Alkene Epoxidations Catalysed by Molybdenum(VI) Supported on Imidazole-containing Polymers. Part 3. Epoxidation of Oct-1-ene and Propene

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Six polymer-supported Mo^{VI} catalysts have been prepared. Two involve supported aminomethyl-2-pyridine (AMP) ligands, and the other four various ligands based on imidazole. All catalysts are active in the epoxidation of propene using *tert*-butyl hydroperoxide in the liquid state at 80 °C and at a pressure of 400 psi (He). The catalysts with AMP ligands show a slight fall in activity on recycling, but this trend is also accompanied by significant and continuing leaching of Mo. In contrast the catalysts based on imidazole-containing polymers generally show better retention of catalyst activity, and most importantly no measurable loss of Mo after the first few cycles. The best species is based on polybenzimidazole, PBI. This shows only modest activity when used initially but when the catalyst is recycled the conversion in the reaction rises to 99.8% and the selectivity is essentially 100%. Thermogravimetric analysis also shows that this polymer-supported catalyst is stable in air to *ca.* 400 °C, and so also offers the possibility of application under even more extreme oxidative conditions than those used to date.

The transition metal-catalysed epoxidation of alkenes using alkyl hydroperoxides as the oxygen source has been extensively employed in the last two decades in both laboratory and industrial processes.[1] In the laboratory Sharpless and co-workers have made extensive studies of regio- and stereo-selective alkene expoxidations using molybdenum and vanadium-based complexes as catalysts,[2] and of enantioselective epoxidations of allylic alcohols with *tert*-butyl hydroperoxide (TBHP) activated by a titanium dialkyltartrate (Katsuki–Sharpless reagent).[3] The most important industrial application is the oxidation of propene, the Halcon or Arco process using homogeneous Mo^{VI}[4] or heterogeneous Ti–silica[5] catalysts.

Research into readily recoverable and recyclable polymer-supported heterogenised catalysts for oxidative processes has grown steadily in recent years, despite initial scepticism about the likely adequate stability of the supports under oxidative conditions.[6] Polymer-supported analogues of the aforementioned epoxidation catalysts have utilised anion,[7] cation[8,9] and chelating ion-exchange resins[10–13] as supports. The majority of these have been based upon porous polystyrene resins, and have displayed favourable activity and selectivity, but in terms of recycling, have been disappointingly unstable, often showing excessive metal leaching. We have recently reported the use of a very thermo-oxidatively stable polymer polybenzimidazole (PBI), as a support for Pd^{II} in Wacker oxidations of higher alkenes,[14] and for Mo^{VI} in TBHP epoxidations of cyclohexene (Parts I and II of this series).[15,16] Most interestingly of all however, we have also made a preliminary disclosure of the remarkable activity and stability of PBI supported Mo^{VI} in the TBHP epoxidation of propene,[17] and we now report in detail on this system, and the use of other polymer supports carrying imidazole residues as ligands.

Experimental

Materials.—Bromobenzene, chlorobenzene, 1,2-epoxyoctane, propene, propylene oxide (Aldrich Chemical), toluene (Analar) (May and Baker), 5-benzimidazole carboxylic acid and molybdenyl acetylacetonate (MoO_2acac_2) (Aldrich Chemical) were all used as supplied. Cyclohexene (Aldrich Chemical) and 1,2-dichloroethane (Fisons Laboratories) and oct-1-ene (Aldrich Chemical) were fractionally distilled prior to use.

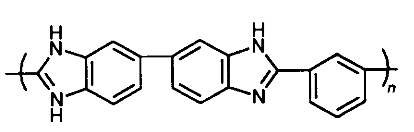
An 'anhydrous' solution of TBHP in toluene was employed throughout since this offers greater thermal and storage stability than anhydrous solutions in halogenated solvents[2,18] as used in previous work.[12,13] The solution was prepared from aqueous TBHP-70 (Aldrich Chemical) using an azeotropic distillation technique according to a literature method.[2,18] The molarity of each batch was determined using an iodometric titration procedure.

Polymer Resin Supports.—Polybenzimidazole resin (PBI) (250–500 μm diameter, microporous, toluene up-take 1.1 g g^{-1} dry resin) was obtained as a gift from the Celanese Corporation.[19] The resin was supplied wetted with water. Prior to use, it was stirred in 1 mol dm^{-3} NaOH solution for a period of 12 h, washed thoroughly with de-ionised water until the pH of the washings was neutral, washed with acetone and dried under vacuum. A polystyrene-based chelating resin functionalised with *N*-(2-hydroxypropyl)aminomethyl-2-pyridine, Ps•HPP, was obtained from the Dow Chemical Company (denoted as resin XFS 43084).[20]

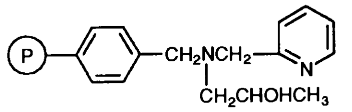
A glycidyl methacrylate-based (GMA) resin functionalised with 2-aminomethyl pyridine (PGMA•AMP) ligands was obtained from BP International.[21] Both of these resins were subjected to the following treatment prior to use: approximately 20 g of the wet resin was filtered and washed with 2 mol dm^{-3} H_2SO_4, followed by 10% NH_3 solution. The resin was then washed thoroughly with de-ionised water until pH = 7, washed with acetone and dried under vacuum at 40 °C.

Synthesis of Other Polymer Resin Supports.—Resins based upon macroporous chloromethylated polystyrene (Ps) and poly(glycidylmethacrylate) (PGMA) functionalised with 2-pyridyl-2-imidazole (PyIm) (Ps•PyIm and PGMA•PyIm, respectively) were prepared as shown in Scheme 1 from PS and PGMA, themselves synthesised in-house using a suspension polymerisation methodology.[21] The 2-pyridyl-2-imidazole ligand itself was synthesised using a previously published procedure.[13,21]

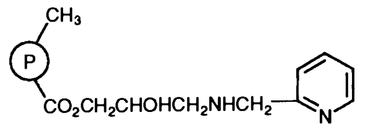
Thus Ps (5.00 g, 0.021 mol $-CH_2Cl$) or PGMA (5.00 g, 0.020 mol epoxide) was refluxed with PyIm (9.14 g, 0.063 mol) in toluene (120 cm^3) for 12 h. The resin was filtered off, washed thoroughly with acetone, extracted with acetone in a Soxhlet apparatus for 24 h and then dried under vacuum at 40 °C.



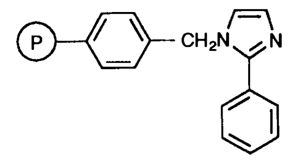
PBI



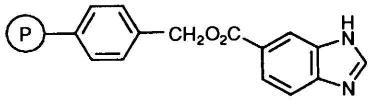
Ps.HPP



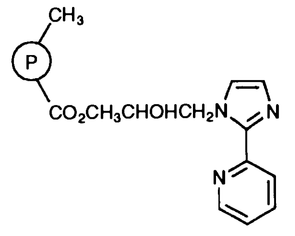
PGMA.AMP



Ps.PyIm



Ps.5BzCOO

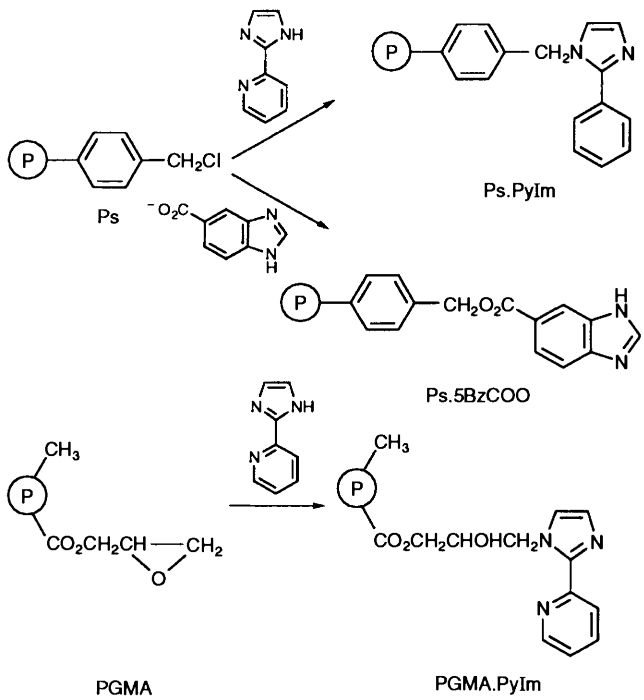


PGMA.PyIm

Polystyrene resin functionalised with a 5-benzimidazole carboxylic acid (5Bz•CO_2H) residues (Ps•5Bz•COO) was prepared from the sodium salt of the acid as follows (Scheme 1): $5BzCO_2H$ (6.80 g, 0.042 mol) and NaOH (1.68 g, 0.042 mol) were stirred in ethanol (150 cm^3) for 4 h. Ps resin (5.00 g, 0.021 mol $-CH_2Cl$) was added and the mixture refluxed for 24 h. The resin was filtered off, extracted with acetone in a Soxhlet apparatus for 48 h and then dried under vacuum at 40 °C.

Preparation of Polymer-supported Mo *Complexes*.—All supported Mo complexes were prepared using a ligand exchange procedure, in which polymer ligands were reacted with $MoO_2(acac)_2$ in the stoichiometric ratio 2:1 $MoO_2(acac)_2$: functional ligand (Scheme 2). Typically PBI resin (5 g, 0.027 mol imidazole group) was refluxed with $MoO_2(acac)_2$ (17.68 g, 0.054 mol Mo) in toluene for a period of 72 h. The resin (PBI•Mo) was filtered off and extracted exhaustively with acetone in a Soxhlet apparatus for 48 h. During extraction a dark-blue colour was evident in the extracting solution. This disappeared eventually upon repeated introduction of fresh solvent. The supported complex was then dried thoroughly under vacuum.

Mo *Loading Analysis of Supported Metal Complexes*.—The metal loading of the supported complexes was determined as follows: supported Mo complex (0.1 g, accurately weighed) was ground finely, and treated with aqua regia (15 cm^3) for a period of approximately 48 h. The solution was made up to 100 cm^3 with de-ionised water and analysed for Mo using atomic absorption spectrophotometry.

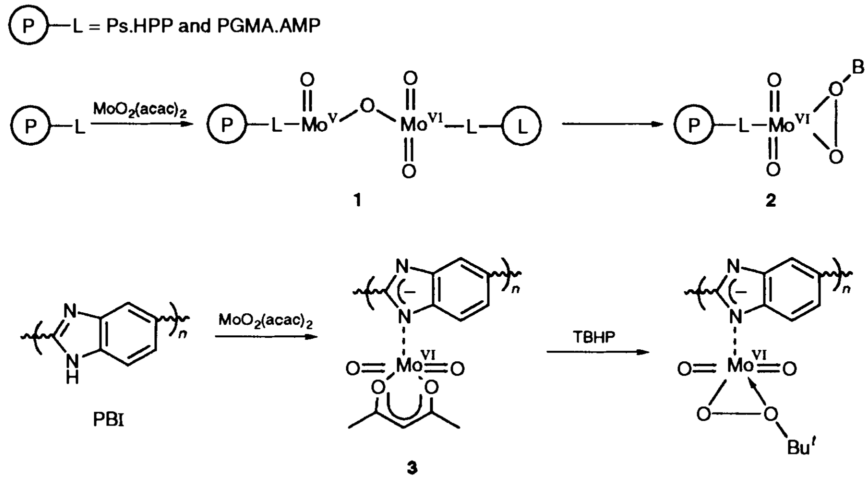


Scheme 1 Synthesis of resins containing imidazole residues

Elemental microanalytical data, functional group loading and relevant IR spectral data for polymer resin supports are shown in Table 1. Mo loading data, ligand:metal ratios and relevant IR spectral data for polymer-supported Mo complexes are shown in Table 2.

Catalyst Activation.—A catalyst activation procedure, in which a sample of the supported Mo complex is pre-treated with TBHP prior to use in an epoxidation, has previously been found to have a pronounced effect upon catalytic activity for supported complexes utilising chelating resins as supports.[12,13] Therefore, certain supported catalysts in this study were subjected to this procedure prior to use. A typical activation procedure was as follows: supported Mo complex (0.02 g, 0.06 mmol Mo) was refluxed with anhydrous TBHP solution (1.3–1.4 cm^3, 5 mmol) in 1,2-dichloroethane for a period of 4 h. During this procedure the colour of the supported complex changed to yellow. The beads were filtered off, washed with 1,2-dichloroethane and used immediately in a reaction.

Catalytic Epoxidation of Oct-1-*ene*.—A typical procedure for the epoxidation of oct-1-ene was as follows: a sample of PBI•Mo catalyst (weight equivalent to 0.06 mmol Mo), oct-1-ene (8.3 cm^3, 0.053 mol), bromobenzene (0.5 cm^3) and 1,2-dichloroethane (0.2 cm^3) were placed in a twin-necked thermostatted reaction vessel equipped with condenser and septum cap, and left to thermally equilibrate at 80 °C for a period of 20 min. 'Anhydrous' TBHP solution (1.4 cm^3, 5 mmol) was added, this point being taken as the commencement of the reaction. Samples were withdrawn by syringe periodically (typically every 20 min) during the 4 h reaction period, and monitored for their 1,2-epoxyoctane concentration by high-resolution capillary GLC. The epoxide concentration was determined from the mean of three injections. The epoxidations were carried out over a range of temperatures, and with differing



Scheme 2 Loading of Mo onto polymeric ligands

Table 1 Elemental microanalytical data, functional group loading and salient IR spectral data for resin supports

Resin	Found (%) C	H	N	Ligand loading mmol g^{-1}	IR spectral data/cm^{-1}
PBI	65.2	4.4	15.2	2.7	1300, 1450, 1610 (C=N, C=C)
Ps•HPP	75.9	6.8	7.1	2.5	810 (arom. ring); 1450 (C=N)
PGMA•AMP	55.4	6.4	4.5	2.5	1450 (C=N); 3400 (O–H)
Ps•PyIm	71.2	5.9	9.2	2.2	810 (arom. ring); 1450 (C=N) (loss 1260 CH_2Cl)
Ps•5BzCO$_2$	74.8	6.3	1.8	0.4	810 (arom. ring); 1590 (C=O); 3400 (N–H) (loss 1260 CH_2Cl)
PGMA•PyIm	56.0	6.3	4.5	1.1	1450 (C=N); 3400 (O–H)

Table 2 Mo loading data, ligand : metal ratios and IR spectral data for polymer-supported complexes

Polymer catalyst	Loading/mmol g^{-1} Ligand[a]	Mo	Ligand : metal ratio	IR Bands/cm^{-1} M=O str.	Mo–O–Mo str.	Appearance[b]
PBI•Mo	2.2	1.8	1.2:1	950, 979	—	Dark blue
Ps•HPP•Mo	2.2	1.3	1.7:1	916, 933	726	Brown
PGMA•AMP•Mo	1.4	1.1	1.3:1	906, 940	720	Dark blue
Ps•PyIm•Mo	2.1	0.5	4.5:1	960, 915	—	Brown
Ps•5BzCO$_2$•Mo	0.41	0.19	2.2:1	960, 904	—	Green
PGMA•PyIm•Mo	0.99	0.66	1.5:1	946, 910	—	Green

[a] (1 − weight Mo g^{-1} supported complex) × (original ligand loading). [b] Some variation in colour seen from bead to bead.

Table 3 Catalytic epoxidation of oct-1-ene with TBHP using homogeneous and PBI-supported[a] Mo catalysts[b]

Catalyst	T/°C	1,2-Epoxyoctane yield (%)[c] 20 min	60 min	240 min
$MoO_2(acac)_2$	80	88.0	94.0	~ 100.0
PBI•Mo	60	22.0	39.6	67.6
PBI•Mo	70	11.8	41.8	78.4
PBI•Mo	80	65.0	81.2	99.6
PBI•Mo[d]	80	30.6	50.0	~ 100.0
PBI•Mo	90	67.8	84.0	~ 100.0
PBI•Mo[d]	90	61.0	79.0	~ 100.0

[a] All PBI•Mo samples were activated for 4 h unless stated. [b] Reaction conditions: [TBHP] = 5 mmol; [Mo] = 0.06 mmol; [oct-1-ene] = 53.5 mmol; $ClCH_2CH_2Cl$ = 0.2 cm^3. [c] Yield based on conversion of TBHP *i.e.* 5 mmol TBHP = 5 mmol 1,2-epoxyoctane ≡ 100% yield. [d] Activated for 24 h.

catalyst activation conditions, as well as with a sample of homogeneous $MoO_2(acac)_2$ catalyst for the purposes of comparison. The results obtained are summarised in Table 3.

Catalytic Epoxidation of Propene.—These epoxidations were carried out using a small-scale batch procedure in a Parr 4560 series 50 cm^3 stainless steel autoclave reactor fitted with a 4841 analogue temperature controller and overhead magnetically coupled stirrer. **CAUTION:** Reactions with propene and powerful oxidants are potentially hazardous and the following procedure was designed with this in mind. The conditions shown were similar to those specified in the original patent describing the industrial process,[4] and our laboratory set-up is shown schematically in Fig. 1. Liquid substrates consisting of 1,2-dichloroethane (17.2 cm^3), anhydrous TBHP solution in toluene (2.8 cm^3, 10 mmol) and chlorobenzene (1.0 cm^3, GLC internal standard) were charged into the reactor along with a sample of catalyst (wt. equiv. to 0.12 mmol Mo). The reactor was sealed and cooled with CO_2–acetone bath. Propene (10 g, 0.238 mol) was distilled into the calibrated Fischer–Porter tube by cooling the latter with a CO_2–acetone bath and opening valve V1, all other valves being closed. Valve V1 was then closed and V3 and V6 opened. The Fischer–Porter tube was then heated with a hot water bath to distill the propene into the pre-cooled reactor. Upon complete transfer of the propene, valves

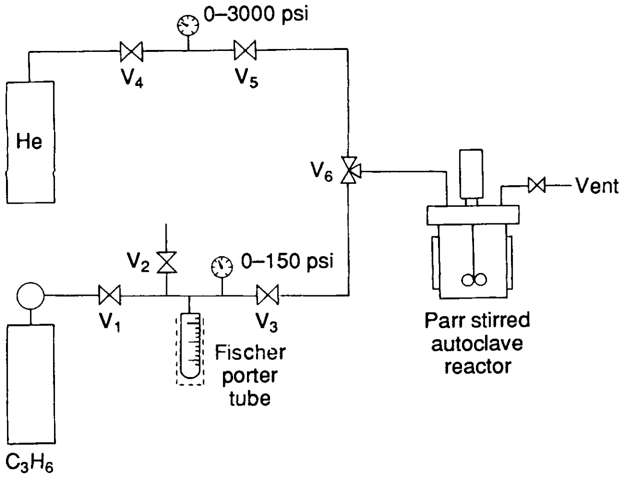


Fig. 1 Schematic representation of apparatus used for propene epoxidations

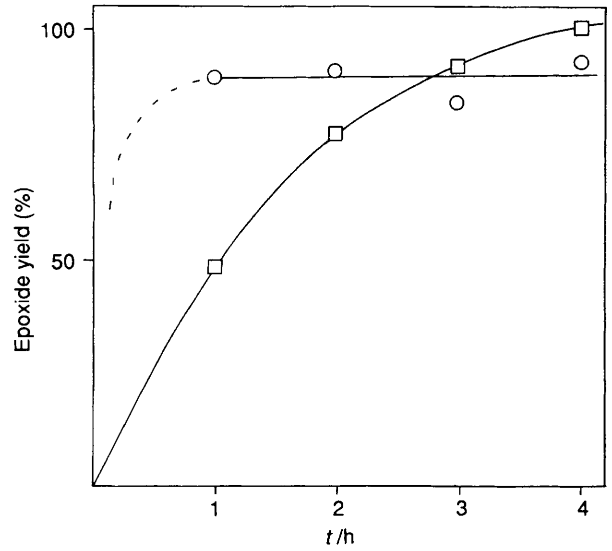


Fig. 2 Conversion–time curves for epoxidation of propene by TBHP catalysed by $MoO_2(acac)_2$ and PBI•Mo (non-activated) (for conditions see Experimental section)

V3 and V6 and the reactor's own inlet valve were closed. The reactor was then heated to room temp. and pressurised to 300 psi with He by opening valves V4, V5 and V6. On heating to the reaction temperature (typically 80 °C) the reactor pressure was adjusted to 400 psi. Raising the temperature was taken as the start of the reaction. After the desired reaction period had expired (usually 1 h), the reactor was cooled to 0 °C with an ice bath and the gases carefully vented off, in order to prevent loss of the relatively voltatile propylene oxide product. The liquid contents of the reactor were then analysed for propylene oxide using high resolution capillary GLC. The concentration was calculated from the average of three sample injections. After the sample of catalyst was filtered off the liquid contents of the reactor were assayed for Mo using standard atomic absorption spectrophotometric techniques to determine the amount of metal leached during use. When not in use the catalyst was stored in a solution of TBHP (1.4 cm^3, 5 mmol) in 1,2-dichloroethane (10 cm^3).

Conversion curves were rather tedious to generate (Fig. 2) because each data point required a separate experiment. The eight experiments shown in Fig. 2 also therefore represent a good estimate of the reproducibility of reactions.

In general polymer catalyst samples were retained and recycled ten times, with reaction supernatants being monitored for the Mo content. The results are shown in Tables 4 and 5.

Thermo-oxidative Stability.—The thermo-oxidative stability of catalysts PBI•Mo, Ps•HPP•Mo and PGMA•AM•P•Mo and their precursor polymer ligands was assessed by thermal gravimetric analysis (TGA) using a Stanton Redcroft TG750/770. A heating rate of 10 °C min^{-1} over the temperature range 0–800 °C in air was employed. Data expressed as % weight remaining as a function of temperature are plotted in Figs. 3–5.

Instrumentation.—Elemental microanalyses were prepared on a Carlo Erba Analyser 1106. FTIR spectra of the polymer samples were run as KBr discs on Nicolet 20SXB and Unicam-Mattson 1000 spectrometers. Atomic absorption spectroscopy was carried out on a Philips PU 1800X instrument. The GLC used was a Carlo-Erba Mega series 5380 high-resolution capillary gas chromatography with a cold on-column injection facility. The column was from J and W Scientific (DB-5, length 30 m; i.d. 0.32 mm; film thickness, 1.0 μm), hydrogen gas carrier 38 cm^3 min^{-1} (40 kPa); oven, 100 °C (1 min) to 120 °C (40 °C min^{-1}); sample, 1 mm^3; FID (200 °C).

Results and Discussion

Synthesis and Structure of Polymer-supported Catalysts.—The successful synthesis of the six polymer catalysts is confirmed by the analytical data in Tables 1 and 2. In particular good loadings of Mo (more than adequate for catalytic applications) were achieved. Generally ligand : metal ratios were in the range *ca*. 1–2, although the low metal content of Ps•PyIm•Mo resulted in a much higher ligand : metal ratio. In all cases the IR spectra contained bands assigned to Mo=O stretching modes[22] in the region 900–950 cm^{-1}, indicating the presence of oxo-molybdenum centres. In addition Ps•HPP•Mo and PGMA•AMP•Mo exhibited IR bands in the region 720–730 cm^{-1} normally associated with the bridged Mo–O–Mo species. The polymers carrying an imidazole residue *e.g.* PBI•Mo also showed evidence in the IR spectrum (Fig. 6) for the retention of an acac ligand. Overall therefore it is believed that the Mo complex formed on Ps•HPP and PGMA•AMP has a bridged bimetallic form **1** which is cleaved on activation with TBHP to form the active catalytic centre **2**, Scheme 2. On the other hand the polymers bearing an imidazole ligand, notably PBI, form a monometallic complex **3** which requires no activation, TBHP simply replacing the acac ligand rather readily. Further details have already been presented in the literature.[15]

*Epoxidation of Oct-*1*-ene*.—We have already reported on the activity of these catalysts in cyclohexene epoxidations including a more detailed analysis of the kinetics and solvent effects.[16] It is also now clear (Table 3) that the PBI•Mo species is of comparable activity to $MoO_2(acac)_2$ in oct-1-ene epoxidation as well. PBI•Mo activated for 4 h is as active as a sample subjected to more severe activation (24 h), indeed as in the case of cyclohexene[15] and propene[17] we believe that activation of this catalyst is unnecessary. An Arrhenius-type temperature dependence has been reported previously for the activity of homogeneous catalysts in these epoxidations.[23] However, although there are changes observed with temperature here, the dependence is not a simple Arrhenius one. The reason for this is probably due to other kinetic factors arising when the polymer-supported catalyst is used. These are usually mass transfer related and arise more specifically from porosity and accessibility limitations, as well as local polarity and substrate–product distribution effects, all of which are absent with homogeneous catalysts.

Table 4 Epoxidation of propene using TBHP.[a] Recycling experiments with catalysts PBI•Mo, Ps•HPP•Mo and PGMA•AMP•Mo

	PBI•Mo[b]		Ps•HPP•Mo[c]		PGMA•AMP•Mo[c]	
Run	Yield propylene[d] oxide (%)	Mo leached[e] (%)	Yield propylene oxide (%)	Mo leached (%)	Yield propylene oxide (%)	Mo leached (%)
1	59.0	2.9	98.7	2.9	84.5	0.7
2	68.4	0[f]	85.8	2.2	82.8	0.7
3	74.8	0	90.1	2.2	94.8	0.7
4	74.1	0	79.9	3.6	88.6	0.7
5	80.4	0	91.3	4.4	96.6	0.7
6	84.6	0	99.0	2.2	93.6	0.7
7	87.4	0	65.2	2.9	99.0	2.1
8	89.7	0	85.9	0.7	83.9	0.7
9	94.8	0	87.0	0.7	82.0	0
10	99.8	0	—	—	81.7	0

[a] Reaction conditions as in Experimental section. [b] Non-activated catalyst. [c] Catalyst activated for 4 h. [d] Yield after 1 h based on conversion of TBHP; *i.e.* 10 mmol TBHP = 10 mmol propylene oxide ≡ 100% yield. [e] Expressed as a % of metal originally loaded on polymer sample. [f] Detection limit indicates < 0.2%.

Table 5 Epoxidation of propene using TBHP.[a] Recycling experiments with catalysts PGMA•PyIm•Mo, Ps•PyIm•Mo and Ps•5BzCO$_2$•Mo

	PGMA•PyIm•Mo[b]		Ps•PyIm•Mo[c]		Ps•5BzCO$_2$•Mo[b]	
Run	Yield propylene[d] oxide (%)	Mo leached[e] (%)	Yield propylene oxide (%)	Mo leached (%)	Yield propylene oxide (%)	Mo leached (%)
1	90.1	1.1	98.9	0[f]	~100	1.1
2	89.3	1.1	53.3	0	88.0	1.1
3	74.1	0	97.7	0	87.4	1.1
4	—[g]	0	—[g]	0	—[g]	0
5	43.4	0	95.0	0	86.5	0
6	53.6	0	—[g]	0	84.9	0
7	—[g]	0	93.4	0	85.5	0
8	55.4	0	92.8	0	86.5	0
9	53.8	0	92.8	0	86.2	0
10	53.9	0	—[g]	0	88.2	0

[a] Reaction conditions as in Experimental section. [b] Non-activated catalyst. [c] Catalyst activated for 4 h. [d] Yield defined in Table 4. [e] Expressed as a % of metal originally loaded on polymer sample. [f] Detection limit indicates < 0.2%. [g] Not recorded.

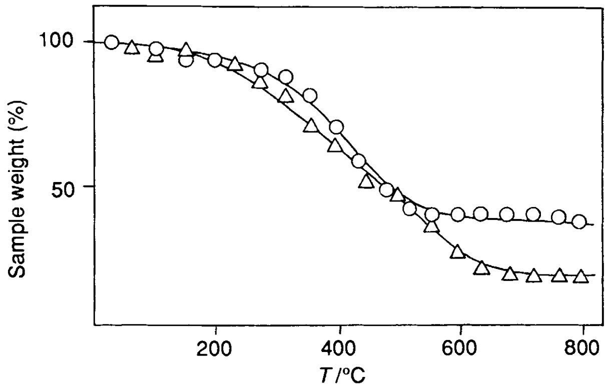


Fig. 3 Thermogravimetric analysis trace for Ps•HPP (△) and Ps•HP•Mo (○)

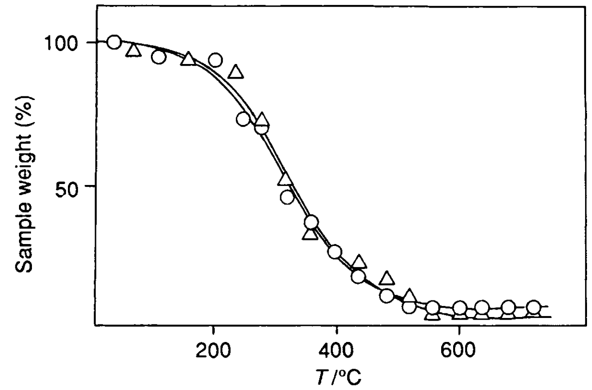


Fig. 4 Thermogravimetric analysis trace for PGMA•AMP (△) and PGMA•AMP•Mo (○)

Epoxidation of Propene.—The conversion curves for propene epoxidation catalysed by MoO$_2$(acac)$_2$ and non-activated PBI•Mo are shown in Fig. 2. Under the conditions used PBI•Mo is the more active but the yield levels at *ca.* 90%. Why this is so is not clear but the favourable activity of PBI•Mo is of potential technical importance. The results of the recycling experiments serve only to reinforce this. All the polymer-supported species retain activity over ten consecutive runs (Tables 4 and 5), although PGMA•PyIm•Mo shows *ca.* 50% loss of activity. Apart from this resin, the catalysts fall into two groups. The first includes Ps•HPP•Mo and PGMA•AMP•Mo. These show a variation in activity with possibly an overall downward trend. Perhaps more importantly, however, they show a sustained leakage of Mo, which over a prolonged period of use would cause loss of activity. This result agrees with previous observations when these catalysts were used in cyclohexene epoxidation at atmospheric pressure.[13] The second group include PBI•Mo, Ps•PyIm•Mo and Ps•5BzCOO. These show good retention of activity over ten runs, and apart from leaching of Mo in runs 1–3, loss of Mo is below the detection limit of our experimental technique. The difference in stability of the two groups of supported complex seems to be related to the presence of the imidazole ligand. The binding of the Mo centre to this seems to be very strong. A lack of leaching on re-

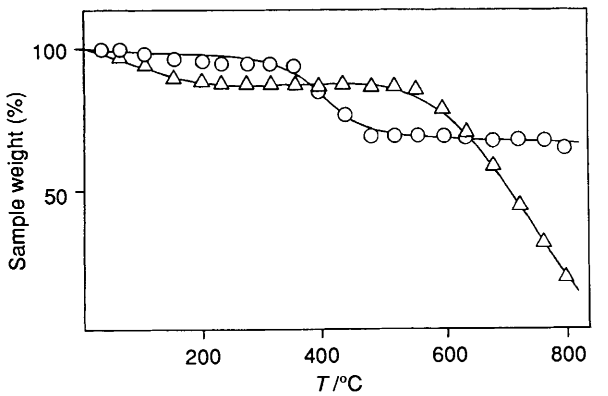


Fig. 5 Thermogravimetric analysis trace for PBI (△) and PBI·Mo (○)

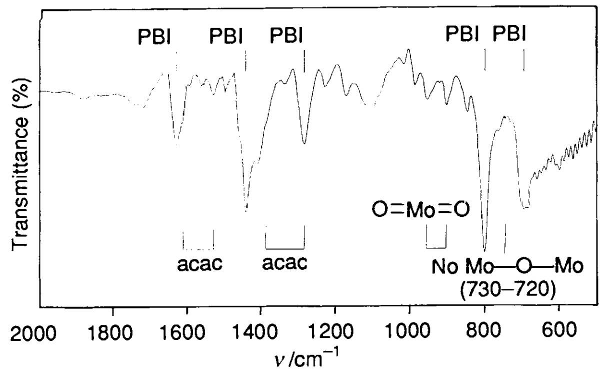


Fig. 6 FTIR spectrum of PBI·Mo

use of PBI·Mo has been observed before in the epoxidation of cyclohexene.[15] However, in the latter case, despite retention of the metal complex, recycling was accompanied by a progressive fall in catalytic activity, and this was tentatively ascribed to accumulation of oligomeric side-product in the heterogeneous support.

The most exciting result here is undoubtedly with the PBI·Mo catalyst. As this ages its initially moderate activity becomes outstanding, with essentially quantitative conversion of propene to propylene oxide with effectively 100% selectivity. Mo is leached only in run one, and thereafter leakage is below the detection limit (< 0.2% Mo). There are a number of possible explanations for the progressive increase in activity of the PBI·Mo catalyst. On balance at the moment we favour the view that progressive morphological and accessibility changes in the support gradually maximise the number of catalytic sites available. Evidence from reactions with other alkenes suggests an opposing process (in addition to Mo loss from some supports) involving build-up of oligomeric side-products which blocks access to catalytic sites. Rapid loss of propylene oxide from PBI·Mo appears to avoid this in the case of propylene.

For applications involving temperatures below *ca.* 200 °C Ps·PyIm·Mo is also a very respectable catalyst. However, the thermo-oxidative stability of Ps and PGMA-based resins is limited as revealed by TGA measurements on Ps·HPP·Mo and PGMA·AMP·Mo (Figs. 3 and 4). Relatively rapid decomposition onsets at *ca.* 200 °C both with metal-free and metal-loaded supports. PBI·Mo however, as anticipated, shows excellent stability (Fig. 5). Significant decomposition is not initiated until *ca.* 400 °C, and again the behaviour of the metal-free and metal-loaded resins is very similar. It should be emphasised, however, that PBI·Mo is also a most suitable catalyst for use in the laboratory under more routine conditions of temperature and pressure.

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