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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 an oxidant have been studied under different reaction conditions in a batch reactor. As alkene representatives we have chosen cyclohexene, limonene, α -pinene and 1-octene (a less reactive terminal alkene). The order of reactivity of the alkenes was found to be: cyclohexene>limonene> α -pinene>1-octene. 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, cyclohexene, limonene, α -pinene and 1-octene, *tert*-butyl hydroperoxide.

1. INTRODUCTION

The growing concern for the environment, increasingly stringent standards for the release of chemicals into the environment and economic competitiveness have 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.

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 MoO₂acac₂ 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 alkenes. 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 epoxidations of alkenes 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. Particle size distribution measurement of the catalysts was carried out using Malvern Mastersizer. BET surface area measurements were carried out by the nitrogen adsorption and desorption method using a Micromeritics ASAP 2010 (Accelerated Surface Area and Porosimetry). The results obtained are summarised in Table 1.

2.2 Preparation of *tert*-butyl hydroperoxide

tert-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 (1979). The molarity of TBHP was determined by iodimetry. The concentration of the TBHP in toluene was found to be 3.65 mol/dm³.

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 0.15 to 0.6 mol% of Mo 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.

Table.1. Mo loading and Mo/ligand ratio and physical properties of polymer-supported Mo catalysts

Properties	PBI.Mo catalyst
Mo loading (mmol Mo/g resin) ^a	0.95
Ligand loading mmol /g resin ^b	2.3
Ligand/Mo ratio	2.4 : 1
Particle size	10% below 228 μ m ; 90% below 331 μ m
BET surface area	22.12 (\pm 0.3) m ² /g

^a: From AAS analysis of digested resins.

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

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 μ m 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 μ L and a complete GC run took about 15 min.

3. RESULTS AND DISCUSSION

The batch experimental results are presented in this section. We studied alkenes epoxidation systems under different reaction conditions, however, in this paper we show the effect of reaction temperature, effect of Mo/TBHP mole ratio (Mo loading), effect of alkene/TBHP ratio and catalyst reusability as these information would be very useful when performing continuous 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 and Sherrington,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 the alkene epoxides was found to be close to 100%.

3.1. Effect of reaction temperature on TBHP conversion catalysed by PBI.Mo

It is evident from Figure 1a that the epoxidation of cyclohexene catalysed by the **PBI. Mo** complex is very fast. After 50 min of the reaction, nearly 100% conversion of TBHP was achieved at 353 K. A distinct exothermic effect was observed when the reaction was carried out at 353 K, with the temperature increasing to 363 K (in about 10 minutes). It was then controlled immediately to maintain the reaction mixture at temperature 353 K. Therefore, the significantly higher conversion and reaction rate at that temperature is probably due to the increase in temperature.

Limonene, which is the main component of the orange essential oil, has a low price, and is thus a particularly important substrate for the production of much higher value products (Gomes and Antunes 2001).Wentzel *et. al* (2000) studied the use of a **PBI.Mo** catalyst in the *aerobic* epoxidation of limonene, however no reaction was observed. In our studies using the same catalyst, with TBHP as an oxidant the main product found in all cases is 1,2-limonene epoxide. GC analysis shows the 1,2-epoxide to be 50:50 mixture of *cis*- and *trans*-diastereoisomers. 8,9-Limonene epoxide is also found as a by-product. Notably neither the diepoxide nor any other by-products were detected during the present study. Regardless of reaction conditions the selectivity of 1,2-limonene oxide reached 94% after 60 min and remained constant at higher conversion until the end of the experiment. The epoxidation of limonene at 353 K catalysed by the **PBI.Mo** complex is not as fast as cyclohexene epoxidation. However, after 120 minutes of the reaction, nearly 90% of TBHP conversion to 1,2-limonene oxide is achieved (Figure 1b). The reaction rate for epoxidations carried out at 353 K and 343 K is very similar whilst a significant drop of reaction rate at 333 K was recorded. However, at the end of the experiment (350 min) at 353 K, 343 K and 333 K similar TBHP conversions to 1,2-limonene oxide were achieved for all three temperatures. An exothermic effect was observed especially when carrying out the reaction at 353 K.

α -Pinene oxide is used as an intermediate in the production of synthetic substitutes for natural aromas (da Silva Rocha *et. al.* 2005). Variation of temperature clearly markedly influences the TBHP conversion to α -pinene oxide which at the end of experiment at 353 K reaches 90% (Figure 1c). For the other temperatures studied the TBHP conversion drops down proportionally giving 70% at 343 K and 50% at 333 K at the end of experiment. The reaction rate is not as fast as it is in case of cyclohexene and limonene epoxidations.

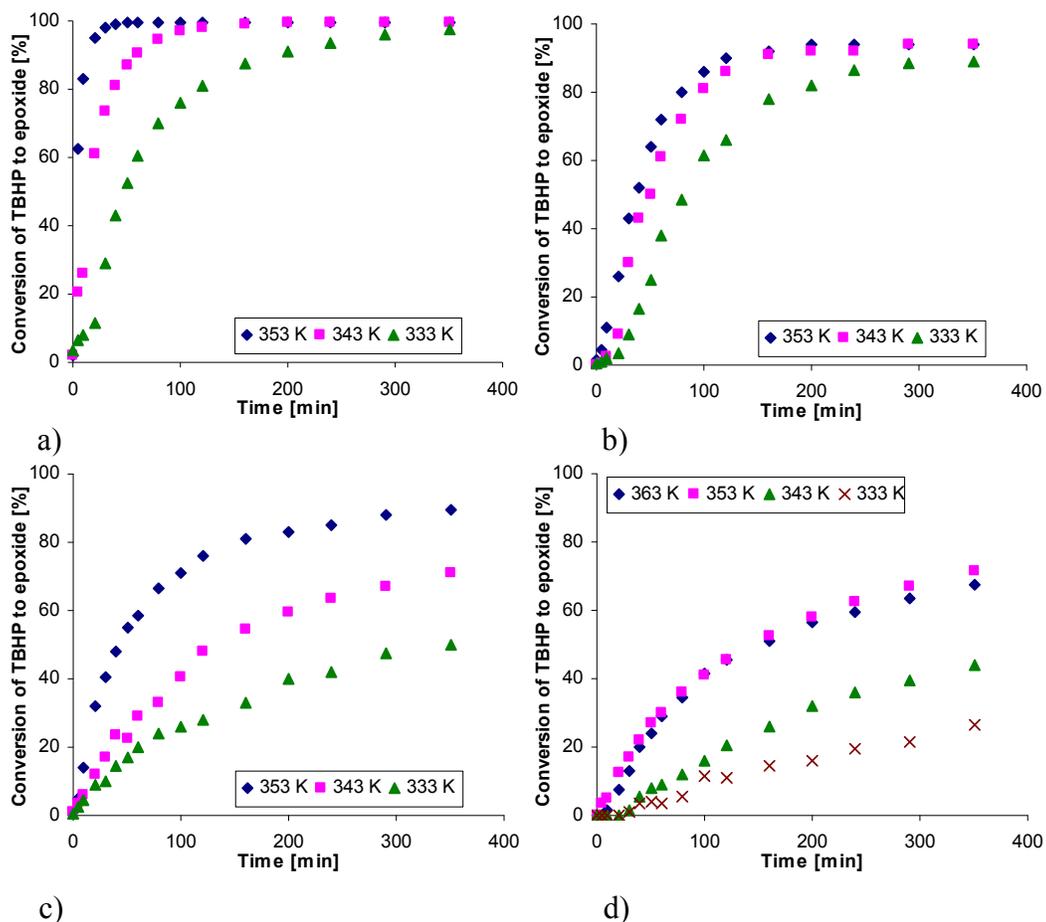


Figure 1. Effect of temperature on TBHP conversion and reaction rate of **PBI.Mo** catalysed epoxidation of alkenes: a) cyclohexene, b) limonene (conversion of TBHP is related to 1,2-limonene epoxide), c) α -pinene, d) 1-octene (at 5/1 molar ratio of alkene to TBHP, catalyst content 0.3 mol% Mo, 400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

The TBHP conversion achieved at the end of reaction time at 353 K for 1-octene epoxidation is the lowest obtained for the epoxidation of all the alkenes studied catalysed by **PBI.Mo**. The fall in conversion with decrease in temperature is also very significant (Figure 1d). In order to achieve higher conversion it was decided to increase the reaction temperature to 363K. It was found that the TBHP conversion carried out at 363 K is nearly identical to those obtained for the epoxidation carried out at 353 K. Therefore, 353K can be considered as an optimum temperature for epoxidation of 1-octene catalysed by the **PBI.Mo** catalyst.

3.2. Effect of Mo/TBHP mole ratio on epoxidation of alkenes catalysed by **PBI.Mo**

The effect of the catalyst level i.e. the Mo/TBHP mole ratio was investigated using mole ratios of Mo/TBHP of $1.5 \times 10^{-3}/1$, $3 \times 10^{-3}/1$, $6 \times 10^{-3}/1$, i.e. 0.15, 0.3 and 0.6 mol% Mo.

For the cyclohexene epoxidation using 0.15 mol% Mo >99% of TBHP conversion is achieved after 120 minutes whilst for catalyst levels of 0.3 and 0.6 mol% Mo, similar TBHP conversions are obtained after 40 minutes (Figure 2a). It is evident that increase in the catalyst level above 0.3 mol% Mo has little effect on the TBHP conversion, and so 0.3 mol% Mo of **PBI.Mo** can be considered as optimal for cyclohexene epoxidation at 353 K with a 5/1 molar ratio of cyclohexene to TBHP.

For limonene epoxidation with 0.15 mol% Mo, 90% TBHP conversion is achieved after 240 minutes, whilst with 0.3 mol% Mo, 90% conversion is achieved after 120 minutes. However, the reaction rate is particularly high when 0.6 mol% Mo is used. In this case 90% TBHP conversion to 1,2-limonene oxide is obtained after 60 minutes, and the reaction is completed after 100 minutes (Figure 2b). The rate dependence on catalyst level is therefore very clear and is the most noticeable among the studied alkenes.

The results for α -pinene epoxidation (Figure 2c) are similar to those found with cyclohexene i.e., the TBHP conversion and reaction rate obtained for the two largest catalyst contents (0.3 and 0.6 mol% Mo) are nearly identical. Slightly higher reaction rate, especially at the beginning of the reaction, for lower Mo loading can be explained by an exothermic effect which at that stage of the reaction was very difficult to control (Figure 2c). The final TBHP conversion at the end of the reaction time is 90% in each case. As for cyclohexene it can be concluded that increasing the level of catalyst above 0.3 mol% Mo neither improves TBHP conversion nor the reaction rate.

For epoxidation of the least reactive alkene i.e. 1-octene, change of the **PBI.Mo** content does not significantly influence the TBHP conversion and reaction rate (Figure 2d). Unlike the situation found with the other alkenes the difference in TBHP conversion (~10%) for 0.15 and 0.6 mol% Mo remains almost the same during the course of reaction.

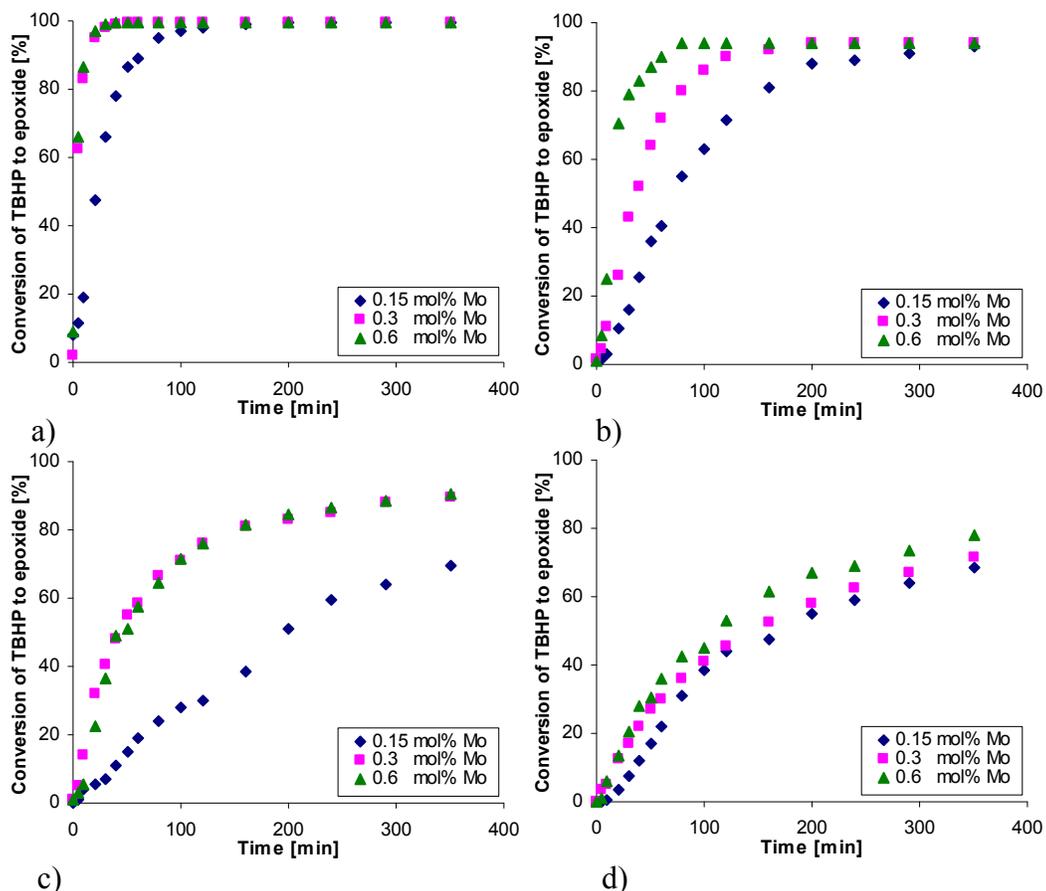


Figure 2. Effect of Mo/TBHP ratio on TBHP conversion and reaction rate of **PBI.Mo** catalysed epoxidation of alkenes: a) cyclohexene, b) limonene (conversion of TBHP is related to 1,2-limonene epoxide), c) α -pinene, d) 1-octene (at 343 K, 5/1 molar ratio of alkene to TBHP, 400 rpm agitation speed).

3.3. 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.

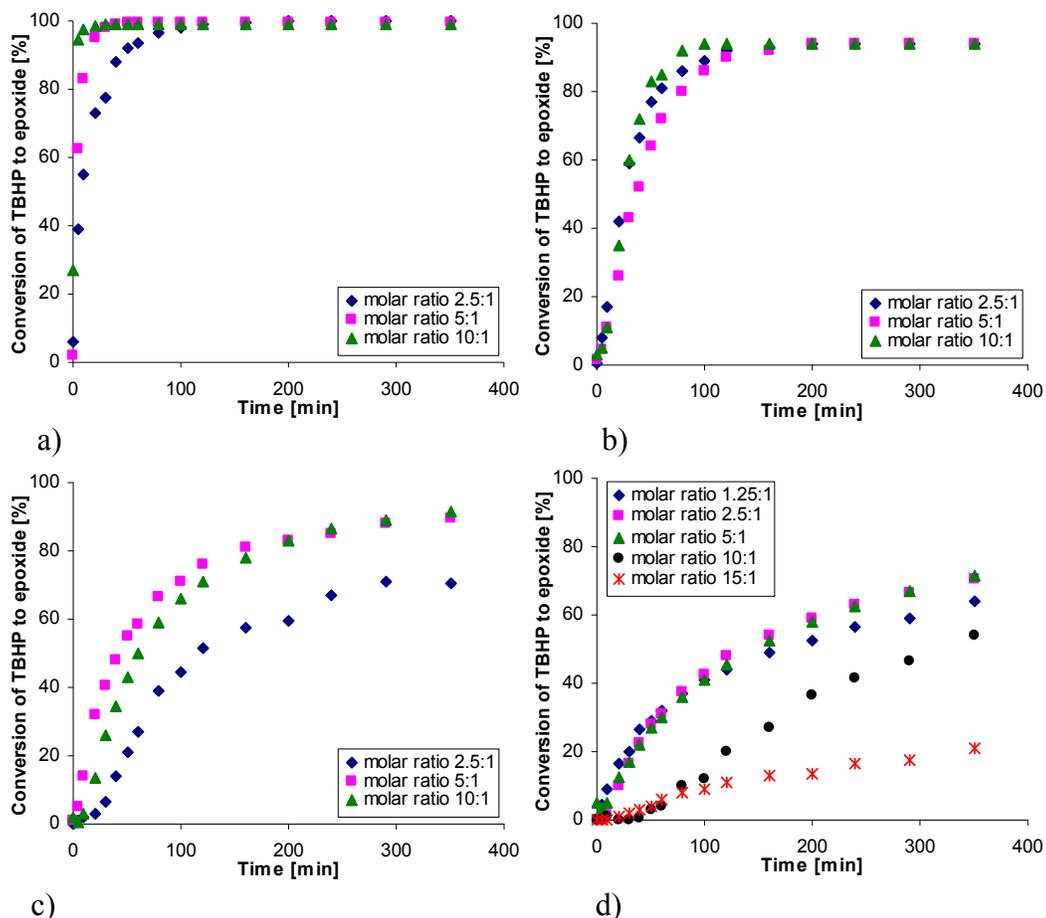


Figure 3. Effect of feed mole ratio (alkene/TBHP) on TBHP conversion and reaction rate of **PbI.Mo** catalysed epoxidation of alkenes: a) cyclohexene, b) limonene (conversion of TBHP is related to 1,2-limonene epoxide), c) α -pinene, d) 1-octene (at 343 K, catalyst content 0.3 mol% Mo, 400 rpm agitation speed).

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 3a). 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 3b that the variation of the limonene/TBHP mole ratio does not affect the TBHP conversion to 1,2-limonene oxide significantly. The reaction rates for different ratio of limonene/TBHP are the same within experimental error.

Similar studies in the epoxidation of α -pinene show that a mole ratio of α -pinene/TBHP of 5/1 can be considered as an optimal one (Figure 3c). The TBHP conversion as well as the reaction rate obtained for 5/1 and 10/1 ratios are very similar (Figure 3c). However, the initial reaction rate when using a 5/1 ratio is slightly higher. The feed mole ratio of 2.5/1 (TBHP: α -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 3d). 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 3d).

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.

3.4. Catalyst reusability studies of **PBI.Mo** in epoxidation of alkenes

In order to check the suitability of the catalyst for continuous epoxidation process, it is essential to study the catalyst reusability in batch reactions using the conditions likely to be used in the continuous process. 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 during the continuous process.

The data for cyclohexene epoxidation shown in Figure 4a indicate that the **PBI.Mo** 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 4b). 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 α -pinene epoxidations are different from that obtained for cyclohexene and limonene. As is shown in Figure 4c 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 **PBI.Mo** catalyst in the epoxidation of α -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 4d) 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.

In our previous work with other alkenes we found that Mo loss in the first run using **PBI.Mo** 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 **PBI.Mo** 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.

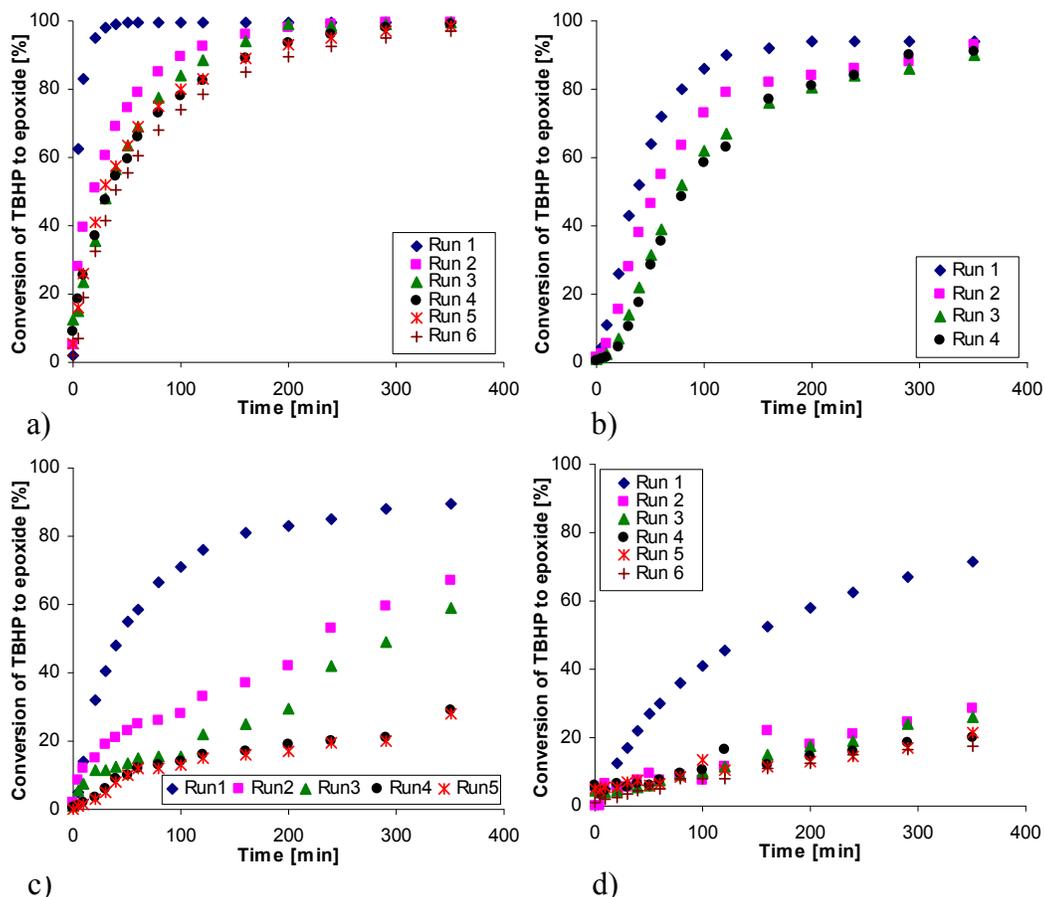


Figure 4. Effect of **PBLMo** catalyst reusability on TBHP conversion and reaction rate of epoxidation of alkenes: a) cyclohexene, b) limonene (conversion of TBHP is related to 1,2-limonene epoxide), c) α -pinene, d) 1-octene (at 343 K, 5/1 molar ratio of alkene ,catalyst content 0.3 mol% Mo, 400 rpm agitation speed).

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 continuous 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 **PBI.Mo** indicate that leaching of Mo usually stops after about 4-5 runs after which only heterogeneous catalysis by **PBI.Mo** 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 **PBI.Mo** 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 fixed bed during the continuous operation as the catalyst will be packed within a structured packing in the packed column.

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