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## **Greener and sustainable method for alkene epoxidations by polymer-supported Mo(VI) catalysts**

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## GREENER AND SUSTAINABLE METHOD FOR ALKENE EPOXIDATIONS BY POLYMER-SUPPORTED Mo(VI) CATALYSTS

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**Abstract.** A polybenzimidazole supported Mo(VI) (PBI.Mo) catalyst has been prepared and characterised. The catalytic activities of the PBI.Mo catalyst in epoxidation of alkenes with *tert*-butyl hydroperoxide (TBHP) as oxidant have been studied under different reaction conditions in a batch reactor. As alkene representatives we have chosen cyclohexene, limonene,  $\alpha$ -pinene and 1-octene as less reactive terminal alkenes.

The stability of each polymer catalyst was assessed by recycling a sample in batch reaction using conditions that will form the basis of the continuous process. The loss of Mo from each support has been investigated by isolating any residue from the reaction supernatant solutions, following removal of the heterogeneous polymer catalyst, and then using the residues as potential catalysts in epoxidation reactions.

**Key-words.** Polymer supported molybdenum catalyst, alkene epoxidation, reactive distillation.

### 1. INTRODUCTION

The growing concern for the environment, increasingly stringent standards for the release of chemicals into the environment and economic competitiveness has prompted extensive efforts to improve chemical synthesis and manufacturing methods, as well as development of new synthetic methodologies that minimise or completely eliminate pollutants. As a consequence, more and more attention has been focused on the use of safer chemicals, through the proper design of clean processes and products.

Reactive distillation (RD) is one of the emerging technologies that has an extremely attractive potential as a process alternative for carrying out equilibrium limited liquid phase chemical reactions (Saha and Sharma, 1996; Saha *et al.* 2005). It is a unit operation which combines simultaneous chemical reaction and multi-component distillation in the same vessel in a single step. RD technology has particular benefit for equilibrium limited reactions. By performing reaction and separation simultaneously, equilibrium can be shifted and in some applications almost complete conversion of the feedstock is economically achieved. RD can also offer heat integration benefits. In the case of exothermic reactions, the heat of reaction replaces some of the energy required for performing the distillation (Sundmacher and Kienle, 2003).

Epoxides are versatile and useful intermediates in organic synthesis and as a consequence the epoxidation of alkenes is a field of both academic and industrial importance (Jørgensen, 1989). Mo(VI) complexes are well known to be potent catalysts for the epoxidation of alkenes by hydroperoxides such as *tert*-butylhydroperoxide, and indeed an industrial example is the Halcon Process that describes the use of a soluble Mo complex to catalyse the formation of propylene oxide from propylene highly selectively in the liquid phase at 373 K (Kollar, 1967).

There has been a considerable amount of academic work published on polymer-supported metal complex alkene epoxidation catalysts with a number of Mo(VI) based systems looking particularly attractive for scale-up and commercial exploitation (Sherrington, 2000). Despite this there appears to have been no

significant attempt to move the chemistry on from being a useful small-scale laboratory procedure to being a viable medium to large-scale production technology. Indeed this is the situation with essentially all the attractive polymer-supported catalysts that have been developed in the last decade or so. One of the reasons for this is the concern that in continuous processes apparently long-lived heterogeneous catalysts may prove to be unstable with even low levels of metal leaching causing more problems than are solved. The other nervousness is associated with the simple lack of engineering experience with polymer-supported species. We are now involved in a chemistry/chemical engineering collaboration aimed at addressing both of these shortcomings and have selected a highly active and selective polymer-supported Mo(VI) alkene epoxidation catalyst (PBI.Mo) employing *t*-butyl hydroperoxide as the oxidant which one of us developed for use in small batch reactions some time ago. The most attractive support is a highly thermo-oxidatively stable polybenzimidazole (PBI) available in a bead form from Hoechst-Celanese which has been loaded with Mo(VI) simply by treatment with excess MoO<sub>2</sub>acac<sub>2</sub> followed by exhaustive washing to yield the PBI.Mo catalyst (Leinonen, *et al.*, 1999).

We are currently re-visiting the use of this catalyst in small batch epoxidations of alkene. We are also developing a detailed knowledge of the repeated use of this catalyst to provide experimental parameters to aid in the design of a reactive-distillation column upon which we are already embarked. The design is based upon a previous successful reactive-distillation column (RDC) rig used for esterifications (Saha and Sharma, 1996; Saha *et al.*, 2000; Saha *et al.* 2005) but will require significant modification to be compatible with the quite different physico-chemical demands of alkene epoxidations.

In this paper we will highlight some batch experimental studies for epoxidation of alkene catalyzed by polymer supported Mo(VI) complex. This information will be useful for performing continuous experiments in our laboratory.

## 2. EXPERIMENTAL

### 2.1 Preparation of Mo(VI) polymer supported catalyst (PBI.Mo)

Polybenzimidazole supported Mo(VI) (PBI.Mo) catalyst was prepared according to the procedure described by (Miller and Sherrington 1995). The method for determining the Mo content of supported catalyst was also as described in the above reference. The results obtained are summarised in Table 1

Table 1. Mo loading and Mo/ligand ratio of PBI.Mo catalyst.

Supported complex	Mo loading <sup>a</sup>		Ligand loading <sup>b</sup>	Ligand/Mo ratio
	mmol Mo/g resin	g Mo/g resin	mmol amine/g resin	
PBI.Mo	0.95	0.091	2.3 (2.0) <sup>b</sup>	2.4 : 1

<sup>a</sup>: From AAS analysis of digested resins.

<sup>b</sup>: From N% elemental analysis of Mo loaded resins assuming ligand = imidazole or aminomethyl pyridine as appropriate.

### 2.2 Preparation of tert-butyl hydroperoxide

*t*-Butyl hydroperoxide (70%) from the Aldrich Chemical Co. was rendered anhydrous by Dean-Stark distillation from a toluene solution following the modified method that was previously reported by Sharpless and Verhoeven (Sharpless and Verhoeven, 1979). The molarity of TBHP was determined by iodimetry. The concentration of the TBHP in toluene was found to be 3.65 mol/dm<sup>3</sup>.

### 2.3 Batch epoxidation studies.

The experiments were conducted in a 250 ml jacketed batch reactor at temperatures from 333 to 353 K and at molar ratios of alkene to *tert*-butyl hydroperoxide from 2.5:1 to 10:1. Catalyst loading varied from 0.25 to 1% (w/w) and the stirrer speed was set at 400 rpm. The effect of temperature, catalyst loading, feed mole ratio and catalyst reusability on the conversion of TBHP and reaction rate was studied.

### 2.4 Analysis

All the reactant and product compositions were analysed by gas chromatography. HP 5080 II Gas Chromatograph (GC) was used to analyse the composition of samples from the liquid phase of the reactive mixture. The GC was fitted with 30 m long J&W DB-5 MS, 0.32 mm diameter and 0.25 μm film capillary column and FID detector. Column temperature was programmed between 313 and 473 K (313 K for 4.5 min, then ramp 25 K/min until 473 K), both injector and detector temperatures were set at 473 K and helium carrier gas flow maintained at 1 ml/min. The sample size for GC was 0.4 μL and a complete GC run took about 15 min.

### 3. RESULTS AND DISCUSSION

The batch experimental results are presented in this section and the RDC results will be presented at the conference. We studied alkenes epoxidation systems under different reaction conditions, however in this paper we only show effect of alkene/TBHP ratio and catalyst reusability as these information would be very useful when performing RDC experiments.

It is to be noted that aerobic oxidation of alkenes involving PBI-supported metal complexes tends to yield allylic oxidation products via a free radical mechanism and that a mono-oxygen source such as TBHP is required to achieve alkene epoxidation via non-free radical selective mechanisms (Olason *et al.*, 1999). There is no significant allylic oxidation detected in the present work and so any participation by molecular oxygen as an oxidant seems minimal. The PBI support itself has been shown to be very oxidatively stable in many earlier publications and indeed for this reason the material is used as an aero-space polymer (Leinonen *et al.*, 1999). It is also a highly thermally stable and displays good resistance to Mo leaching. Simple thermal decomposition of TBHP under the conditions of the epoxidations carried out is negligible. For all alkenes except limonene the selectivity towards alkene epoxides was found to be close to 100%.

#### 3.1. Effect of the alkene/TBHP feed mole ratio on epoxidation of alkenes catalysed by PBI.Mo

Typically in medium to large scale alkene epoxidation processes the reactions are run with a substantial excess of alkene in order to achieve high consumption of the oxidant, to avoid over oxidation and hence to deliver high selectivity towards the epoxide. In addition this ensures that no explosion limit is reached.

When the cyclohexene/TBHP mole ratio is increased to 10/1, more than 99% conversion of TBHP is achieved after 20 minutes of reaction, whilst for a 5/1 and 2.5/1 mole ratio it took about 50 and 120 minutes, respectively (Figure 1a). As already mentioned, excess of alkene can improve the selectivity of the reaction, however for limonene epoxidation, regardless of feed mole ratio, the selectivity towards 1,2-limonene oxide did not change in all three experiments and remained at the same value of 94%. It can be seen from Figure 1b that variation of the limonene/TBHP mole ratio does not affect the TBHP conversion to 1,2-limonene oxide significantly. Unexpectedly, the slightly higher reaction rate obtained using a mole ratio of limonene/TBHP of 2.5/1 might be explained by a temperature increase (exothermic effect) that was observed when fresh catalyst was used. Similar studies in the epoxidation of  $\alpha$ -pinene show that a mole ratio of  $\alpha$ -pinene/TBHP of 5/1 can be considered as an optimal one. The TBHP conversion as well as the reaction rate obtained when 5/1 and 10/1 ratios are used are very similar. However, the initial reaction rate when using a 5/1 ratio is slightly higher (Figure 1c). The feed mole ratio of 2.5/1 (TBHP:  $\alpha$ -pinene) gives a distinctly lower conversion and reaction rate compared to those obtained using higher ratios.

In the case of 1-octene epoxidation under different 1-octene/TBHP molar ratio, we have obtained unexpected results. After using 2.5/1 and 5/1 alkene/TBHP mole ratios we observed that the TBHP conversion and the reaction rate were very similar for both cases (Figure 1d). These results were not entirely surprising since we had already noticed similar behaviour in the limonene epoxidations. However, when a 1-octene/TBHP mole ratio of 10/1 is employed surprisingly the TBHP conversion and reaction rate both decreased markedly. This experiment was repeated several times, but similar results were obtained for all cases. Furthermore using a 1-octene/TBHP mole ratio of 15/1 the final conversion of TBHP drops to only 21% (Figure 1d).

In explaining why an increase in the 1-octene/TBHP mole ratio leads to a decrease in the TBHP conversion and reaction rate, it was interesting to find out what happened when a ratio *below* that of the normal range was employed. In fact the results obtained for a reaction using a 1.25/1 mole ratio are very similar to those obtained using mole ratios of 5/1 and 2.5/1. Clearly the effect of the alkene/TBHP feed ratio is alkene dependent and in the case of a rather unreactive alkene, such as 1-octene, it seems that increasing this ratio beyond 5/1 decreases the TBHP *concentration* to such an extent as to cause a reduction in the rate of conversion of TBHP to epoxide. Similar unpublished results showing a decrease of TBHP conversion with an increase in alkene/TBHP feed mole ratio have recently been obtained in our laboratory for **PBI.Mo** catalysed epoxidation of 1-dodecene, another rather unreactive alkene. It seems therefore that this effect is characteristic of such alkenes.

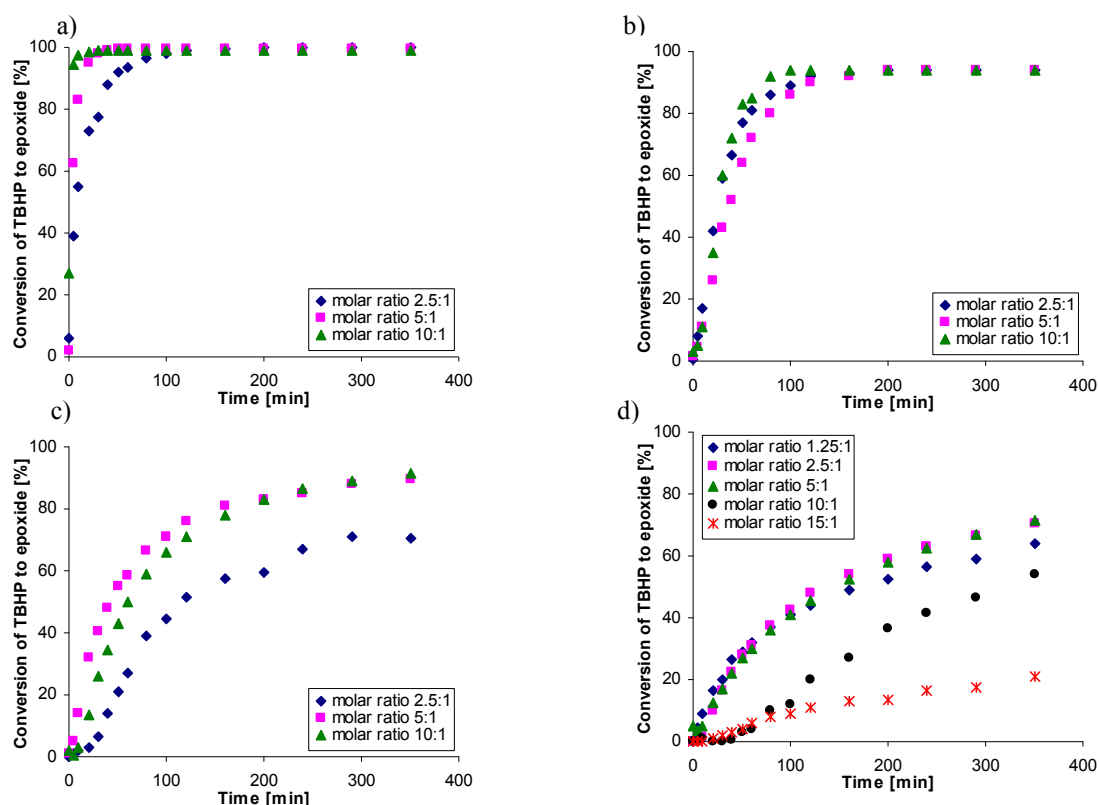


Figure 1. Effect of feed mole ratio (alkene/TBHP) on TBHP conversion and reaction rate of **PBLMo** catalysed epoxidation of alkenes: a) cyclohexene, b) limonene (conversion of TBHP is related to 1,2-limonene epoxide), c)  $\alpha$ -pinene, d) 1-octene (at 343 K, catalyst content 0.3 mol% Mo, 400 rpm agitation speed)

### 3.2. Catalyst reusability studies of **PBLMo** in epoxidation of alkenes

In order to check the suitability of the catalyst for continuous use in the RD studies, it is essential to study the catalyst reusability in batch reactions using conditions likely to be used in the RD rig. In the batch epoxidations of all the alkenes reported so far some attrition of catalyst particles was noticed when they had been reused more than three times under the stirring conditions used in the batch reactor. However it is anticipated that this problem will be absent with the catalyst in a fixed bed in the RDC rig.

The data for cyclohexene epoxidation shown in Figure 2a indicate that the **PBLMo** catalyst remains active over many cycles. The high reaction rate in run 1 might be explained by the significant exothermic effect which is observed when fresh catalyst is used. Although the rate of reaction is slower when the catalyst is reused more than two times, nearly quantitative conversion of TBHP was obtained at the end of the experiment for all the runs.

In the case of limonene epoxidation more than 90% yield of 1,2-limonene oxide is achieved at the end of experiments for all runs (Figure 2b). The rate of epoxide formation seems to decrease for the first three runs, however it becomes stabilised after run 3 with the yield and reaction rate for run 3 and run 4 being nearly identical. For all the runs the selectivity towards 1,2-limonene oxide remains constant during the course of reaction and is found to be 94% at the end of each experiment. The results from similar studies of  $\alpha$ -pinene epoxidations are different from that obtained for cyclohexene and limonene. As is shown in Figure 2c the TBHP conversion and reaction rate decrease gradually but the difference between consecutive runs, especially after run 3, is more significant than was recorded for cyclohexene and limonene. The conversion curves for runs 4 and 5 look very similar and the final conversion for both experiments is low (~30%). Therefore, it can be concluded that the activity of the **PBLMo** catalyst in the epoxidation of  $\alpha$ -pinene remains stable after run 4 but this activity is decreased significantly compared to that in the first three runs.

In the case of 1-octene (Figure 2d) analogous experiments show a significant decrease in the reaction rate and final TBHP conversion after run 1. The final TBHP conversion in run 2 drops by ~40% compared to run 1 but in subsequent reactions the activity decreases very slowly and finally shows stable behaviour for run 4-6.

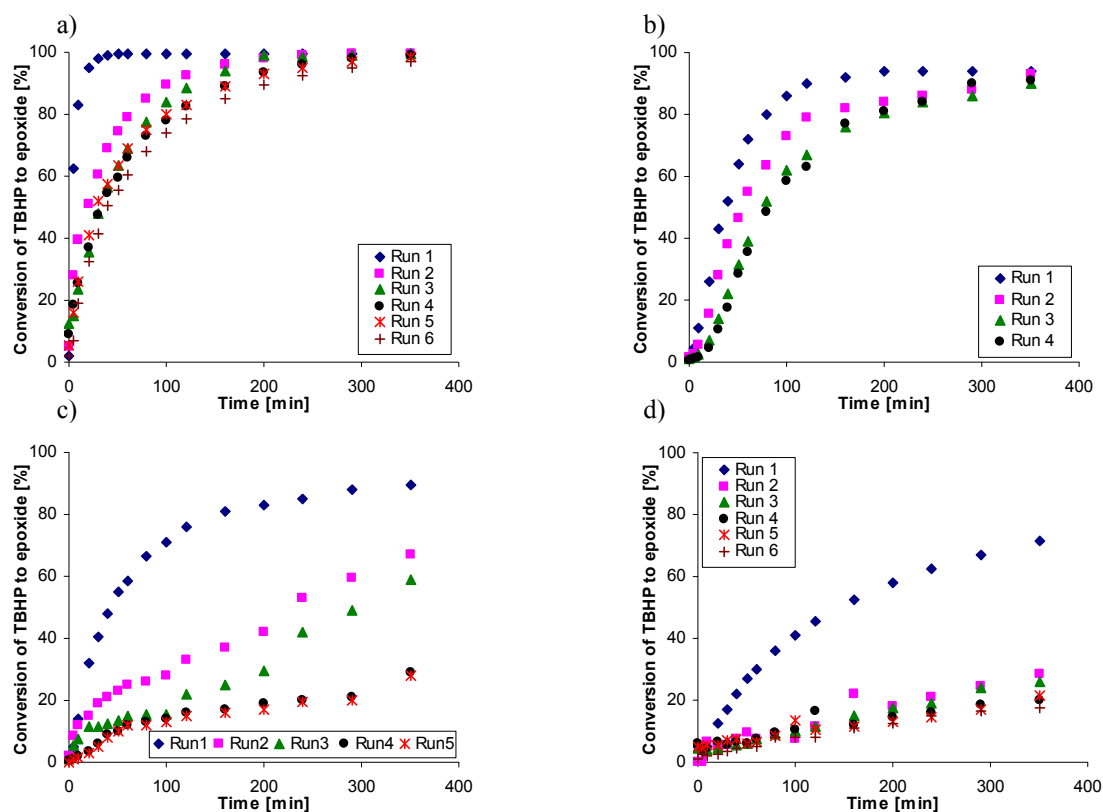


Figure 2. Effect of **PBLMo** catalyst reusability on TBHP conversion and reaction rate of epoxidation of alkenes: a) cyclohexene, b) limonene (conversion of TBHP is related to 1,2-limonene epoxide), c)  $\alpha$ -pinene, d) 1-octene (at 343 K, 5/1 molar ratio of alkene, catalyst content 0.3 mol% Mo, 400 rpm agitation speed)

In our previous work with other alkenes we found that Mo loss in the first run using **PBLMo** could be in the range of 2-5% (Sherrington, 2000). This might be due to the presence of some weakly bound or physically trapped Mo complex. The high reactivity with fresh catalyst might therefore be attributed to leaching of this weakly bound Mo thereby catalysis of epoxidation in a homogenous manner. In the present study when the **PBLMo** catalyst is used for a run 2 with 1-octene, the amount of Mo leaching to the system may well be less. Hence the TBHP conversion achieved might be lower because the reaction is catalysed mostly by heterogeneous Mo species. For runs 2-6, therefore, the amount of soluble Mo species present in the reaction mixture (if any at all), does not significantly influence the TBHP conversion. It seems clear therefore that catalysis in the early reactions arises from the heterogeneous Mo complexes immobilised on each support *and* active Mo species lost from the support. However, once the catalyst has been recycled the contribution to catalysis from the Mo species lost from the support become negligible. Overall however the activity of the **PBLMo** catalyst in 1-octene epoxidation is significantly lower than that observed with the other more electron rich alkenes.

#### 4. CONCLUSIONS

The present study has shown that it is possible to produce stable long-lived polymer-supported Mo alkene epoxidation catalysts. The catalyst could be reused several times in the RD experiments without losing any significant catalytic activity. The batch experimental work demonstrated the effectiveness of polymer supported catalysts in the epoxidation of all the alkenes studied. The results from alkene epoxidations catalyzed by **PBLMo** indicate that leaching of Mo usually stops after about 4-5 runs after which only heterogeneous catalysis by **PBLMo** occurs. However in the case of 1-octene, leaching of active Mo species becomes negligible after run 1. Despite this however the overall heterogeneous activity of **PBLMo** with this alkene is poor.

In the epoxidations of the alkenes studied some attrition of catalyst particles was noticed when they were reused more than three times under the vigorous agitation condition in the batch reactor and this might be a facilitating factor in Mo loss. However this effect will be absent in the RDC as the catalyst will be packed within a structured packing in the reactive section of the column.

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