

Polybenzimidazole-supported Molybdenum(vi) Propene Epoxidation Catalyst

Matthew M. Miller and David C. Sherrington*

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, UK G1 1XL

A polybenzimidazole-supported molybdenum(vi) complex was found to be a highly active, stable and long-lived catalyst for the high pressure epoxidation of propene using *tert*-butyl hydroperoxide (Halcon process).

Recently, heterogeneous polymer-supported metal complex oxidation catalysts have been the subject of much interest.¹ For instance, poly(benzimidazole) (PBI) has been used to support palladium catalysts for Wacker-type oxidation² and hydrogenation.³ We now report the first use of PBI to immobilise Mo^{VI} catalysts for the epoxidation of propene using *tert*-butyl hydroperoxide as the oxygen source. This process, known as the Halcon (or Arco) process, is reported to be carried out industrially using both a homogeneous Mo^{VI} catalyst⁴ and a heterogeneous titanium/silica catalyst⁵ with yields of and selectivities for propylene oxide in excess of 90% for both catalysts. To date, polymer-supported analogues of these epoxidation catalysts have used anion exchange,⁶ cation exchange^{7,8} and chelating ion exchange resins^{9–11} as supports, the majority of these being based on macroporous polystyrene resins. While high activity and good selectivity for epoxide formation have been recorded, the catalysts to date have been unstable and offer no real prospect for technological application. Highly oxidatively and thermally stable PBI can be synthesised as porous beads using a precipitation or dispersion procedure.¹²

The supported catalyst was synthesised from porous PBI beads and molybdenyl acetylacetonate using a ligand exchange procedure, as shown in Scheme 1. After exhaustive extraction with acetone to remove unbound metal species, and thorough drying *in vacuo*, the supported complex was found to have a metal loading of 1.88 mmol Mo g⁻¹ using atomic absorption analysis. FTIR analysis of the polymer catalyst indicated the presence of residual acetylacetonate (acac) ligand (e.g. 1530 cm⁻¹, C=O) and the appearance of the Mo=O stretching modes in 900–930 cm⁻¹ region,¹³ but no indication of any Mo–O–Mo bridge (ca. 725 cm⁻¹). The active centre therefore appears to be BIMO₂acac (where BIH is a benzimidazole residue), and the polymer catalyst is designated, PBI·MoO₂acac. This sample was used throughout all the catalytic epoxidations.

The catalytic epoxidation reactions were carried out in batch-type procedures using a small scale autoclave reactor, employing conditions similar to those specified in the original patent⁴ and indicated in Table 1. Initial studies were carried out using homogeneous MoO₂(acac)₂ and the heterogeneous PBI·MoO₂acac catalyst. Reactions were monitored by GLC and yields calculated as shown in Table 1.

The activity of the PBI·MoO₂acac catalyst compares extremely favourably with that of the homogeneous catalyst and, indeed, with other polymer-supported Mo catalysts for

the same reaction^{7,8} with propylene oxide in excess of 90% observed. Propylene oxide was the only oxidation product detected, agreeing with previously reported selectivities for epoxide in excess of 90% for the reaction.^{4,5,7}

To assess long-term stability for the PBI·MoO₂acac catalyst, recycling experiments were carried out with a single sample of catalyst used over a series of ten reactions, with the catalyst being removed by filtration at the end of each reaction, washed with 1,2-dichloroethane and re-used. The yields and metal leaching data obtained are listed in Table 2.

The increase in activity observed during recycling is remarkable, with the 'aged' catalyst (run 10) giving essentially quantitative conversion and selectivity in 1 h. An increase in activity has also been observed for PBI-supported Pd hydrogenation catalysts.³ The latter was loosely attributed to changes in polymer microstructure during the reaction. In the present case a more likely explanation¹⁴ is that prolonged exposure of PBI·MoO₂acac to *tert*-butyl hydroperoxide gradually maximises the proportion of 'active' Mo^{VI} sites available, and that subtle changes in the polymer support morphology (pore size, distribution *etc.*) also maximises site accessibility. In addition, the binding of the Mo catalyst centres by the

Table 1 Epoxidation of propene using homogeneous and PBI-supported heterogeneous Mo^{VI} catalysts^a

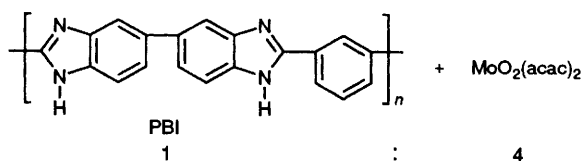
t/h	Propylene oxide yield (%) ^{b,c}	
	MoO ₂ (acac) ₂	PBI·MoO ₂ acac
1	47.6	89.4
2	77.1	90.6
3	97.7	83.4
4	100.0	92.6

^a Reaction conditions: [catalyst] mass equiv. to 0.12 mmol Mo, [TBHP] (anhydrous solution in toluene) vol. equiv. to 10 mmol, propene 10 g, 238 mmol, 1.0 ml chlorobenzene (GLC int. std), 22 ml 1,2-dichloroethane, 400 psi He at 80°C. ^b Products analysed by high-resolution capillary GLC. ^c GLC yield based on conversion of TBHP *i.e.* 10 mmol TBHP = 10 mmol propylene oxide = 100% yield.

Table 2 Recycling of PBI·MoO₂acac catalyst in the epoxidation of propene using *tert*-butyl hydroperoxide^a

Run	Propylene oxide yield (%) ^b	Mo leached ^c (%) ^d
1	59.0	2.9
2	68.4	
3	74.8	
4	74.1	
5	80.4	<0.2% (below detection limit of AAS)
6	84.6	
7	78.4	
8	89.7	
9	94.8	
10	99.8	

^a Reaction conditions: identical with those in Table 1, footnote a. Reaction time = 1 h. ^b Propylene oxide yield determined as detailed previously in Table 1, footnotes b and c. ^c Reaction solution assayed for Mo using ASS (atomic absorption spectroscopy). Detection limit 0.5 ppm. For procedure see ref. 11. ^d Expressed as a percentage of Mo originally present on resin.



Toluene, reflux 72 h
↓
PBI·MoO₂(acac)
Scheme 1

imidazole functionalities present in the PBI resin appears to be strong, accounting for the extremely low levels of metal leaching observed during recycling (below the detection limits of our analysis from run 2 onwards). This is much lower than those previously reported for analogous polystyrene chelating resin-supported catalysts for the liquid phase epoxidation of cyclohexene,¹¹ a process utilising much less severe reaction conditions.

In comparison with other reported polymer-supported Mo^{VI} epoxidation catalysts,⁶⁻¹¹ the performance of the PBI·MoO₂acac catalyst can only be described as outstanding. This, coupled with the potential for use under much more severe temperature and pressure conditions, means that the PBI·MoO₂acac catalyst offers a real prospect for technological application of a polymer-supported epoxidation catalyst.

In addition, of course, the use of PBI·MoO₂acac is not restricted to propylene epoxidation, it is an extremely active and convenient catalyst for epoxidation of other alkenes on a laboratory scale, and displays no release of heavy metal.

Financial support of this research by the SERC and BP Chemicals Ltd is acknowledged.

Received, 26th July 1993; Com. 3/04413K

References

- 1 D. C. Sherrington, *Pure Appl. Chem.*, 1988, **60**, 401.
- 2 D. C. Sherrington and H. G. Tang, *Polymer*, 1993, **34**, 282; *J. Catal.*, 1993, **142**, 540.
- 3 N. H. Li and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.*, 1985, 1100; *Makromol. Chem. Macromol. Symp.*, 1986, **1**, 191; *React. Polym.*, 1987, **6**, 311.
- 4 J. Kollar, US Pat., 3 350 422, 1967; 3 357 635, 1967; 3 507 809, 1970; 3 625 981, 1971 to Halcon International.
- 5 H. P. Wulff, Br. Pat., 1 249 079, 1971; US Pat., 3 923 843, 1975 to Shell Oil.
- 6 J. Sobezak and J.-J. Ziolkowski, *J. Mol. Catal.*, 1978, **3**, 165.
- 7 S. Ivanov, R. Boeva and S. Tanielyan, *J. Catal.*, 1979, **56**, 150.
- 8 R. Boeva, S. Kotov and N. I. Jordanov, *React. Kinet. Catal. Lett.*, 1984, **24**, 239.
- 9 S. Bhaduri and H. Khwaja, *J. Chem. Soc., Dalton Trans.*, 1983, 415.
- 10 T. Yokoyama, M. Nishizawa, T. Kimura and T. M. Suzuki, *Bull. Chem. Soc. Jpn*, 1985, **58**, 3271.
- 11 D. C. Sherrington and S. Simpson, *J. Catal.*, 1991, **131**, 115.
- 12 P. N. Chen and R. D. Tucker, US Pat., 4 628 067, 1986; T. Brock and D. C. Sherrington, *Polymer*, 1992, **33**, 1773.
- 13 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4** 867; F. W. Moore and R. E. Rice, *Inorg. Chem.*, 1968, **7**, 2510.
- 14 M. M. Miller, PhD Thesis, University of Strathclyde, 1993.