

**Greener and sustainable approach for the synthesis of commercially important epoxide building blocks using polymer-supported Mo(VI) complexes as catalysts**

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## 1. Introduction

Chemical industries are continuously faced with increasing challenges of regulatory requirements and rising cost of manufacturing intermediates. Hence, a greener and efficient route for chemical synthesis that could improve manufacturing efficiency by reducing operational cost and minimising waste products is highly desired. Alkene epoxidation is the addition of oxygen to alkene to yield epoxide. The reaction is very useful in organic synthesis as the resultant epoxide is a highly reactive compound that is used as a raw material or intermediate in the production of commercially important products for flavours, fragrances, paints and pharmaceuticals.<sup>1-9</sup>

The conventional epoxidation methods in the fine chemicals industries employs either stoichiometric peracids such as peracetic acid and *m*-chloroperbenzoic acid<sup>10</sup> or chlorohydrin<sup>11</sup> as oxidising reagents in liquid phase batch reactions. However, such processes are not environmentally benign as the former produces equivalent amount of acid waste, whilst the later yields chlorinated by-products and calcium chloride waste. In recent years, more and more attention has been focused on developing greener and more efficient epoxidation processes, employing environmentally benign oxidants such as *tert*-butyl hydroperoxide (TBHP) since it is atom efficient and safer to handle.<sup>12,13</sup> A notable industrial implementation of alkene epoxidation with TBHP was the Halcon process described by Kollar (1967),<sup>14</sup> which employs homogenous molybdenum (VI) as a catalyst for liquid phase epoxidation of propylene to propylene oxide. On the other hand, homogenous catalysed epoxidation processes are not economically viable for industrial applications due to major requirements in terms of work-up, product isolation and purification procedures. Therefore, researchers have focused on developing stable heterogeneous catalysts for epoxidation by immobilisation of catalytically active metal species on organic or inorganic materials.<sup>15-17</sup>

Polymers have gained attention as suitable support for transition metal catalysts as they are inert, nontoxic, insoluble and often recyclable.<sup>18</sup> A number of polymer supported molybdenum complexes have been prepared and used as catalysts for batch alkene epoxidation with TBHP as an oxidant and have shown good catalytic activity and product selectivity.<sup>19-31</sup> However, despite numerous published works on polymer supported Mo(VI) catalysed alkene epoxidation with TBHP, there appears to have been no significant efforts to move the chemistry on from small-scale laboratory batch reaction to continuous flow process.

In this chapter we discuss the preparation and characterisation of an efficient and selective polystyrene 2-(aminomethyl)pyridine supported molybdenum complex (Ps.AMP.Mo) and a polybenzimidazole supported molybdenum complex (PBI.Mo), which have been used as catalysts for epoxidation of 1-hexene and 4-vinyl-1-cyclohexene (i.e. 4-VCH) using TBHP as an oxidant. The process is considered to be clean as (i) it employs efficient and selective heterogeneous catalysts, (ii) it is solvent less, (iii) it uses a benign oxidant (TBHP), which becomes active only on contact with the catalyst and (v) it is atom efficient and the alcohol by-product itself is an important chemical feedstock.

An extensive assessment of the catalytic activity, stability and reusability of Ps.AMP.Mo and PBI.Mo catalysts has been conducted in a classical batch reactor. Experiments have been carried out to study the effect of reaction temperature, feed molar ratio (FMR) of alkene to TBHP and catalyst loading on the yield of 1,2-epoxyhexane and 4-vinyl-1-cyclohexane 1,2-epoxide (i.e. 4-VCH 1,2-epoxide) to optimise the reaction conditions in a batch reactor. A detailed evaluation of molybdenum (Mo) leaching from the polymer supported catalyst has been investigated by isolating any residue from reaction supernatant solutions and then using these residues as potential catalyst in epoxidation reactions. Furthermore, the efficiency of the

heterogeneous catalysts for continuous epoxidation studies have been assessed using a FlowSyn reactor by studying the effect of reaction temperature, feed molar ratio (FMR) of alkene to TBHP and feed flow rate on the conversion of the oxidant and the yield of corresponding epoxide. The continuous flow epoxidation using FlowSyn reactor has shown a considerable time savings, high reproducibility and selectivity along with remarkable improvements in catalyst stability compared to reactions carried out in a batch reactor.

### **1.1. Applications of epoxides**

A wide range of epoxides are produced on a large scale due to their high global demand either as end products or as building blocks in organic synthesis. On the other hand, a number of epoxides are produced in small scale for specialised, but important applications. The scale of epoxides production ranges from millions of tons per year to a few grams per year depending on requirements and usage.

Over 85% of worldwide consumption of ethylene oxide (EO) is in the production of ethylene glycol, which is widely employed in the manufacture of products such as pharmaceuticals, textiles, automobiles and detergents.<sup>32</sup> Additionally, EO is used as a sterilant for spices, cosmetics and medical equipment, and as a fumigant in certain agricultural products.<sup>33</sup> Propylene oxide (PO) is employed in the production of polyurethane polyols, which are largely used for the production of polyurethane foams and plastics. Other applications of PO are found in the production of cosmetics, drugs, plasticisers as well as in the manufacture of unsaturated polyester resins used in the textile and construction industries.<sup>34</sup> Epichlorohydrin is an important epoxide that is employed as a building block in the manufacture of epoxy resins, glycerols, plastics and elastomers. One of the largest world consumption of

epichlorohydrin is in the production of epoxy resins such as aryl glycidyl ethers,<sup>35</sup> which has several commercial and industrial applications.<sup>36</sup>

Hydroxyethers are useful solvents in the manufacture of lotions, ointments and creams for pharmaceutical and cosmetic applications. They serve as oil-soluble bases in which a number of lipid-soluble solids can be dissolved efficiently. Hydroxyethers are prepared by acid or alkaline catalysed reaction of aliphatic alcohols with terminal epoxides, i.e. having 6 to 18 carbon atoms including 1,2-epoxyhexane, 1,2-epoxyoctane and 1,2-epoxydecane or their *iso*-derivatives.<sup>37</sup> Epoxides of terminal and internal alkenes are also used as resin modifiers, reactive diluents for epoxy resins, stabilisers for halogen hydrocarbons and as coating materials.<sup>38</sup> Furthermore, epoxide of cyclic alkenes such as 1,2-epoxycyclohexane is an intermediate for the production of perfumes, pharmaceuticals and dyestuffs, while 4-vinyl-1-cyclohexane 1,2-epoxide (i.e 4-VCH 1,2-epoxide) is used in the production of coatings and adhesives coupling agent as well as electronic chips encapsulant.

The terpene,  $\alpha$ -pinene can be epoxidised to obtain a valuable  $\alpha$ -pinene oxide. One of the major industrially important reactions of  $\alpha$ -pinene oxide is the one-step synthesis of  $\alpha$ -campholenic alcohol, also known as naturanol, which is a key ingredient used in the perfumery and food industries due to its natural and sweet berry-like fragrance.<sup>39</sup>

Additionally,  $\alpha$ -pinene oxide has found use in the manufacture of some vital unsaturated alcohols that are employed as a sandalwood scent in the fragrance industry. Limonene, which is the main component of the orange essential oils, is an abundant, cheap, monoterpene that accumulate in bulk quantities as by-product of fruit juice industry.<sup>40,41</sup> Oxidation of limonene mostly yields 1,2-limonene oxide, which is an intermediate for production of fragrances, perfumes, food additives and pharmaceuticals.<sup>38</sup>

## 1.2. Polymeric supports for the immobilisation of catalyst

Polymer supported catalysts are made by immobilising a robust polymer support with an active species either by forming chemical bonds or through physical interactions such as hydrogen bonding or donor-acceptor interactions. Suspension polymerisation is one of the most popular and effective methods of synthesising polymers in spherical or beads form. The polymerisation reaction is of two types depending on the nature of monomers. For instance, inverse suspension polymerisation is employed for hydrophilic monomers such as acrylamide using hydrocarbon or chlorinated hydrocarbon as the bulk liquid phase in the reaction.<sup>42</sup> On the other hand, water is used as the bulk liquid phase in suspension polymerisation involving hydrophobic monomers such as styrene. The polymer resins intended for use as support are normally cross-linked using a bi-functional co-monomer such as divinylbenzene to form an infinite network.<sup>43</sup> The uniformity shape and sizes of the polymer beads prepared by suspension polymerisation method depends on the shape of the reactor, impeller diameter, stirring speed, porogen and other reaction conditions.<sup>44</sup> Basically, there are two factors that are responsible for the internal porous structure of polymer beads. These include the amount of cross-linking present and the type of organic solvent or porogen incorporated into the polymer resin. The former determines the level of swelling of the polymer, while the later creates the pores and influence the pore size, pore volume and surface area of the polymer particles.<sup>44,45</sup>

Cross-linked polystyrene based polymer and polybenzimidazole (PBI) polymer resins have been used as support for Mo(VI) complexes used as catalysts in this study. The cross-linked resin beads are commonly used as catalyst support due to their high porosity, large surface area and robust spherical particles with uniform size distribution.<sup>43</sup> On the other hand, PBI resins are well known class of polymers due to their high degree of thermal stability and



chemical resistance, and have found applications in a wide variety of uses including chromatographic processes (i.e. ion-exchange, purifications and separations), fuel cells, electronics, aerospace, as well as replacement for asbestos in high temperature applications such as conveyor belts, plastic composites and gloves.<sup>46-50</sup>

### **1.3. *tert*-Butyl hydroperoxide (TBHP) as a terminal oxidant for alkene epoxidation**

Epoxidation with alkyl hydroperoxides has received a considerable scientific attention in recent times since the reagents are readily available and inexpensive. The commonly employed alkyl hydroperoxides for epoxidation are *tert*-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP) and ethyl benzyl hydroperoxide (EBHP). There are numerous advantages of using TBHP as an oxidant for epoxidation which include high thermal conductivity, good solubility in polar solvents and neutral pH.<sup>1</sup> In addition, the oxidant is non-corrosive, safer to handle and yields *tert*-butanol as by-product, which can easily be separated from the reaction mixture by distillation. Therefore, TBHP was chosen as terminal oxidant for all the epoxidation experiments reported in this chapter. The commercially available TBHP is in the form of 70% (w/w) solution in 30% water, which serves as stabilisers. However, the water content could inhibit epoxidation reaction by causing epoxide opening and formation of diols by-products.<sup>4</sup> As a result, the oxidant is usually rendered anhydrous in toluene, benzene or dichloroethane using phase separation and azeotropic distillation technique.<sup>51</sup>

## **2. Catalysts preparation and characterisation**

The heterogeneous catalysts employed in the present study, i.e. a polystyrene 2-(aminomethyl)pyridine supported Mo(VI) complex (Ps.AMP.Mo) and a polybenzimidazole supported Mo(VI) complex (PBI.Mo) were prepared by immobilisation of molybdenum

metal species derived from molybdenyl acetylacetonate ( $\text{MoO}_2(\text{acac})_2$ ) on two types of polymers, namely a polystyrene 2-aminomethyl(pyridine) (Ps.AMP) and a polybenzimidazole (PBI). A ligand known as 2-(aminomethyl)pyridine (AMP) was firstly attached to the polystyrene based resin to act as the site for coordination of the metal centre. On the other hand, no separate ligand was introduced onto the PBI resin since the benzimidazole residue of the backbone acts as the coordination point for Mo(VI) centre.<sup>52</sup> The catalysts have been characterised extensively to determine their molecular structures, morphological and physico-chemical properties.

## **2.1. Preparation of polystyrene 2-(aminomethyl)pyridine supported Mo(VI) complex (Ps.AMP.Mo)**

The procedure for the preparation of Ps.AMP.Mo catalyst involves three main stages, which are described in the following sections:

### **2.1.1. Synthesis of poly (divinylbenzene-co-vinylbenzyl chloride-co-styrene) resin (Ps.VBC)**

The polystyrene based resin used for immobilisation of Mo was prepared by suspension polymerisation method. The aqueous continuous phase for the reaction was prepared by dissolving 7.5 g of polyvinyl alcohol (PVOH) in water at ~373 K followed by addition of 33 g of sodium chloride. The mixture was stirred until the solids dissolved completely. The solution was allowed to cool down to room temperature and then more water was added until the volume was brought to 1 L, to give a 0.75% PVOH and 3.3% sodium chloride solution. The resulting solution (634 mL) was added to a 1 L parallel-sided, jacketed glass baffled reactor equipped with a condenser, double impeller and mechanical stirrer. The volume ratio of organic to the aqueous phase was 1:20.

A flash column chromatography was used to purify each of the organic monomers (divinylbenzene (DVB), vinylbenzyl chloride (VBC) and styrene) using silica gel and nitrogen gas. The organic phase for the synthesis of 15 g of the resin (Ps.VBC) was prepared by stirring the mixture of DVB (1.95 mL, 12%, 1.8 g), VBC (3.5 mL, 25%, 3.75 g), styrene (10.39 mL, 63%, 9.45 g), 0.15 g of 2,2-azobis isobutyronitrile (AIBN) (equivalent to 1% by weight of the co-monomers) and 2-ethylhexanol (15.84 mL, 1/1 by volume ratio of the co-monomers, 17.03 g) as a porogen in a 0.25 L conical flask. The resulting organic solution was added to the aqueous phase in a 1 L reactor and nitrogen gas was bubbled through the stirred mixture for 30 minutes before starting the reaction.

The suspension polymerisation reaction was carried out under nitrogen atmosphere at 353 K for a period of 6 hours, with stirrer speed set at 500 rpm. After the reaction was completed, the resulting beads were filtered off and washed exhaustively with distilled water. A sonic bath was used to remove other impurities such as traces of NaCl and PVOH that remains in the beads. Finally the beads were washed successively with methanol and acetone, and then with acetone only. The beads were dried in a vacuum oven at 313 K. The reaction for the synthesis of Ps.VBC is illustrated by Figure 1.

### **2.1.2. Synthesis of polystyrene 2-(aminomethyl)pyridine (Ps.AMP) beads**

The synthesis of Ps.AMP resin involves a nucleophilic substitution of the  $-\text{CH}_2\text{Cl}$  functional group of the chloromethylated polystyrene resin (Ps.VBC) by amino group of 2-aminomethyl pyridine (AMP). The amination reaction was carried out with an excess of AMP, using 1:4 mole ratio of Ps.VBC to AMP. For instance, Ps.VBC (35 g, 0.07315 mol of Cl) was refluxed with AMP (31.643 g, 30.4 mL, 0.2926 mol) in ~500 mL of ethanol for 48 h, with stirring at

~150 rpm using an overhead mechanical device. The beads were filtered off at the end of the reaction, washed with acetone/water and then stirred gently overnight in pyridine. The beads were again filtered off and washed successively with water, water/methanol and acetone, and finally dried in a vacuum oven at 313 K. The reaction for the synthesis of polystyrene 2-(aminomethyl)pyridine (Ps.AMP) is shown in Figure 2.

### **2.1.3. Loading of Mo(VI) complex onto Ps.AMP resin**

Ps.AMP resin (17.5g) was refluxed with an excess of molybdenyl acetylacetonate ( $\text{MoO}_2(\text{acac})_2$ ) (20.77g) in anhydrous toluene for a period of 4 days. The reaction is illustrated by Figure 3. The ratio of  $\text{MoO}_2(\text{acac})_2$  to functional ligand used was 1:2. The reaction was carried out in a 0.25 L reactor at ~378 K (i.e. close to the boiling point of toluene) and stirred gently with overhead mechanical device at ~150 rpm. The particles changed colour from brown to blue during the reaction. The catalyst particles were filtered off at the end of the reaction and extracted exhaustively with acetone to remove the excess  $\text{MoO}_2(\text{acac})_2$ . The dark-blue colour for the washings gradually disappeared upon repeated introduction of fresh solvent until the solution remained colourless. Finally, the Ps.AMP.Mo catalyst particles were collected and dried under vacuum oven at 313 K.

### **2.2. Preparation of polybenzimidazole supported Mo(VI) complex (PBI.Mo)**

The wet polybenzimidazole (PBI) resin beads were supplied by Celanese Corporation, USA, and were pre-treated by stirring in 1 M NaOH solution overnight. The polymer beads were then washed with deionised water until the pH of the washings turns neutral, and then washed with acetone before being dried under vacuum at 313 K.

The polymer supported Mo(VI) catalyst (PBI.Mo) was prepared by using a ligand exchange procedure in which the treated PBI resin was reacted with an excess of  $\text{MoO}_2(\text{acac})_2$  in the stoichiometric ratio of 2:1  $\text{MoO}_2(\text{acac})_2$  to functional ligand. For instance, 5 g of the treated PBI resin was refluxed with 17.68 g of  $\text{MoO}_2(\text{acac})_2$  in anhydrous toluene. The loading of Mo(VI) complex onto PBI resin was carried out using the same procedure as described in Section 2.1.3. The PBI beads changed colour from brown to green during this period. At the end of the reaction, the PBI.Mo catalyst particles were filtered off and extracted exhaustively with acetone to remove the excess  $\text{MoO}_2(\text{acac})_2$  in a similar way as described in Section 2.1.3. The catalyst was then dried under vacuum oven at 313 K. The reaction is illustrated by Figure 4.

### 2.3. Catalysts characterisation

The polymer supported Mo(VI) catalysts, i.e. Ps.AMP.Mo and PBI.Mo have been characterised extensively to determine their molecular structure, morphological and physico-chemical properties. The infrared spectra of Ps.AMP.Mo and PBI.Mo catalysts were observed on a Thermal Nicolet Avectar 370 DTGS. The spectrum of Ps.AMP.Mo catalyst (Figure 5) has revealed some bands at the range of  $\sim 760\text{ cm}^{-1}$  to  $\sim 800\text{ cm}^{-1}$ , which are characteristic of Mo=O symmetrical and antisymmetric stretches. On the other hand, the band recorded at  $\sim 700\text{ cm}^{-1}$  could most likely be associated with stretching of Mo-O-Mo bridges.<sup>52</sup> Similarly, the PBI.Mo spectrum showed Mo=O and Mo-O-Mo vibrations characteristics with absorptions around  $\sim 690\text{ cm}^{-1}$  to  $\sim 900\text{ cm}^{-1}$  (Figure 5). Therefore, the FTIR spectra of both Ps.AMP.Mo and PBI.Mo catalysts confirm the incorporation of Mo centers in both resins due to the presence of Mo=O and M-O-Mo features.

The molybdenum content of the prepared catalysts was analysed using Perkin-Elmer AAnalyst 200 spectrophotometer. A sample of each polymer supported complex (~0.1 g) was grounded to fine powder and digested in 15 mL aqua regia for 3 days. Aqua regia is a mixture of concentrated HNO<sub>3</sub> and HCL in the volume ratio of 1:3. The resulting mixture was diluted to 100 mL with distilled water and Mo content was analysed using an atomic absorption spectrophotometer (AAS). The Mo content of Ps.AMP.Mo and PBI.Mo catalyst and the corresponding ligand:Mo ratio are given in Table 1.

The morphology of Ps.AMP.Mo and PBI.Mo catalysts particles were observed using a JEOL JSM-6300F scanning electron microscope (SEM). The SEM images of Ps.AMP.Mo and PBI.Mo (Figure 6) revealed an obvious similarity in the morphology of the two polymer supports. Neglecting mechanical damages to the samples, the SEM images of both catalysts have a well dispersed spherical smooth surface, a characteristic of macroporous polymer resins.<sup>52</sup> Apparently, the sizes of PBI.Mo catalyst beads (Figure 6b) are approximately double in size than those of Ps.AMP.Mo catalyst (Figure 6a).

The particle size measurement was carried out using Malvern Mastersizer and true density of the catalysts was measured using micrometrics multivolume pycnometer-1305. As shown in Table 1, Ps.AMP.Mo catalyst has particles sizes in the range of 119–153 μm, which are smaller compared to PBI.Mo catalyst with the particle size range of 243–335 μm. The average densities of Ps.AMP.Mo and PBI.Mo catalyst particles were found to be 1.44 g cm<sup>-3</sup> and 1.74 g cm<sup>-3</sup>, respectively. The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore diameter were determined by nitrogen adsorption and desorption method using Micromeritics ASAP (accelerated surface area and porosimetry) 2010. The results obtained

for BET surface area, pore volume and pore diameter of Ps.AMP.Mo and PBI.Mo catalysts are presented in Table 1.

### **3. Batch epoxidation studies**

Batch epoxidation experiments have been carried out in a classical batch reactor to evaluate the catalytic activity and stability of Ps.AMP.Mo and PBI.Mo catalysts using TBHP as an oxidant. The suitability and efficiency of both catalysts for alkene epoxidation have been compared by studying the effect of various parameters such as reaction temperature, feed molar ratio of alkene to TBHP and catalyst loading on the yield of epoxide for optimisation of reaction conditions in a batch reactor. A detailed evaluation of molybdenum (Mo) leaching from the polymer supported catalysts has been conducted by assessing the catalytic activity of the residue obtained from the supernatant solutions of the reaction mixture after removal of the heterogeneous catalyst. The results of batch epoxidation form the basis for continuous epoxidation experiments in a FlowSyn reactor.

#### **3.1. Preparation of *tert*-butyl hydroperoxide (TBHP) solution**

TBHP solution in water (70% w/w) was purchased from Sigma-Aldrich Co. Ltd and the water content was removed by Dean-Stark apparatus from a toluene solution following a modified procedure that was previously reported by Sharpless and Verhoeven.<sup>51</sup> For instance, 130 mL of TBHP solution in water (70% w/w) and 160 mL of toluene were placed in a 0.5 L separating funnel. The mixture was swirled vigorously for about one minute and allowed to settle, forming organic and aqueous layers. Approximately 30 mL of the aqueous layer was removed from the mixture and the remaining portion (organic layer) was transferred into a 0.5 L doubled-necked round bottom flask equipped with thermostat, Dean-Stark apparatus and reflux condenser. The flask was immersed in paraffin oil contained in a 1 L Pyrex glass

basin. The mixture was heated on a hot plate via the paraffin oil. A magnetic stirrer was placed both in the mixture and in the paraffin oil to enhance heat distribution. The solution was refluxed for about 2 h and the temperature of the paraffin oil was kept at 413–418 K using a thermostat. The distillate, which is mostly water was collected from the side arm and the remaining solution of anhydrous TBHP in toluene was cooled at room temperature and stored over 4A molecular sieves in a fridge at 275–281 K. The concentration of TBHP in toluene solution was determined by iodometric titration.<sup>51</sup>

### **3.2. Batch epoxidation procedure**

Batch epoxidation of alkenes with TBHP as an oxidant in the presence of polymer supported Mo(VI) catalyst was conducted in a 0.25 L jacketed four neck glass reactor. The batch reactor was equipped with a condenser, overhead stirrer, digital thermocouple, sampling point and water bath.

Known quantities of alkene and TBHP were weighted out and introduced into the reactor vessel and stirring was started. Feed molar ratio (FMR) of alkene to TBHP of 1:1–10:1 was selected for charging the reactor and agitation was started at the desired rate (400 rpm). Heating to the reaction mixture was supplied through water bath via the reactor jacket and monitored by digital thermocouple. The temperature of the reaction mixture was allowed to reach the desired value, i.e. 323 K–343 K and was maintained in the range of  $\pm 0.5$  K throughout the batch experiment. Known amount of catalyst (0.15–0.6 mol% Mo loading) was added into the reactor when the reaction mixture reached a constant desired temperature. A sample was collected after the catalyst was added and the time was noted as zero time, i.e.  $t = 0$ . Subsequent samples were taken from the reaction mixture at specific time and analysed



using Shimadzu GC-2014 gas chromatography (GC). The reactions for epoxidation of the model alkenes are illustrated by Figure 7.

### **3.3. Method of analysis**

Shimadzu GC-2014 gas chromatography was used for the analysis of samples collected during epoxidation experiments. The instrument was fitted with a flame ionisation detector (FID), auto-injector and a 30 m long Econo-CapTM-5 (ECTM-5) capillary column (purchased from Alltech Associates, Inc., USA) with internal diameter 320  $\mu\text{m}$  and film thickness 0.25  $\mu\text{m}$ . The carrier gas used was helium at a flow rate of 1  $\text{mL}/\text{min}^{-1}$ .

A split ratio of 100:1 and injection volume of 0.5  $\mu\text{L}$  were selected as part of the GC method. Both injector and detector temperatures were maintained at 523 K. A ramp method was developed to separate all the components in the sample. In the ramp method, the oven temperature was initially set at 313 K, and the sample was then injected by the auto injector. The oven temperature was maintained at 313 K for 4 min after the sample was injected and ramped from 313 K to 498 K at the rate of 293  $\text{K}/\text{min}^{-1}$ . Each sample took  $\sim 13$  min to be analysed by GC and the oven temperature was cooled back to 313 K before the next run was started.

### **3.4. Batch epoxidation results**

Batch epoxidation of 1-hexene and 4-vinyl-1-cyclohexene (4-VCH) with TBHP as an oxidant have been carried out under different reaction conditions to study the effect of reaction temperature, feed molar ratio (FMR) of alkene to TBHP and catalyst loading on the yield of epoxide. The reusability and supernatant studies have been carried out to evaluate the long term stability of each of the catalyst as well as the leaching of Mo from the polymer support. Both Ps.AMP.Mo and PBI.Mo catalysts have been found to be selective in the formation of

1,2-epoxyhexane and 4-vinyl-1-cyclohexane 1,2-epoxide (i.e. 4-VCH 1,2-epoxide) in the epoxidation of 1-hexene and 4-VCH with TBHP, respectively. The GC analysis of the reaction mixtures for 4-VCH epoxidation showed no evidence of either terminal or diepoxide products.

### **3.4.1. 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 polymer supported Mo(VI) catalysts. 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. Therefore, it can be concluded that external mass transfer resistances was absent in this study. On the other hand, most of the particles of Ps.AMP.Mo and PBI.Mo lie within the size range of 119–335  $\mu\text{m}$ , which are fairly uniform. According to Clerici and Kholdeeva,<sup>53</sup> mass transfer limitation could be eliminated when the catalyst particles are small and fairly uniform. Therefore, it was presumed that internal mass transfer resistance would be negligible for both Ps.AMP.Mo and PBI.Mo catalysed epoxidation reactions due to the nature of the catalysts particles. On the basis of these investigations, all batch epoxidation experiments were carried out with stirrer speed of 400 rpm using Ps.AMP.Mo and PBI.Mo catalysts as prepared.

### 3.4.2. Effect of reaction temperature

Alkene epoxidation with alkyl hydroperoxides essentially require a thorough screening of reaction temperature in order to achieve high conversion of the oxidant and high product selectivity. Hence, epoxidation of 1-hexene and 4-VCH with TBHP have been carried out at 333 K, 343 K and 353 K to study the effect of reaction temperature on the yield of corresponding epoxide.

As expected, higher reaction temperatures gave higher yield of epoxide at fixed reaction time for all the alkene studied. Figure 8a shows that the yield of 1,2-epoxyhexane using Ps.AMP.Mo catalyst at 260 min was 83% and 88% at 343 K and 353 K, respectively, whilst a significant drop in the yield of 1,2-epoxyhexane (57%) was recorded over the same period when the experiment was carried out at 333 K. Similar trends in the yield of 1,2-epoxyhexane (Figure 8b) and the yield of 4-VCH 1,2-epoxide (Figure 8d) were observed when PBI.Mo catalyst was used. On the other hand, epoxidation of 4-VCH 1,2-epoxide in the presence of Ps.AMP.Mo reached equilibrium within the first 5 min for the experiment carried out at 353 K as shown in Figure 8c. This was due to distinct exothermic effect observed during that period. The temperature was controlled immediately to maintain the reaction at 353 K. Therefore, significantly higher yield of 4-VCH 1,2-epoxide obtained at that temperature was probably due to the exothermic effect. The yield of 4-VCH 1,2-epoxide during first 5 min at 353 K was ~94%. The effect was not so noticeable at 343 K and 333 K. However, the yield of 4-VCH 1,2-epoxide obtained at 260 min was ~95% for all the three temperature ranges. The experiments were replicated twice and the same behavior was observed in both cases. Ambroziak et al.<sup>5</sup> observed similar exothermic effect while studying the effect of reaction temperature on cyclohexene epoxidation with TBHP catalysed by polymer supported Mo(VI)

complex. Therefore, it can be concluded that 353 K is the preferred reaction temperature for both Ps.AMP.Mo and PBI.Mo catalysed epoxidation of 1-hexene and 4-VCH (Figures 8a–d).

### 3.4.3. Effect of feed molar ratio (FMR)

In most of the catalysed alkene epoxidation processes, reactions are conducted with a substantially excess of alkene in order to avoid over oxidation, achieve high conversion of the oxidant and high yield of epoxide. Consequently, a number of batch experiments have been carried out to study the effect of different feed molar ratio of alkene to TBHP on the yield of epoxide.

In case of Ps.AMP.Mo catalysed epoxidation of 1-hexene and 4-VCH, an increase in feed molar ratio of alkene to TBHP from 2.5:1 to 10:1 resulted in a marked increase in the yield of 1,2-epoxyhexane (Figure 9a) and 4-VCH 1,2-epoxide (Figure 9c). For instance, the yield of 1,2-epoxyhexane obtained at 260 min for 2.5:1 and 10:1 molar ratio of 1-hexene to TBHP was 61% and 97%, respectively (9a). The experiments conducted at 2.5:1 and 10:1 molar ratio of 4-VCH to TBHP gave 92% and 98% yield of 4-VCH 1,2-epoxide, respectively at 260 min (Figure 9c). Similarly, a significant increase in the rate of epoxides formation was observed when the feed molar ratio of alkene to TBHP was increased from 2.5:1 to 5:1 for PBI.Mo catalysed epoxidation of 1-hexene (Figure 9b) and 4-VCH (Figure 9d). Surprisingly, for PBI.Mo catalysed epoxidation of 1-hexene (Figure 9b) and 4-VCH (Figure 9d), an increase in the feed molar ratio of alkene to TBHP from 5:1 to 10:1 decreases the rate of formation of corresponding epoxide which is unusual. However, similar unexpected results were reported by Ambroziak et al.<sup>5</sup> for 1-octene epoxidation with TBHP in the presence of polymer supported Mo(VI) catalyst when the molar ratio of 1-octene to TBHP was increased from 5:1 to 10:1.

Based on the results obtained from this study, it can be concluded that the effect of alkene to TBHP feed ratio is dependent not only on the type of alkene but also the catalyst used. In the case of PBI.Mo catalysed epoxidation of 1-hexene and 4-VCH, increasing the feed molar ratio of alkene to TBHP beyond 5:1 decreases the TBHP concentration to such an extent as to cause a reduction in the yield of epoxide. Therefore, the feed molar ratio of 10:1 (alkene to TBHP) can be considered as the optimum for Ps.AMP.Mo catalysed epoxidation of 1-hexene and 4-VCH (Figures 9a and c), while feed molar ratio of 5:1 can be regarded as the optimum for epoxidation of both alkenes in the presence of PBI.Mo catalyst (Figures 9b and d).

#### **3.4.4. Effect of catalyst loading**

In this chapter, the catalyst loading was defined based on the active Mo content instead of the total mass of the polymer supported catalysts in order to take into account the slight differences in Mo loading that could arise from different batches of the prepared catalysts. However, all the experiments in this study were conducted from one batch of the prepared catalysts.

An increase in catalyst loading increases the number of active sites per unit volume of reactor leading to an increase in the yield of epoxides. Thus, the effect of catalyst loading (i.e. mole ratio of Mo to TBHP  $\times$  100%) for epoxidation of 1-hexene and 4-VCH with TBHP was investigated by conducting batch experiments using 0.15 mol% Mo, 0.3 mol% Mo and 0.6 mol% Mo catalyst loading. Epoxidation of 1-hexene catalysed by Ps.AMP.Mo catalyst shows identical trends in the rate of epoxidation when the catalyst loading was increased from 0.3 mol% Mo to 0.6 mol% Mo as shown in Figure 10a. On the other hand, 4-VCH epoxidation in the presence of Ps.AMP.Mo reached equilibrium within the first 20 min for catalyst loading of 0.6 mol% Mo, whilst it took 100 min to achieve equilibrium for reaction

conducted at 0.3 mol% Mo loading (Figure 10c). It should be noted that Ps.APM.Mo catalyst demonstrates a remarkable catalytic performance for 4-VCH epoxidation as evident by the higher yield of 4-VCH 1,2-epoxide (~90%) obtained at 260 min using 0.15 mol% Mo (Figure 10c) compared to the yield of epoxide achieved with other experiments carried out at 0.15 mol% Mo (Figures 10a, b and d). It can be concluded from Figures 10a–d that the catalyst loading of 0.6 mol% Mo was found to be the optimum for both Ps.AMP.Mo and PBI.Mo catalysed epoxidation of 1-hexene and 4-VCH.

### **3.4.5. Catalyst reusability studies**

Transition metal catalysts that could be reused several times without significant loss in activity are generally attractive for commercial applications as most of the metal complexes are very expensive to purchase and difficult to prepare. The reusability potentials of Ps.AMP.Mo and PBI.Mo catalysts for 1-hexene and 4-VCH epoxidation have been investigated by recycling the catalysts several times in batch experiments. The results are presented in Figure 11.

In this study, a fresh catalyst was used for 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 313 K. The stored catalyst particles were reused in the subsequent experiment and plotted as Run 2. This procedure was repeated for the successive catalyst reusability experiments, i.e. Run 3–Run 6. In addition, uncatalysed epoxidation experiment was carried out and plotted for comparison with the catalysed experimental results. As shown in Figures 11a–d, high rate of epoxidation was observed in Run 1 as compared to subsequent runs. This is due to the sufficient active sites that are available for adsorption by the reacting species in the fresh

catalyst sample compared with subsequent runs. The rate of formation of epoxide for Run 2 and Run 3 were quite similar in Ps.AMP.Mo catalysed epoxidation of 1-hexene (Figure 11a) and 4-VCH (Figure 11c). The yield of 1,2-epoxyhexane obtained at 260 min was ~80% in both Run 2 and Run 3 (Figure 11a), while ~96% yield of 4-VCH 1,2-epoxide was obtained for Run 1–Run 3 over the same period (Figure 11c). However, a significant drop in the rate of epoxide formation was observed in the subsequent Run 4–Run 6 in Ps.AMP.Mo catalysed epoxidation of 1-hexene and 4-VCH (Figures 11a and c). Similarly, for epoxidation in the presence of PBI.Mo catalyst, the yield of 1,2-epoxyhexane and 4-VCH 1,2-epoxide was decreased to ~11% after Run 6 as compared to Run 1 (Figures 11b and d).

The most distinguishing parameter that differentiates Ps.AMP.Mo catalyst from PBI.Mo catalyst is the ligand to Mo ratio. In case of Ps.AMP.Mo catalyst, the ligand to Mo ratio is 0.68:1, while it is 2.58:1 for PBI.Mo catalyst. It is obvious that Ps.AMP.Mo has an excess of Mo to ligand content as compared to PBI.Mo. Therefore, Mo is lost during reaction with Ps.AMP.Mo catalyst since a significant proportion of Mo introduced at the outset cannot be coordinated by polymer immobilised ligand. In case of PBI.Mo catalyst, it seems most of the Mo introduced at the outset is coordinated by polymer immobilised ligand and the Mo species that becomes mobile during catalysis are effectively recaptured by the presence of excess ligand on the support. On the other hand, Mo species containing microgel are lost from both Ps.AMP.Mo and PBI.Mo catalysts as a result of mechanical agitation. It could be concluded that the reason for the decrease in catalytic activity after each successive experimental run for both catalysts was due to loss of catalytically active Mo from the polymer supports, either as soluble leached complexes or as traces of Mo containing microgel released as a result of mechanical attrition of the beads or both.

### 3.4.6. Supernatant studies

The aim of this analysis is to investigate the extent of Mo leaching from the polymer supported catalysts. Once each reusability study experiment was completed (see Section 3.4.5), the catalyst particles were filtered out and the reaction mixture was vacuum distilled to recover the residue from reaction supernatant solutions. The isolated residue from supernatant solution of fresh catalyst was used as a potential catalyst for epoxidation and plotted as Run 1 in Figures 12. The same procedure was repeated for all the subsequent reusability studies and the corresponding residue obtained was used as catalyst for the supernatant studies. Furthermore, a control experiment was carried out in the absence of residue and plotted in Figures 12 for comparison with the experiments carried out in the presence of residue.

The residue isolated from Ps.AMP.Mo catalysed epoxidation of 1-hexene and 4-VCH revealed high content of catalytically active Mo as shown in Figures 12a and c. This was evident by the catalytic effect observed when the experiments were conducted in the presence of residue. The amount of Mo retained by the catalyst after Run 1 was  $0.70 \text{ mmol g}^{-1}$ , while it was  $0.62 \text{ mmol g}^{-1}$  and  $0.56 \text{ mmol g}^{-1}$  after Run 2 and Run 3, respectively as compared to the Mo content in the fresh Ps.AMP.Mo, i.e.  $0.74 \text{ mmol g}^{-1}$  resin (see Table 1). The yield of epoxide achieved from the supernatant studies of 1-hexene and 4-VCH after Run 1 was 67% (Figure 12a) and 47% (Figure 12c), respectively. The yield of epoxide decreased steadily for the subsequent experimental runs and became negligible after 4–6 runs (Figures 12a and c).

It can be seen from Figure 12b that epoxidation of 1-hexene catalysed by residue of PBI.Mo revealed the presence of some catalytically active Mo species after Run 1 as evident by the minor catalytic effect displayed by the reaction. However, the residue obtained from subsequent experimental runs show no signs of catalytic effect (Figure 12b). On the other



hand, 4-VCH epoxidation in the presence of residue of PBI.Mo failed to show any trace of Mo leaching as shown in Figure 12d. Thus, it can be concluded that the leaching of Mo in Ps.AMP.Mo catalysed epoxidation becomes negligible after 4–5 experimental runs.

### **3.4.7. Optimisation study of alkene epoxidation**

Further study aimed at achieving a set of optimum reaction conditions that would produce maximum yield of epoxide for 1-hexene epoxidation have been carried out using the optimum reaction parameters. For 1-hexene epoxidation catalysed by Ps.AMP.Mo catalyst, the optimisation study was conducted at a reaction temperature of 353 K, catalyst loading of 0.6 mol% Mo and feed molar ratio of 1-hexene to TBHP of 10:1. In case of PBI.Mo catalysed epoxidation of 1-hexene, reaction temperature has the most pronounced effect on the yield of epoxide as shown in Figure 8b, while the influence of catalyst loading was not very distinct (Figures 10b). Furthermore, the reaction conducted at a feed molar ratio of 1-hexene to TBHP of 5:1 achieved higher yield of epoxide than the one carried out at a feed molar ratio of 10:1 (Figure 9b). Hence, optimisation study for 1-hexene epoxidation in the presence of PBI.Mo was carried out at a reaction temperature of 353 K, catalyst loading of 0.6 mol% Mo and feed molar ratio of 1-hexene to TBHP of 5:1. The maximum yield of 1,2-epoxyhexane obtained at the optimum reaction conditions for Ps.AMP.Mo catalysed reaction at 260 min was ~97% (13a), while the yield of epoxide achieved at the same period with the optimum conditions using PBI.Mo was ~86% (Figure 13b).

## **4. Continuous alkene epoxidation in a Flowsyn reactor**

Continuous epoxidation of 1-hexene and 4-vinyl-1-cyclohexene (4-VCH) have been carried out in a FlowSyn continuous flow reactor supplied by Uniqsis ltd, in the presence of Ps.AMP.Mo and PBI.Mo as catalysts. The instrument is equipped with two independent

HPLC pumps, control interface and SquirrelView software with data logger (supplied by Grant Instruments). The catalytic fixed bed is made of stainless steel (SS) column of length 130 mm (internal diameter 7 mm and outer diameter 10 mm). The fluid paths in FlowSyn reactor were connected with each other using a perfluoropolymer tubing of 0.5 mm internal diameter. Each HPLC pump was primed before starting the experiment to remove air bubbles that may be present in the fluid paths. All the reaction parameters including reaction temperature, feed flow rate and pressure limits were set using the control interface of FlowSyn reactor. The SquirrelView software and data logger were employed as additional components to the FlowSyn unit to precisely monitor and record the temperature profile of the mobile phase in the fixed bed column. The stainless steel column reactor was packed with the catalyst ( $1.5 \pm 0.02$  g) and enclosed in an electronically controlled column heater. The schematic of the experimental set-up of FlowSyn reactor is shown in Figure 14.

Continuous epoxidation studies was carried out following optimisation of the reaction conditions as well as extensive evaluation of the activity and reusability of the heterogeneous catalysts for alkene epoxidation in a 0.25 L jacketed stirred batch reactor (see Section 3).

#### **4.1. Continuous epoxidation procedure in a FlowSyn reactor**

Before starting continuous epoxidation experiment using a FlowSyn reactor, the alkene was fed continuously by an HPLC pump until the column reactor and tubings are completely saturated. The heating to the column was set to the required value and the temperature of the mobile phase was allowed to reach the desired level and maintained at  $\pm 2$  K. Once the column was saturated with alkene and the desired temperature was achieved, continuous epoxidation experiment was started.

The reactants were continuously fed at a desired flow rate by two HPLC pumps to the packed column via a mixing chamber. As soon as the reactants entered the column, reaction takes place in the presence of the catalyst to produce epoxide. The fluid from the outlet port of the packed column was collected in a fraction collector. The samples were taken at specific time intervals and were analysed by Shimadzu GC-2014 gas chromatography (see Section 3.3). The fluid paths in FlowSyn reactor were properly cleaned by flushing with *iso*-propanol (solvent) at the end of each experimental run.

#### **4.2. Continuous epoxidation results**

In continuous epoxidation experiment using a FlowSyn reactor, a small volume of the reaction mixture is in contact with a relatively large volume of the catalyst in the stainless steel column reactor. Moreover, particle size distribution is one of the most important properties that suggest the adaptability of a catalyst to continuous flow reaction since fine powdered catalyst materials may cause high pressure drop in the fixed bed reactor. The particle size range of Ps.AMP.Mo catalyst (i.e. 119–153  $\mu\text{m}$ ) allow a stable system pressure during the reaction, thereby providing a constant flow of the feed through the reactor channels. Optimisation of reaction conditions have been carried out by studying the effect of different parameters such as reaction temperature, feed flow rate and feed molar ratio of the alkene to TBHP on the conversion of TBHP and the yield of epoxide at steady state, i.e. at 2 h. Figure 15 shows the steady state mole fractions of the various constituents in the reaction mixture for continuous epoxidation of 4-VCH with TBHP as an oxidant. The long term stability of Ps.AMP.Mo catalyst for continuous epoxidation has been evaluated by reusing the same catalytic packing several times under similar reaction conditions. Furthermore, continuous epoxidation of 1-hexene and 4-VCH with TBHP have been carried out in the presence of PBI.Mo as a catalyst using the optimum reaction conditions recorded when

Ps.AMP.Mo catalyst was used, so as to compare the catalytic performances of both catalysts for continuous epoxidation.

#### **4.2.1. Effect of reaction temperature**

Continuous epoxidation of 1-hexene and 4-VCH with TBHP in the presence of Ps.AMP.Mo as a catalyst was carried out at 333 K, 343 K and 353 K to study the effect of reaction temperature on the conversion of TBHP and the yield of epoxide. The experiments were conducted using 5:1 molar ratio of alkene to TBHP and the feed flow rate was maintained at 0.1 mL/min. The temperature of the mobile phase in the catalytic column was monitored with the aid of SquirrelView software.

It can be seen from Figure 16a that ~45% conversion of TBHP and ~42% yield of 1,2-epoxyhexane was achieved at steady state for epoxidation of 1-hexene conducted at 333 K, whilst the reactions carried out at 353 K gave ~79% conversion of TBHP and ~64% yield of 1,2-epoxyhexane. The effect of reaction temperature on continuous epoxidation of 4-VCH with TBHP revealed higher conversion of TBHP and yield of epoxide compared to 1-hexene epoxidation for all the temperature ranges studied as shown in Figure 16b. The conversion of TBHP and the yield of 4-VCH 1,2-epoxide at 333 K was found to be ~66% and ~64%, respectively (Figure 16b). However, a significant increase in the conversion of TBHP (~95%) and the yield of 4-VCH 1,2-epoxide (~82%) was obtained for reaction carried out at 353 K (Figure 16b). Hence, 353 K was selected for further optimisation studies of 1-hexene and 4-VCH epoxidation in a FlowSyn reactor.

#### **4.2.2. Effect of feed flow rate**

The effect of feed flow rate was investigated at 0.1 mL/min, 0.13 mL/min and 0.16 mL/min. These flow rates correspond to the feed residence time in the reactor of ~5 min, ~4 min and ~3 min, respectively. The experiments were carried out at 353 K (i.e. the optimum reaction temperature) and at a feed molar ratio of 5:1 (alkene to TBHP) using Ps.AMP.Mo as a catalyst.

An increase in feed residence time in the catalytic feed bed reactor by reducing the flow rate could have a positive impact on the catalytic performance in a continuous flow reaction. In case of 1-hexene epoxidation, experiments carried out at a flow rate of 0.16 mL/min achieved ~68% conversion of TBHP and ~51% yield of 1,2-epoxyhexane as shown in Figure 17a. On the other hand, for 4-VCH epoxidation at a feed flow rate of 0.16 mL/min gave ~84% conversion of TBHP and ~73% yield of 4-VCH 1,2-epoxide (Figure 17b). However, when the residence time of the feed was increased to ~4 min by reducing the flow rate to 0.13 mL/min, ~70% conversion of TBHP and ~55% yield of 1,2-epoxyhexane were recorded for 1-hexene epoxidation (Figure 17a), whilst the conversion of TBHP and the yield of 4-VCH 1,2-epoxide obtained at 0.13 mL/min increased to ~90% and ~77%, respectively in case of 4-VCH epoxidation (Figure 17b). Thus, it can be concluded that an increase in feed flow rate caused reduction in feed residence time in the reaction zone (packed column), which consequently led to decrease in both the conversion of TBHP and the yield of corresponding epoxides in the continuous flow epoxidation.

#### **4.2.3. Effect of feed molar ratio of alkene to TBHP**

The effect of feed molar ratio of alkene to TBHP of 1:1, 2.5:1 and 5:1 was studied. The continuous epoxidation experiments have been carried out at a feed flow rate of 0.1 mL/min

and at a reaction temperature of 353 K. Figure 18 illustrates that both TBHP conversion and the yield of epoxide increases with an increase in feed molar ratio of alkene to TBHP. The experiment conducted at a feed molar ratio of 1-hexene to TBHP of 1:1 resulted in similar TBHP conversion and yield of 1,2-epoxyhexane (~18%) as shown in Figure 18a. However, when a feed molar ratio of 1-hexene to TBHP of 2.5:1 was used, ~73% conversion of TBHP and ~63% yield of 1,2-epoxyhexane was achieved. Similarly, the reaction carried out at a feed molar ratio of 4-VCH to TBHP of 1:1 recorded ~50% conversion of TBHP and ~43% yield of 4-VCH 1,2-epoxide (Figure 18b). However, a significant increase in both the conversion of TBHP (~78%) and the yield of 4-VCH 1,2-epoxide (~70%) was obtained at a feed molar ratio of 4-VCH to TBHP of 2.5:1 (Figure 18b). Therefore, it can be concluded that the feed molar ratio of 5:1 (alkene to TBHP) is the appropriate molar ratio for continuous epoxidation of 1-hexene and 4-VCH with TBHP in the presence of Ps.AMP.Mo catalyst.

#### **4.2.4. Catalyst reusability studies**

Reusability studies of Ps.AMP.Mo catalyst in batch epoxidation of 1-hexene and 4-VCH with TBHP was slightly affected by attrition of catalyst particles and leaching of Mo containing microgel from the polymer support when the catalyst was reused under stirred condition in a batch reactor (see Figures 11a and c). In continuous epoxidation of 1-hexene and 4-VCH with TBHP using FlowSyn reactor, Ps.AMP.Mo catalyst was firmly packed inside a stainless steel column and there was no stirring involved. The reusability studies were carried out in a FlowSyn reactor using the same catalyst packing for four consecutive experimental runs, and each experiment lasted for 6 h. Therefore, the catalyst packing was used in continuous experiments for a period of 24 h. All the experiments for this study were carried out at a feed flow rate of 0.1 mL/min, reaction temperature of 353 K and feed molar ratio of alkene to TBHP of 5:1.

The reusability studies showed Ps.AMP.Mo catalyst which was reused for four consecutive experimental runs under the same conditions had negligible loss in catalytic activity. In case of 4-VCH epoxidation, the conversion of TBHP and the yield of 4-VCH 1,2-epoxide at steady state was found to be in the range of  $95\pm 4\%$  and  $82\pm 4\%$ , respectively for all the four experimental runs. On the other hand, 1-hexene epoxidation under similar conditions gave  $79\pm 4\%$  and  $64\pm 4\%$  conversion of TBHP and yield of 1,2-epoxyhexane, respectively when the catalyst was reused for four times. It could be concluded that the problems of attrition of catalyst particles and leaching of Mo observed in batch studies have been eliminated in continuous flow experiments. Therefore, Ps.AMP.Mo catalyst could be reused several times for continuous epoxidation of alkene with TBHP in a fixed bed column.

### **4.3. Continuous epoxidation catalysed by polybenzimidazole supported Mo(VI) complex (PBI.Mo) in a FlowSyn reactor**

It should be noted that continuous epoxidation of 1-hexene and 4-VCH catalysed by Ps.AMP.Mo using a FlowSyn reactor achieved the highest conversion of TBHP and the yield of corresponding epoxides when the reactions were conducted at a reaction temperature of 353 K, feed flow rate of 0.1 mL/min and at a feed molar ratio of alkene to TBHP of 5:1 (see Figure 17a and b). Hence, these conditions were employed for continuous epoxidation of 1-hexene and 4-VCH with TBHP as an oxidant using FlowSyn reactor in the presence of PBI.Mo as a catalyst, so as to compare the performance of both polymer supported catalysts for continuous epoxidation.

The results show that epoxidation of 1-hexene in the presence of PBI.Mo achieved  $\sim 35\%$  conversion of TBHP and  $\sim 32\%$  yield of 1,2-epoxyhexane, whereas, the same reaction

conducted in the presence of Ps.AMP.Mo as a catalyst gave ~79% conversion of TBHP and ~64% yield of 1,2-epoxyhexane (Figure 17a). On the other hand, continuous epoxidation of 4-VCH catalysed by PBI.Mo gave appreciable conversion of TBHP (~84%) and yield of 4-VCH 1,2-epoxide (~69%), although the values are lower when compared with the conversion of TBHP (~95%) and the yield of 4-VCH 1,2-epoxide (~82%) obtained when Ps.AMP.Mo was used as a catalyst (Figure 17b). Therefore, it can be concluded that Ps.AMP.Mo catalyst shows higher catalytic performance for continuous epoxidation of both 1-hexene and 4-VCH in a FlowSyn reactor as compared to PBI.Mo catalyst.

#### **4.4. Comparison between batch and continuous epoxidation**

In order to compare the efficiency of batch and continuous epoxidation, it is worth noting that epoxidation experiments were carried out in a batch reactor for a period of 240 min.

However, continuous epoxidation experiment in a FlowSyn reactor conducted at a feed flow rate of 0.1 mL/min has a feed residence time of ~5 min in the fixed bed column. As shown in Figure 16a, continuous epoxidation of 1-hexene carried out in the presence of Ps.AMP.Mo at a reaction temperature of 343 K using 5:1 molar ratio of 1-hexene to TBHP achieved ~58% yield of 1,2-epoxyhexane within ~5 min residence time, whereas it takes >40 min to achieve similar yield of epoxide in a batch reactor using the same conditions (see Figure 8a).

Similarly, ~80% yield of 4-VCH 1,2-epoxide was obtained for continuous epoxidation catalysed by Ps.AMP.Mo at 343 K using feed flow rate of 0.1 mL/min and feed molar ratio of 4-VCH to TBHP of 5:1 (Figure 16b), while batch epoxidation of 4-VCH achieved similar yield of epoxide (80%) after 40 min of the reaction (8c). Therefore, based on the results obtained from this study, continuous epoxidation of alkene in a FlowSyn reactor can be considered to be more efficient than the batch reaction. Moreover, the continuous flow reaction in a FlowSyn reactor shows substantial benefits that include short setup and reaction



times, flexibility of scaling-up reactions, safer and more environmentally friendly operating procedures.

## 5. Conclusions

The catalytic performance of polymer supported Mo(VI) complexes, i.e. Ps.AMP.Mo and PBI.Mo have been assessed for alkene epoxidation using TBHP as an oxidant. Ps.AMP.Mo catalyst demonstrates better catalytic performance for epoxidation of 1-hexene and 4-VCH as compared to PBI.Mo catalyst. For example, Ps.AMP.Mo catalysed epoxidation of 4-VCH at 0.15 mol% Mo loading achieved ~91% yield of 4-VCH 1,2-epoxide at 260 min, whereas epoxidation of 4-VCH in the presence of PBI.Mo under similar conditions gave ~25% yield of epoxide over the same period. The catalyst reusability and supernatant studies have been carried out in a batch reactor to assess the long term stability of the polymer supported catalysts for alkene epoxidation using conditions that form the basis for continuous epoxidation experiments in a FlowSyn reactor. The supernatant studies confirmed the presence of some catalytically active Mo that might have contributed to catalysis in the Ps.AMP.Mo catalysed reactions. The leaching of Mo from the polymer support was due to soluble leached complex or Mo-containing microgel released as a result of mechanical attrition of the beads or both.

Continuous alkene epoxidation using a FlowSyn reactor has enabled rapid evaluation of catalytic performance of Ps.AMP.Mo and PBI.Mo from a small quantity of reactants under different reaction conditions. Both catalysts have demonstrated higher catalytic performance in the continuous epoxidation of 4-VCH as compared to 1-hexene. However, this observation was not quite surprising due to the presence of electron withdrawing vinyl group in 4-VCH, which increased the reactivity of the double bond in the cyclic structure. Experiment carried

out in the presence of Ps.AMP.Mo as a catalyst at a feed molar ratio of 4-VCH to TBHP of 5:1, reaction temperature of 353 K and feed flow rate of 0.1 mL/min resulted in ~95% conversion of TBHP and ~82% yield of 4-VCH 1,2-epoxide at steady state. On the other hand, ~84% conversion of TBHP and ~69% yield of 4-VCH 1,2-epoxide was achieved for continuous epoxidation of 4-VCH catalysed by PBI.Mo under similar reaction conditions. The results obtained in this study show that a thorough screening of reaction parameters including reaction temperature, feed flow rate and feed molar ratio of alkene to TBHP could have a positive impact on the efficiency of a continuous flow alkene epoxidation in the presence of a heterogeneous catalyst.

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