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Efficient epoxidation of cyclododecene and dodecene catalysed by polybenzimidazole supported Mo(VI) complex

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ABSTRACT

A polybenzimidazole supported Mo(VI) complex (PBI.Mo) has been prepared and characterised. The catalytic activity of PBI.Mo for the epoxidation of cyclododecene and dodecene with *tert*-butyl hydroperoxide (TBHP) as an oxidant has been studied under different reaction conditions in a batch reactor. The stability of heterogeneous Mo(VI) catalyst was evaluated by recycling a sample in batch reaction using conditions that will form the basis of continuous process. The leaching of Mo species from PBI.Mo has been investigated by isolating any residue from reaction supernatant solutions following the removal of the heterogeneous catalyst, then using the residues as potential catalyst in epoxidation reactions. The batch epoxidation experimental data provided useful information for conducting continuous epoxidation in a reactive distillation column (RDC).

1. Introduction

Alkene epoxidation has emerged as an indispensable tool for chemical synthesis since it allows the direct oxidation of two adjacent carbon atoms from alkenes through the use of oxidising reagents including molecular oxygen, peracids or hydroperoxides in the presence of transition metal complexes as catalysts [1–4]. The use of solvents for alkene epoxidation has been a serious issue from environmental and economic viewpoint. The production of epoxides in the industries often uses the stoichiometric peracid such as peracetic acid and m-chloroperbenzoic acid in batch reactions. However, the employment of peracids is not an environment friendly synthesis since equivalent amounts of acid waste are produced. Therefore, there is a strong need for cleaner catalytic epoxidation methods which employ safer oxidants and produce little waste. Currently, extensive efforts have been focused on developing efficient and cleaner processes that minimise or completely eliminate pollutants such as toxic solvents and by-products.

Epoxides are versatile and useful intermediates for organic synthesis because they can be converted into a variety of chemicals, such as pharmaceuticals to plastics and paints to adhesives [5–7]. The versatile nature of epoxides is due to the high reactivity of the three-membered ring in their structure. As a consequence, epoxidation of alkenes is a field of both academic and industrial importance. Homogeneous molybdenum (VI) [8] and heterogeneous titanium-on-silica (TiO_2–SiO_2) [9] are notable examples of catalysts used for industrial epoxidation of propylene to propylene oxide using alkyl hydroperoxides as oxidising reagents.

A wide range of polymer supported Mo(VI) complexes have been successfully applied as catalysts for alkene epoxidation over the last few decades [10–19]. The application of supported metal complex as a catalyst for a laboratory scale epoxidation could considerably facilitate product work-up and isolation, while on a large scale process, heterogeneous catalyst allow reaction to be run continuously using packed or fluidised bed columns with considerable financial advantages [20–24].

In this work, we report a new process which is considered to be clean as it employs an efficient and selective polybenzimidazole

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Abbreviations: AAS, atomic absorption spectrophotometer; ASAP, accelerated surface area and porosimetry; BET, Brunauer–Emmett–Teller; FID, flame ionisation detector; GC, gas chromatography; Mo, molybdenum; $MoO_2(acac)_2$, molybdenyl acetylacetonate; PBI.Mo, polybenzimidazole supported Mo(VI) complex; RDC, reactive distillation column; TBHP, *tert*-butyl hydroperoxide.

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supported Mo(VI) complex (PBI.Mo) as a catalyst for epoxidation of cyclododecene and dodecene. The process uses environmentally benign *tert*-butyl hydroperoxide (TBHP) as a terminal oxidant.

Experiments have been carried out to study the effect of reaction temperature, catalyst loading and feed molar ratio of alkene to TBHP on the conversion of TBHP to epoxide for optimisation of reaction conditions in a batch reactor. The long term stability of the heterogeneous catalyst has been evaluated by recycling a sample of the catalyst several times in batch experiments. The extent of Mo leaching from the polymer supported catalyst has been investigated by isolating any residue from reaction supernatant studies after removal of the heterogeneous catalyst and using the residue as potential catalyst for epoxidation reaction. This information will be useful for conducting a large scale continuous epoxidation process in a reactive distillation column (RDC).

2. Experimental methods

2.1. Materials

Cyclododecene (96%), dodecene (95%), dry toluene (99.8%), molybdenyl acetylacetonate (MoO_2acac_2) and *tert*-butyl hydroperoxide (TBHP) solution in water (70% w/w) were purchased from Sigma–Aldrich Co. Ltd. Microporous polybenzimidazole (PBI) resin beads were supplied by Celanese Corporation. The water content of TBHP was removed by Dean-Stark apparatus from toluene solution and the concentration of the resulting anhydrous TBHP solution was determined by iodometric titration [25].

2.2. Synthesis of polybenzimidazole supported Mo(VI) complex (PBI.Mo)

Polybenzimidazole (PBI) resin is employed in various applications such as ion-exchange, separations, purifications and catalysts preparation due to its high degree of thermal stability and chemical resistivity. The polymer supported Mo(VI) complex (PBI.Mo) was prepared by using a ligand exchange procedure in which PBI resin was reacted with an excess of molybdenyl acetylacetonate (MoO_2acac_2) relative to polymer bound ligand under reflux in toluene for a period of 4 days (Fig. 1). The catalyst particles were filtered off at the end of the reaction and the excess MoO_2acac_2 was removed by exhaustive extraction with acetone. The dark-blue colour of the washings gradually disappeared upon repeated introduction of fresh acetone until the solution remained colourless. Molybdenum in the prepared catalyst was found to be homogeneously distributed in the polymer matrix. The molybdenum content of the prepared catalyst was determined using Perkin-Elmer AAnalyst 200 spectrophotometer. A sample of PBI.Mo catalyst (~0.1 g) was grounded to fine powder and digested in 15 mL aqua regia. The resulting mixture was diluted to 100 mL with distilled water and Mo content was analysed using an atomic absorption spectrophotometer (AAS). The particle size distribution of the catalyst was measured using Malvern Mastersizer and the BET surface area was determined by nitrogen adsorption and desorption method using Micromeritics ASAP (accelerated surface area and porosimetry) 2010. The properties of the prepared PBI.Mo catalyst are presented in Table 1.

Table 1
Physical and chemical properties of polybenzimidazole supported Mo(VI) catalyst.

Catalyst properties	PBI.Mo catalyst
BET surface area ($m^2 g^{-1}$)	24.8
Ligand loading (mmol g^{-1} resin)[a]	2.4
Mo loading (mmol Mo g^{-1} resin)[b]	0.93
Ligand to Mo ratio	2.58:1
Particle size (μm)	243–335
Average pore diameter (nm)	11.5
Total pore volume ($cm^3 g^{-1}$)	0.07

[a] From N% elemental analysis of Mo loaded resins assuming ligand = imidazole.
[b] From AAS analysis of digested resin.

2.3. Batch epoxidation studies

Batch epoxidation experiments were conducted in a 0.25 L jacketed four necked glass reactor equipped with condenser, overhead stirrer, digital thermocouple, sampling point and water bath. The feed mole ratio of alkene to TBHP, catalyst loading and reaction temperature ranges were selected based on numerous experiments that were conducted for epoxidation of the substrates studied. Alkene and TBHP in toluene were weighed out and introduced into the reactor (no solvent was added) and stirring was started. Feed mole ratio of alkene to TBHP of 1:1–10:1 was selected. Heating to the reaction mixture was supplied through water bath via the reactor jacket and monitored by a digital thermocouple. A known amount of PBI.Mo catalyst (0.15–0.6 mol% Mo) was added to the reactor when the reaction mixture in the reactor reached the required temperature, i.e. 323–353 K and was maintained in the range of ±0.5 K throughout the batch experiment. The first sample was collected from the mixture after all the catalyst was added to the reactor and the time was noted as zero time, i.e., $t = 0$. Subsequent samples were taken from the reaction mixture at specific time intervals and were analysed by An HP 5080 II gas chromatography (GC). The reaction scheme is shown in Fig. 2.

3. Method of analysis

An HP 5080 II gas chromatograph (GC) was used to analyse the composition of samples collected from both cyclododecene and dodecene epoxidation. The GC was fitted with a flame ionisation detector (FID) and a 30 m long J&W DB-5ms capillary column with 0.32 mm internal diameter and a film thickness of 0.25 μm. Both injector and detector temperatures were set at 473 K and the helium carrier gas flow rate was maintained at 1 mL min^{-1}. A ramp method was used to separate all the components present in the sample mixture using injection volume of 0.4 μL and a split ratio of 1:100. The method was programmed to hold oven temperature at 323 K for 5 min after the sample was injected and then ramped from 323 K to 388 K at the rate of 4 K min^{-1}. The oven temperature then ramped at 25 K min^{-1} until 473 K.

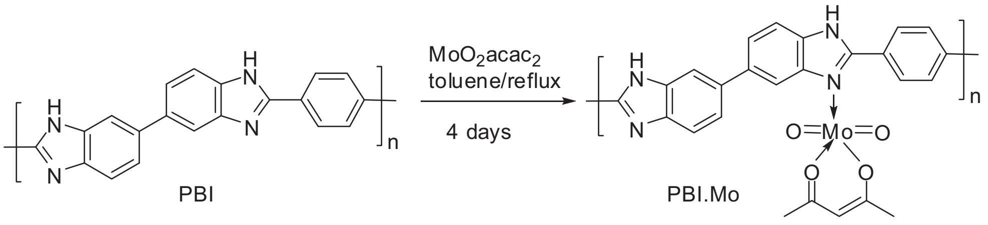

Fig. 1. Schematic of PBI.Mo complex synthesis.

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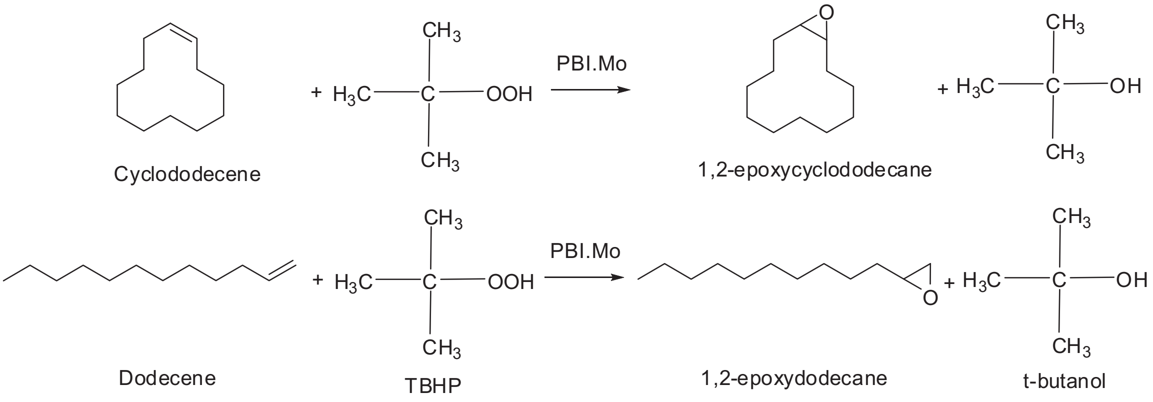

Fig. 2. Reaction scheme for epoxidation of cyclododecene and dodecene catalysed by PBI.Mo complex.

4. Results and discussion

In this work, we have studied the catalytic activity of PBI.Mo for cyclododecene and dodecene epoxidation by studying the effect of reaction temperature, catalyst loading and alkene to TBHP molar ratio on the conversion of TBHP to epoxide. In addition, the catalyst reusability and supernatant studies have been carried out to evaluate the long term stability of the polymer supported catalyst for epoxidation reaction. This information will be very useful when performing continuous epoxidation experiments. It should 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 a non-free radical selective mechanisms [26]. However, no allylic oxidation was detected in the present system, thus, any participation by molecular oxygen as an oxidant seems unlikely. Thermal decomposition of TBHP was also negligible under the reaction conditions employed in the present study. The analytical error for this study was found to be within ±3% for all the experiments.

4.1. Investigation of mass transfer resistances

Two types of mass transfer resistances exist in heterogeneous catalysed alkene epoxidation with TBHP. One across the solid–liquid interface, i.e. the influence of external mass transfer resistance caused as a result of stirring the reaction mixture. The other mass transfer resistance occurs in the intraparticle space, i.e. internal mass transfer resistance that is connected with the different catalyst particle size and catalyst internal structure such as the chemical structure, pore size distribution and porosity. A jacketed stirred batch reactor was used to study the existence of mass transfer resistance for alkene epoxidation with TBHP catalysed by PBI.Mo complex. It was observed that there was negligible external mass transfer resistance when epoxidation experiments were carried out using the stirrer speed of 300–400 rpm under otherwise identical conditions. On the other hand, PBI.Mo catalyst particles are within the size rage of 243–335 μm, which are fairly uniform. A negligible change in catalytic performance was observed within this size range. Therefore, it can be concluded that both external and internal mass transfer resistances were absent in this work. On the basis of these investigations, all batch epoxidation experiments were carried out with stirrer speed of 400 rpm using PBI.Mo catalyst as prepared.

4.2. Effect of reaction temperature on the epoxidation of cyclododecene and dodecene catalysed by PBI.Mo

Reactions were carried out at 333 K, 343 K and 353 K in order to study the effect of reaction temperature on the conversion of TBHP to the corresponding epoxide. As shown in Fig. 3, it is evident that variation of temperature clearly influences the outcome of cyclododecene and dodecene epoxidation catalysed by PBI.Mo.

Epoxidation of cyclododecene at 353 K gave ~98% yield of 1,2-epoxycyclododecane after 350 min, while the reactions conducted at 343 K and 333 K achieved 86% and 59% yield of 1,2-epoxycyclododecene, respectively during the same period (Fig. 3a). In case of dodecene epoxidation, the conversion of TBHP to epoxide is much lower than the values obtained for epoxidation of cyclododecene. For instance, ~77% yield of 1,2-epoxydodecane was achieved after 350 min for reaction conducted at 353 K, whilst the conversion of TBHP decreased significantly to 51% and 28%, when the reactions were carried out at 343 K and 333 K, respectively (Fig. 3b).

The effect of temperature for batch epoxidation experiments gives us important information about the optimum reaction temperature required for obtaining high yield of epoxide for the continuous epoxidation of cyclododecene and dodecene in a reactive distillation column (RDC).

4.3. Effect of catalyst loading on the epoxidation of cyclododecene and dodecene catalysed by PBI.Mo

In this work, catalyst loading was defined based on the active Mo component instead of the total mass of PBI.Mo catalyst in order to take into account any differences in Mo content between different batches of the prepared PBI.Mo catalyst. However, all experiments in this work were carried out using one batch of the prepared catalyst. The effect of catalyst loading (i.e. mole ratio of Mo to TBHP × 100%) was investigated at 0.15 mol% Mo, 0.3 mol% Mo and 0.6 mol% Mo. Fig. 4a shows that the kinetic profiles of TBHP conversion to 1,2-epoxycyclododecane were similar for epoxidation of cyclododecene carried out at 0.15 mol% and 0.3 mol% Mo, i.e. the yield of epoxide at 350 min was ~97% in both cases. On the other hand, the rate of epoxide formation increases slightly when 0.6 mol% Mo was used and the conversion of TBHP to 1,2-epoxycyclododecane reached ~100% at 290 min.

In case of dodecene epoxidation, the rate of TBHP conversion to 1,2-epoxydodecane are almost identical throughout the reaction for all the catalyst loadings investigated (Fig. 4b). The experiments conducted using 0.15 mol% Mo and 0.3 mol% Mo achieved ~70% conversion of TBHP to 1,2-epoxydodecane at 350 min, while a slight increase in the conversion of TBHP (76%) was recorded when 0.6 mol% Mo was used. Thus, it can be concluded that epoxidation of dodecene with TBHP was slightly influenced by increasing the PBI.Mo loading above 0.15 mol% Mo. Indeed dodecene being an unreactive alkene seems to react slowly with PBI.Mo catalyst. Hence, a longer reaction time may be required to achieve a high conversion of TBHP to epoxide.

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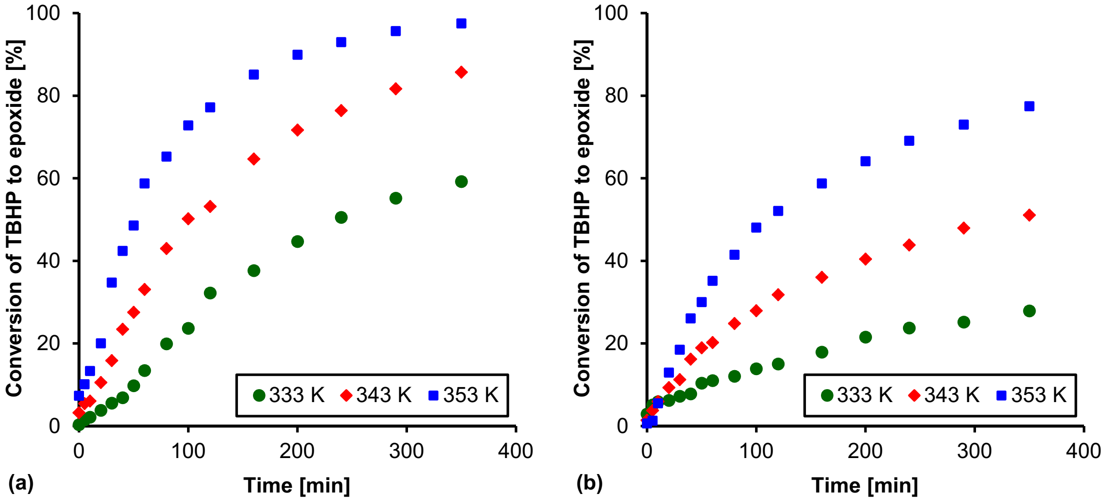

Fig. 3. Effect of reaction temperature on the conversion of TBHP to epoxide for PBI.Mo catalysed epoxidation of (a) cyclododecene and (b) dodecene with TBHP as an oxidant at feed molar ratio of alkene to TBHP: 5:1; catalyst loading: 0.3 mol% Mo; stirrer speed: 400 rpm.

4.4. *Effect of alkene to TBHP molar ratio on the epoxidation of cyclododecene and dodecene catalysed by PBI.Mo*

Typically in medium to large scale alkene epoxidation processes, the reactions are carried out with a substantial excess of alkene in order to obtain higher conversion of hydroperoxide, to avoid overoxidation and to achieve high selectivity to the desired product. In addition, the use of excess amount of alkene ensures that reactions are conducted below the explosion limit. The effect of feed molar ratio of alkene to TBHP was investigated at 2.5:1, 5:1 and 10:1.

Fig. 5a shows that the conversion of TBHP to epoxide was >92% at 240 min for all the feed molar ratios studied. However, the rate of epoxide formation for reaction carried out at 2.5:1 molar ratio of cyclododecene to TBHP was faster than the rate achieved for experiments conducted at 5:1 and 10:1 molar ratio, which is unusual. We observed from our previous work that for cyclic alkenes such as cyclohexene, the rate of formation of epoxide was slightly higher when the molar ratio of cyclohexene to TBHP was increased from 2.5:1 to 10:1 [21]. In case of dodecene epoxidation, experiments carried out at 2.5:1 and 5:1 show similar rate of epoxide formation throughout the reaction and achieved the same conversion of TBHP to 1,2-epoxydodecane (73%) at 290 min (Fig. 5b). On the other hand, when the molar ratio of cyclododecene to TBHP was increased to 10:1, the conversion of TBHP to 1,2-epoxydodecane dropped to 64%. These outcomes were not entirely surprising since we had already noticed similar results in the case of unreactive alkenes such as 1-octene [27] and 1-hexene [4]. Overall, it seems that the feed molar ratio of alkene to TBHP of 5:1 would be suitable for carrying out continuous epoxidation studies in an RDC.

4.5. *Catalyst reusability studies of PBI.Mo for the epoxidation of cyclododecene and dodecene*

In order to check the suitability of PBI.Mo catalyst for continuous epoxidation process, it is essential to study the catalyst reusability in batch reactions at the conditions likely to be used in the continuous process. In the batch epoxidation of alkenes, we have reported that some attrition of catalyst particles was noticed when PBI.Mo was reused several times under stirring conditions used in the batch reactor [4,21,28,29]. However it is anticipated that this problem will be absent in the continuous epoxidation process using an RDC since the catalyst would be systematically packed in a fixed bed reactor.

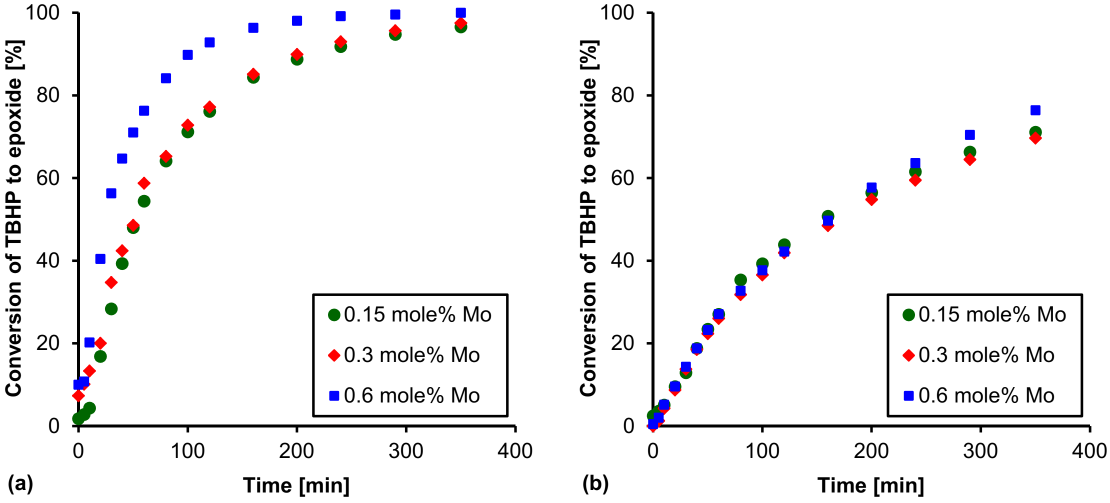

Fig. 4. Effect of catalyst loading on the conversion of TBHP to epoxide for PBI.Mo catalysed epoxidation of (a) cyclododecene and (b) dodecene with TBHP as an oxidant at reaction temperature: 353 K; feed molar ratio of alkene to TBHP: 5:1; stirrer speed: 400 rpm.

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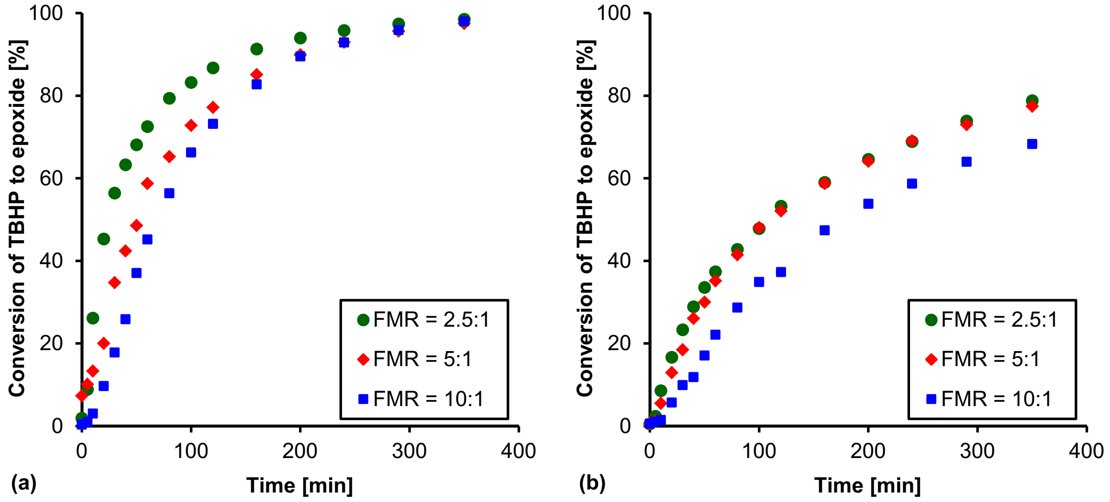

Fig. 5. Effect of feed molar ratio (FMR) of alkene to TBHP on the conversion of TBHP to epoxide for PBI.Mo catalysed epoxidation of (a) cyclododecene and (b) dodecene with TBHP as an oxidant at reaction temperature: 353 K; catalyst loading: 0.3 mol% Mo; stirrer speed: 400 rpm.

In this study, fresh PBI.Mo catalyst was used in epoxidation experiment and plotted as Run 1. At the end of the experiment, i.e. Run 1, the catalyst particles were filtered from the reaction mixture, washed carefully with 1,2-dichloroethane and stored in a vacuum oven at 40 °C. The stored PBI.Mo catalyst particles were reused in the subsequent experiment and plotted as Run 2. This procedure was repeated for the remaining catalyst reusability experiments. It can be seen from Fig. 6a and b that high conversion of TBHP to epoxide was recorded in Run 1 as compared to subsequent runs for epoxidation of both cyclododecene and dodecene. This is due to the availability of sufficient active sites in fresh PBI.Mo catalyst that are available for adsorption by the reacting species. The reusability studies for cyclododecene epoxidation (Fig. 6a) indicate that PBI.Mo remains active over six cycles. The conversion of TBHP to 1,2-epoxycyclododecane was >85% for all the catalyst reusability experiments. However, in case of dodecene epoxidation (Fig. 6b), a significant decrease in the conversion of TBHP to 1,2-epoxydodecane was recorded in Run 2 (68%) and in subsequent experimental runs as compared to Run 1 (79%). However, the rate of epoxide formation at Run 4 and Run 5 were identical (Fig. 6b). Thus, it was concluded that PBI.Mo catalyst became stable for dodecene epoxidation after 4–5 experimental runs.

It is to be noted that PBI.Mo demonstrated high catalytic performance for epoxidation of cyclododecene as compared to dodecene. This observation was not quite surprising due to the electronic effect, which favours epoxidation of more substituted (electron-rich) double bond present in cyclododecene structure. It appears that the efficiency of epoxidation is highly dependent on the electronic effect of the substrates. Hence, more substituted alkenes tend to be more reactive than electron deficient ones [30,31]. Supernatant studies for the epoxidation of cyclododecene and dodecene catalysed by PBI.Mo.

The aim of supernatant studies is to investigate the leaching of any catalytically active Mo species from the polymer supported catalyst. Therefore, after each reusability study was completed (see Section 4.5), PBI.Mo catalyst particles were filtered out and the filtrate obtained was vacuum distilled to recover the residue of the catalyst particles. The residue isolated from supernatant solution of fresh PBI.Mo catalyst was used as a potential catalyst in epoxidation reaction and plotted as “after Run 1” in Fig. 7. The same procedure was repeated for all the subsequent reusability studies and the corresponding supernatant solution obtained was used as a catalyst for epoxidation. In addition, an experiment was carried out in the absence of residues and plotted as “uncatalysed” in Fig. 7 to

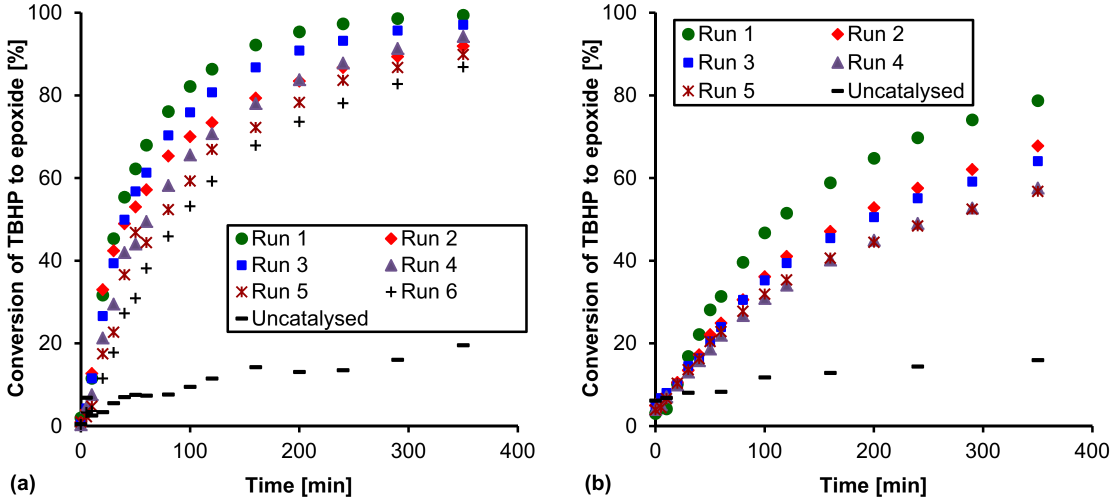

Fig. 6. PBI.Mo catalyst reusability studies for epoxidation of (a) cyclododecene and (b) dodecene with TBHP as an oxidant at reaction temperature: 353 K; feed molar ratio of alkene to TBHP: 5:1; catalyst loading: 0.3 mol% Mo; stirrer speed: 400 rpm.

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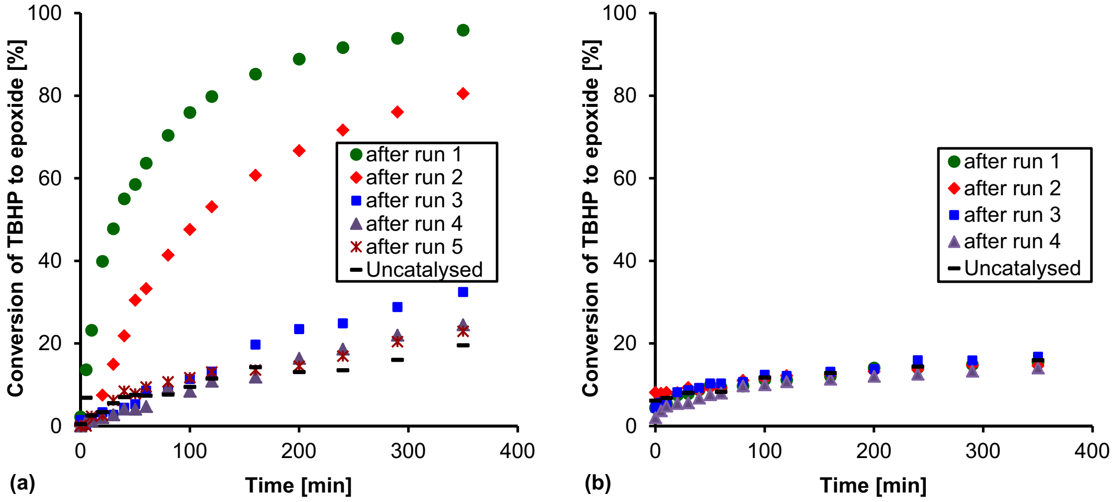

Fig. 7. Supernatant studies for epoxidation of (a) cyclododecene and (b) dodecene with TBHP as an oxidant catalysed by residue isolated from supernatant solutions where PBI.Mo catalyst is reused at reaction temperature: 353 K; feed molar ratio of alkene to TBHP: 5:1; stirrer speed: 400 rpm.

compare with the reactions conducted in the presence of isolated residues.

The conversion curves in Fig. 7a indicate the presence of catalytically active Mo species in the supernatant solutions for cyclododecene epoxidation. This is evident by the catalytic effect shown by the residues isolated from supernatant solutions of catalyst reusability experiments. The leaching of Mo was more pronounced at the first three consecutive reactions, i.e. after Run 1–after Run 3, where the conversion of TBHP to epoxide reaches 96%, 81% and 31%, respectively (Fig. 7a). However, the leaching of Mo decreased progressively afterwards until it became negligible “after Run 5” (Fig. 7a). In contrast, the catalytically active Mo species present in the residues isolated from all the successive supernatant studies experiments was negligible for epoxidation of dodecene (Fig. 7b), due to the low reactivity of dodecene (a terminal alkene) as compared to a more electron rich cyclic alkene, cyclododecene. The conversion curves for all the supernatant studies (after Run 1–after Run 4) were approximately the same with the control experiment conducted in the absence of isolated residues, i.e. “uncatalysed” curve (Fig. 7b). We suggest that the leaching of Mo species from PBI.Mo may be due of the release of Mo species contained in the microgels as a result of mechanical attrition of the polymer catalyst beads. However, this effect will be absent in the fixed bed during continuous epoxidation process as the catalyst will be packed within a structured packing containers located in the reactive section of reactive distillation column (RDC).

5. Conclusions

A polymer supported Mo(VI) complex (PBI.Mo) has been successfully prepared and characterised. The catalytic efficiency of the complex has been assessed for epoxidation of cyclododecene and dodecene in a batch reactor using TBHP as an oxidant. Experiments have been carried out to study the effect of reaction temperature, catalyst loading and feed molar ratio of alkene to TBHP on the conversion of TBHP to epoxide for optimisation of reaction conditions. PBI.Mo has been proved to suitable catalyst for the epoxidation of cyclododecene and dodecene. The optimum reaction condition for epoxidation of both cyclododecene and dodecene was found at 353 K, 0.3 mol% Mo catalyst loading and 2.5:1 feed molar ratio of alkene to TBHP, which gave $\sim$98% yield of 1,2-epoxycyclododecane and $\sim$79% yield of 1,2-epoxydodecane, respectively at 350 min. However, the results of supernatant studies of cyclododecene epoxidation reveal that catalytically active Mo species is leaching from the polymer matrix, which stops after about 4–5 experimental runs, whereas, supernatant studies for dodecene epoxidation show no evidence of Mo leaching. It was established that Mo leaching was due to soluble leached complex or Mo-containing microgel released as a result of mechanical attrition of the beads or both. Therefore, industrial use of PBI.Mo for batch alkene epoxidation is somewhat limited unless its stability is further increased. Nonetheless, Mo leaching would not be a problem in continuous epoxidation process using an RDC as the catalyst will be firmly packed inside a fixed column. Hence, PBI.Mo could be reused several times for continuous epoxidation without any significant loss in catalytic activity.

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