromethane. Usually, alcohols are to be avoided owing to their ability to compete for coordination sites around the metal center. Nevertheless, since *t*-butanol is a byproduct when the epoxidation is performed with *tert*-butylhydroperoxide and is also environmental friendly, we decided to use this alcohol as the solvent. In the absence of PEO, reactions carried out in *t*-butanol are just slightly slower than those per-

formed in non-coordinating solvents, [2] warranting the studies of the biphasic system *t*-butanol/PEO/heptane. Preliminary experiments showed that the addition of PEO to the reaction mixture caused a precipitation of the polymer along with the molybdenum complex even in the absence of heptane. In fact, we later observed that the presence of the reactants was not necessary for the precipitation of a PEO–Mo complex (vide infra). Under the reaction conditions, the PEO–Mo complex begins to precipitate in the first half hour as a green or yellow-greenish solid.

The first studies aimed at determining the effects of the amounts of PEO in the catalytic activity of the molybdenum complex in the epoxidation of *cis*-cyclooctene. As it can be seen in Fig. 1, the presence of PEO leads to a decrease in the catalytic activity which depends on the ratio $MoO_2(acac)_2$/PEO. When this ratio is around 1:25 to 1:50 (w/w) the catalytic activity is only slightly affected. For higher amounts of PEO, the decrease in activity can be explained by diffusion problems owing to the increased viscosity of the solution. Leaching of the catalyst to the supernatant, however, decreases when the amount of PEO increases, as shown in Table 1. In order to compromise catalytic activity with catalyst recovery, a $MoO_2(acac)_2$/PEO ratio of 1:50 (w/w) was chosen for recycling experiments. Fig. 2 shows the results obtained in six runs. Although further ICP-EAS analyses of the reaction solutions revealed a significant loss of molybdenum in the first run (Table 1), the catalytic activity was kept almost constant for three runs. In the fourth run a slight decrease in the reaction rate was observed, with molybdenum losses around 1 wt.% in each run (Table 1). Such losses, however, seemed not to affect the catalytic activity, which remained almost constant. The large loss of molybdenum in the first run may be due to its complexation to lower molecular weight fractions of the PEO employed, becoming inactivated already in the beginning of the reaction. In six runs (with a reaction time of 5 h) a total turnover number of 647 was reached with a total loss of molybdenum to the organic phase around 20%. In spite of the leaching, this system leads to higher turnovers than the best heterogenized molybdenum

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[2] Using [Mo]/[alkene]/[TBHP] = 1/153/153, the time needed to reach 80% conversion in *t*-butanol was 60 min; in 1,2-dichloroethane, 15 min.
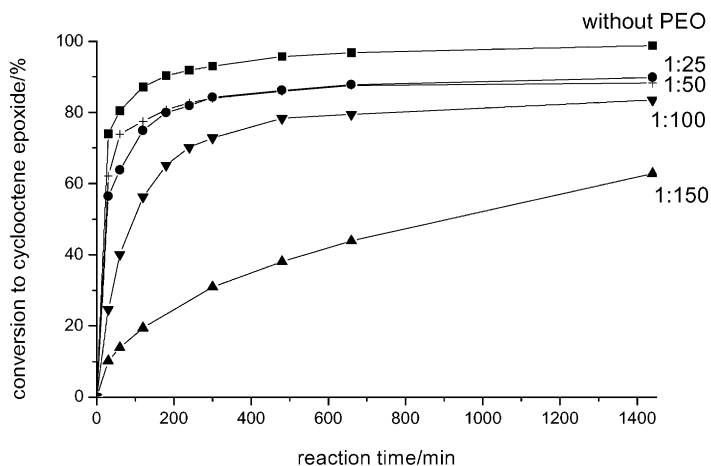
Fig. 1. Epoxidation of *cis*-cyclooctene with $MoO_2(acac)_2$ with increasing amounts of PEO in the reaction solution ($MoO_2(acac)_2$: PEO = wt:wt). Reaction conditions: initial amount of PEO: 1 g; *t*-BuOH: 5 ml, [Mo]/[alkene]/[TBHP] = 1/153/153; 70 °C.

catalysts reported so far [8,9], without requiring the synthesis of functionalized polymers or previous activation. Hence, the present investigation provides an easy and efficient alternative strategy that may be tailored for use in similar catalytic processes, provided an intense polymer/catalyst interaction occurs, and that this complex does not loose its catalytic activity.

Some infrared studies were performed in order to verify the integrity of the polymer after a catalytic re-

Table 1
Epoxidation of *cis*-cyclooctene with $MoO_2(acac)_2$[a]

	PEO (g)	$MoO_2(acac)_2$/ PEO (w/w)	TON[b]	Mo leaching mg (%)[c]
First run	1	50	129	3.07 (15.3)
Second run			133	0.13 (0.6)
Third run			125	0.16 (0.8)
Fourth run			95	0.13 (0.6)
Fifth run			86	0.13 (0.7)
Sixth run			79	0.23 (1.1)
	0	20/0	142	–
	0.5	1/25	128	3.59 (17.8)
	1	1/50	129	3.07 (15.3)
	2	1/100	111	0.82 (4.0)
	3	1/150	47	0.20 (0.9)

[a] Reaction conditions: 20 mg $MoO_2(acac)_2$; 5 ml *t*-BuOH; 9.408 mmol alkene; molar ratio [Mo]/[alkene]/[TBHP] = 1/153/153 in the first run; 70 °C; 24 h.
[b] After 5 h (values corrected for Mo leaching).
[c] Calculated as mg of $MoO_2(acac)_2$.

action (Fig. 3). A slight change in the set of bands around 1200–1000 cm^{-1} assigned to the asymmetric stretching of the C–O–C bonds [15] was observed both in a solid prepared by heating PEO with $MoO_2(acac)_2$ in $CDCl_3$ and in the reaction mixture (Fig. 3c and d). A second set of bands belonging to PEO, in 962 and 947 cm^{-1}, disappeared. In both systems (reaction mixture and PEO + $MoO_2(acac)_2$ in $CDCl_3$) new bands appeared, around 957, 878 and 806–802 cm^{-1}, suggesting the formation of a PEO–Mo complex. The bands at 879 and 806 cm^{-1} can be tentatively assigned to Mo=O vibrations. The spectra also suggest that the acac ligands are removed from the coordination sphere
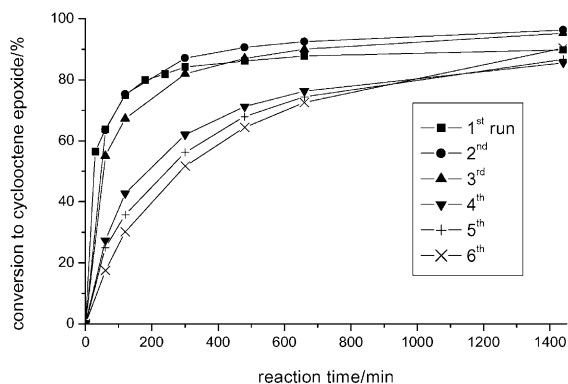

Fig. 2. Epoxidation of *cis*-cyclooctene with $MoO_2(acac)_2$ in six runs. Reaction conditions as stated in Fig. 1.

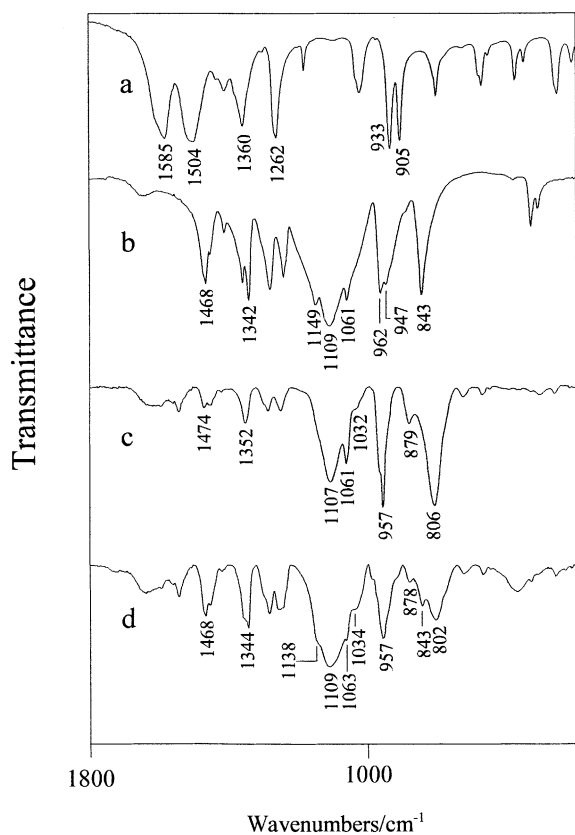Fig. 3. FT-IR spectra (KBr-pellets) of: (a) $Mo_2(acac)_2$; (b) PEO 3350; (c) PEO–Mo complex after 0.5 h of reaction with *cis*-cyclooctene in *t*-butanol; (d) PEO–Mo complex prepared by heating (70 °C) PEO 3350 and $MoO_2(acac)_2$ in $CDCl_3$.

of molybdenum during the catalytic reaction since the bands at 1585 and 1504 cm^{-1}, assigned to these ligands, were no longer present. Since a PEO–Mo complex prepared from PEO and $MoO_2(acac)_2$ in $CDCl_3$ gave a spectrum very similar to that obtained from a catalytic reaction in *t*-butanol, we can also conclude that there is no *t*-butanol bonded to the MoO_2 unit in the PEO–Mo complex.

4. Conclusions

Addition of poly(ethylene oxide) to the catalytic system $MoO_2(acac)_2$/TBHP/*t*-butanol used for epoxidation of *cis*-cyclooctene allowed an easy strategy for catalyst recycling and product recovery. Infrared studies suggest that a PEO–Mo complex is formed. This procedure does not require the synthesis of functionalized polymers nor previous activation. In spite of molybdenum losses, a global turnover number close to 650 was achieved in six runs, with the catalyst still active, results that are, at least, comparable to other heterogenized Mo catalysts. In more general terms, the present study provides another encouraging example of the potential of these polymer-mediated catalyst recycling strategies.

Acknowledgements

References

[1] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, Wiley, New York, 1992.

[2] J. Sobczak, J.J. Ziólkowski, J. Mol. Catal. 3 (1977/1978) 165.

[3] S. Ivanov, R. Boeva, S. Tanielyan, J. Catal. 56 (1979) 150.

[4] R. Boeva, S. Kotov, N.I. Jordanov, React. Kinet. Catal. Lett. 24 (1984) 239.

[5] S. Bhaduri, H. Khwaja, J. Chem. Soc., Dalton Trans. (1983) 415.

[6] T. Yokoyama, M. Nishizawa, T. Kimura, T.M. Suzuki, Bull. Chem. Soc. Jpn. 58 (1985) 3271.

[7] D.C. Sherrington, S. Simpson, J. Catal. 131 (1991) 115.

[8] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 368.

[9] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 377.

[10] J.-H. Ahn, D.C. Sherrington, Chem. Commun. (1996) 643.

[11] D.E. Bergbreiter, Catal. Today 42 (1998) 389.

[12] X. Zheng, J. Jiang, X. Liu, Z. Jin, Catal. Today 44 (1998) 175.

[13] L.H.M. da Silva, W. Loh, Chem. Commun. (1998) 787.

[14] R.G. da Rosa, L. Martinelli, L.H.M. da Silva, W. Loh, Chem. Commun. (2000) 33.

[15] R.M. Silverstein, G.C. Bassler, T.C. Morril, Spectrometric Identification of Organic Compounds, 3rd Edition, Wiley, New York, 1974.