

Efficient and selective molybdenum based heterogeneous catalyst for alkene epoxidation using batch and continuous reactors

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A polystyrene 2-(aminomethyl)pyridine supported molybdenum(VI) complex (Ps.AMP.Mo) has been prepared, characterised and used as a catalyst for epoxidation of 1-hexene and 4-vinyl-1-cyclohexene (4-VCH) using TBHP as an oxidant. The catalytic performance of the polymer supported Mo(VI) complex has been evaluated for epoxidation of 1-hexene and 4-VCH in a classical batch reactor. Experiments have been carried out to study the effect of 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. The long term stability of the polymer supported Mo(VI) catalyst has been evaluated by recycling the catalyst several times in batch experiments using conditions that form the basis for continuous epoxidation studies. The extent of Mo leaching from the polymer supported catalyst has been investigated by isolating any residue from reaction supernatant studies after removal of heterogeneous catalyst and using the residue as potential catalyst for epoxidation. The efficiency of Ps.AMP.Mo catalyst has been assessed for continuous epoxidation of 1-hexene and 4-vinyl-1-cyclohexene with TBHP as an oxidant using a FlowSyn reactor by studying the effect of reaction temperature, feed molar ratio of alkene to TBHP and feed flow rate on the conversion of TBHP and the yield of epoxide. The catalyst was found to be active and selective for batch and continuous epoxidation of the substrates using TBHP as an oxidant. The continuous epoxidation in a FlowSyn reactor has shown considerable time savings, high reproducibility and selectivity along with remarkable improvements in catalyst stability compared with the reactions carried out in a batch reactor.

Introduction

Epoxides are versatile and useful intermediates in the production of commercially important products for flavours, fragrances, paints and pharmaceuticals.¹⁻⁹ Consequently, the epoxidation of alkenes is a field of both academic and industrial importance. The conventional epoxidation methods in the fine chemicals industries employ either stoichiometric peracids such as peracetic acid and *m*-chloroperbenzoic acid¹⁰ or chlorohydrin¹¹ 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 latter 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.^{12,13} Mo(VI) complexes are well known to be potent catalysts for the epoxidation of alkenes by hydroperoxides

immobilisation of catalytically active metal species on organic or inorganic materials such as polymers,^{15,16} ion-exchange resins,^{17,18} alumina,^{19,20} zeolite^{21,22} and silica.^{23,24} Polymers have gained attention as suitable supports for transition metal catalysts as they are inert, nontoxic, insoluble and often recyclable²⁵. 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.²⁶⁻³⁸ 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 work, we discuss the preparation and characterisation of an efficient and selective polystyrene 2-(aminomethyl)pyridine supported molybdenum complex (Ps.AMP.Mo), which has been used as catalyst 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 catalyst, (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 catalyst has been conducted in a classical batch reactor. Experiments have been carried out to study the effect of reaction temperature, feed molar ratio of alkene to TBHP and catalyst loading on the yield of 1,2-epoxyhexane and 4-vinyl-1-cyclohexene 1,2-epoxide (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

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† Electronic Supplementary Information (ESI) available: Catalyst preparation methods and relevant calculation, Experimental set-up for suspension polymerisation, FTIR spectrum and SEM image of the catalyst.

such as TBHP, and indeed an industrial example is the Halcon Process that describes the use of a soluble Mo complex as a catalyst for liquid phase epoxidation of propylene to propylene oxide.¹⁴ 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.

There have been considerable amount of research efforts on developing stable heterogeneous catalysts for epoxidation by

heterogeneous catalyst for continuous epoxidation studies have been assessed using a FlowSyn continuous flow reactor by studying the effect of reaction temperature, feed molar ratio 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 considerable time savings, high reproducibility and selectivity along with remarkable improvements in catalyst stability compared to reactions carried out in a batch reactor.

Experimental section

Materials

All chemicals used for this study were purchased from Sigma-Aldrich Co. Ltd and the purity of each chemical was verified by gas chromatography (GC). The preparation of polystyrene 2-(aminomethyl)pyridine supported Mo(VI) complex, i.e. Ps.AMP.Mo catalyst was carried out using 2-(aminomethyl)pyridine (AMP) (99%), 2,2-azobis isobutyronitrile (AIBN), divinylbenzene (DVB) (technical grade, 80% purity), ethanol ($\geq 99.5\%$), 2-ethylhexanol ($\geq 99.6\%$), molybdenyl acetylacetonate ($\text{MoO}_2(\text{acac})_2$), methanol (99.8%), Silica gel for flash chromatography 223-400 mesh, sodium chloride (BioXtra, $\geq 99.5\%$), styrene ($\geq 99\%$), Sodium hydroxide (purum p.a. $\geq 98\%$), toluene (anhydrous, 99.8%) and vinylbenzyl chloride (VBC) (97%). The catalyst was washed with 1, 2-dichloroethane (anhydrous, 99.8%) after each experimental run. Reactants involved in this study were 4-vinyl-1-cyclohexene (≥ 99.5) and *tert*-butyl hydroperoxide (TBHP) solution in water (70% w/w). The water content of TBHP was removed by Dean-Stark apparatus from toluene solution and the concentration of the resulting TBHP solution was determined by iodometric titration.³⁹ The quantification of samples collected from batch and continuous reactors were carried out using internal standard method in the GC and *iso*-octane (anhydrous, 99.8%) was used as an internal standard.

Catalyst preparation

Synthesis of polystyrene 2-(aminomethyl)pyridine supported molybdenum complex (Ps.AMP.Mo). The procedure for the preparation of Ps.AMP.Mo catalyst involves three main stages: (a) Suspension polymerisation: The cross-linked polystyrene based resin used for immobilisation of Mo was prepared by suspension polymerisation method that involves DVB (12% (w/w)), VBC (25% (w/w)) and styrene (63% (w/w)) with 2-ethylhexanol as a porogen. The aqueous continuous phase for the reaction was prepared by dissolving 7.5 g of polyvinyl alcohol (PVOH) in water at $\sim 100^\circ\text{C}$ 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 i.e. DVB, VBC and styrene using silica gel and

nitrogen gas. The organic phase for the synthesis of the resin 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), AIBN (0.15 g) (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 a speed set at 500 rpm. After the reaction was completed, the resulting poly(divinylbenzene-co-vinylbenzyl chloride-co-styrene) beads i.e. (Ps.VBC) were filtered off and washed exhaustively with distilled water. Finally the beads were washed successively with methanol and acetone, and were dried in a vacuum oven at 313 K.

The elemental analysis of Ps.VBC resin was carried out using Perkin-Elmer AAnalyst 200. The procedure employed was as follows: a sample of the resin was weighed on an aluminium foil and placed in the instrument. The flash combustion process was conducted at 1800°C (2073 K) and helium gas was used to purge the system before the analysis was started. A thermal conductivity detector was used to quantify the gaseous combustion products. The result of elemental analysis for Ps.VBC gives C, 86.60, H, 7.40 and Cl, 4.70%. On the other hand, the percentage contents of all the elements, with the exception of Cl are consistent with their respective theoretical qualities employed in the synthesis of the resin, assuming full conversion of the co-monomer feed was achieved. The experimentally determined chlorine content (Cl, 4.70%) was found to be less than that expected from full conversion (Cl, 7.42%), possibly due to partial hydrolysis of the VBC co-monomer during the polymerisation process.⁴⁰

(b) Amination reaction to produce polystyrene 2-(aminomethyl)pyridine beads (Ps.AMP): This involves a nucleophilic substitution of the $-\text{CH}_2\text{Cl}$ functional group of the chloromethylated polystyrene resin (Ps.VBC) by the 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.

(c) Loading of Mo(VI) complex onto Ps.AMP resin. Ps.AMP resin (17.5g) was refluxed with an excess of $\text{MoO}_2(\text{acac})_2$ (20.77g) in anhydrous toluene for a period of 4 days. The reaction is illustrated by Fig. 1. 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 an 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 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.

Catalyst characterisation

The infrared spectra of Ps.AMP.Mo catalyst was observed on a Thermal Nicolet Avectar 370 DTGS equipped with a smart orbit accessory. A finely grounded sample of the catalyst was placed on the sample stage and the spectra were recorded with the aid of OMNIC (version 7.1) software. The spectrum of Ps.AMP.Mo catalyst has revealed the bands around $\sim 760\text{ cm}^{-1}$ to $\sim 800\text{ cm}^{-1}$, a 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.⁴¹

The molybdenum content of the prepared catalyst was analysed using a Perkin-Elmer AAnalyst 200 spectrophotometer. A sample of the catalyst ($\sim 0.1\text{ g}$) was grounded to fine powder and digested in 15 mL aqua regia for 3 days. Aqua regia is a mixture of concentrated HNO₃ 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 catalyst and the corresponding ligand:Mo ratio are given in Table 1.

The morphology of the catalyst particles was observed using a JEOL JSM-6300F scanning electron microscope (SEM). Neglecting mechanical damages to the samples, the SEM image of the catalyst revealed a well dispersed spherical smooth surface, a characteristic of macroporous polymer resins⁴¹.

The particle size measurement was carried out using Malvern Mastersizer and true density of the catalyst was measured using micrometrics multivolume pycnometer-1305. As shown in Table 1, the catalyst has particles sizes in the range of 119–153 μm and average density of 1.44 g cm^{-3} . 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 are presented in Table 1.

Batch epoxidation studies

Batch epoxidation of alkenes with TBHP as an oxidant in the presence of Ps.AMP.Mo 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 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. 323–343 K and was maintained in the range of $\pm 0.5\text{ K}$ 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 a Shimadzu GC-2014 gas chromatography (GC).

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 reactor (supplied by Uniqsis Ltd) in the presence of Ps.AMP.Mo as a catalyst. 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 perfloropolymer 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 ($1.5 \pm 0.02\text{ g}$) and enclosed in an electronically controlled column heater. The schematic of the experimental set-up of FlowSyn reactor is shown in Fig.2.

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 $\pm 2\text{ K}$. 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. The fluid paths in FlowSyn reactor were properly cleaned by flushing with *iso*-propanol (solvent) at the end of each experimental run. 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 catalyst for alkene epoxidation in a 0.25 L jacketed stirred batch reactor.

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 μm and film thickness 0.25 μm . The carrier gas used was helium at a flow rate of 1 mL/min.

A split ratio of 100:1 and injection volume of 0.5 μL 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 K min⁻¹. Each sample took ~13 min to be analysed by GC and the oven temperature was cooled back to 313 K before the next run was started.

Determination of epoxide yield

The yield of epoxide was calculated based on the moles of TBHP consumed, i.e.

$$\text{Epoxide yield (\%)} = \frac{\text{Moles of epoxide formed}}{\text{Initial moles of TBHP}} \times 100$$

It should be noted that the density of TBHP in toluene solution was determined from the volume of toluene and pure TBHP collected after removing the water content of TBHP with Dean-Stark apparatus.

Results and discussion

Batch epoxidation results

Batch epoxidation of 1-hexene and 4-vinyl-1-cyclohexene (4-VCH) with TBHP as an oxidant 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 epoxide. The reusability and supernatant studies have been carried out to evaluate the long term stability of the catalyst as well as the leaching of Mo from the polymer support. The analytical error was within ±3% for all the experiments.

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 speed or speed of agitation. 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) catalyst. 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 were absent in this study. On the other hand, most of the particles of Ps.AMP.Mo lie within the size range of 119–335 μm, which are fairly uniform. According to Clerici and Kholdeeva,⁴² 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 Ps.AMP.Mo catalysed epoxidation reactions due to the nature of the catalyst particles. On the basis of these investigations, all batch epoxidation experiments

were carried out with stirrer speed of 400 rpm using Ps.AMP.Mo catalyst as prepared.

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 alkenes studied. Fig. 3a shows that the yield of 1,2-epoxyhexane 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. On the other hand, epoxidation of 4-VCH in the presence of Ps.AMP.Mo reached a plateau within the first 5 min for the experiment carried out at 353 K as shown in Fig. 3b. 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 behaviour was observed in both cases. Ambroziak et al.⁵ 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 Ps.AMP.Mo catalysed epoxidation of 1-hexene and 4-VCH.

Effect of feed molar ratio. In most of the catalysed alkene epoxidation processes, reactions are conducted with a substantially excess of alkene in order to avoid over oxidation, and to 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.

As shown in Fig. 4a and 4b, 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 and 4-VCH 1,2-epoxide. 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 (Fig. 4a). 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 (Fig. 4b).

Effect of catalyst loading.

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 × 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 Fig. 5a. On the

other hand, 4-VCH epoxidation in the presence of Ps.AMP.Mo reached a plateau within the first 20 min for catalyst loading of 0.6 mol% Mo, whilst it took 100 min to achieve a plateau for reaction conducted at 0.3 mol% Mo loading (Fig. 5b). 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 (Fig. 5b) compared with the yield of 1,2-epoxyhexane (70%) achieved over the same period when experiment was carried out at 0.15 mol% Mo (Fig. 5a). It can be concluded that the catalyst loading of 0.6 mol% Mo was found to be the optimum for Ps.AMP.Mo catalysed epoxidation of 1-hexene and 4-VCH.

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 catalyst for 1-hexene and 4-VCH epoxidation have been investigated by recycling the catalyst several times in batch experiments. The results are presented in Fig. 6.

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 Fig. 6a and b, 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 for 1-hexene (Fig. 6a) and 4-VCH (Fig. 6b). The yield of 1,2-epoxyhexane obtained at 260 min was ~80% in both Run 2 and Run 3 (Fig. 6a), while ~96% yield of 4-VCH 1,2-epoxide was obtained for Run 1–Run 3 over the same period (Fig. 6b). However, a significant drop in the rate of epoxide formation was observed in the subsequent Run 4–Run 6 in epoxidation of 1-hexene and 4-VCH (Fig. 6a and b). The amount of Mo retained by the catalyst after Run 1 was 0.70 mmol Mo g⁻¹ resin, while it was 0.62 mmol Mo g⁻¹ resin and 0.56 mmol Mo g⁻¹ resin after Run 2 and Run 3, respectively. However, the Mo content of the catalyst recovered from subsequent experimental runs (i.e. Run 4 to Run 6) remain stable (0.56±0.02 mmol Mo g⁻¹). Furthermore, the SEM images of the Ps.AMP.Mo catalyst particles collected after Run 6 did not show any noticeable change in the surface morphology of the beads. A control reaction was also carried out with fresh sample of the catalyst without stirring, and no trace of Mo leaching was detected. The reason for the decrease in the yield of epoxide may be explained by the ligand to Mo ratio of Ps.AMP.Mo catalyst which is 0.68:1. It is obvious that Ps.AMP.Mo catalyst has an excess of Mo to ligand content, therefore Mo is lost during reaction since a significant proportion of Mo introduced at the outset cannot be coordinated by polymer immobilised ligand. It could be concluded that catalytically active Mo species lost from Ps.AMP.Mo could either be soluble leached complex or as traces of Mo containing

microgel released as a result of mechanical attrition of the beads or both. However, despite the gradual decrease in catalytic activity, Ps.AMP.Mo catalyst remained active even after Run 6 as compared to the uncatalysed reaction.

Supernatant studies. The aim of this analysis is to investigate the extent of Mo leaching from the polymer supported catalyst. Once each reusability study experiment was completed, 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 Fig. 7. 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 Fig. 7 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 Fig. 7a and b. This was evident by the catalytic effect observed when the experiments were conducted in the presence of residue. The yield of epoxide achieved from the supernatant studies of 1-hexene and 4-VCH after Run 1 was 67% (Fig. 7a) and 47% (Fig. 7b), respectively. The yield of epoxide decreased steadily for the subsequent experimental runs and became negligible after 4–6 runs (Fig. 7a and b). Thus, it can be concluded that the leaching of Mo in Ps.AMP.Mo catalysed epoxidation becomes negligible after 4–5 experimental runs.

Continuous epoxidation results. Continuous epoxidation was carried out in a FlowSyn continuous flow reactor to study the effect of reaction temperature, feed molar ratio of alkene to TBHP and feed flow rate on the conversion of TBHP and the yield of epoxide at steady state, i.e., at 2 h. Fig. 8 shows a sample plot for 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. The analytical error was within ±3% for all the experiments.

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 Fig. 9a 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 Fig. 9b. The conversion of TBHP and the yield of 4-VCH 1,2-epoxide at 333 K was found to be ~66% and ~64%, respectively (Fig. 9b).

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 (Fig. 9b). Hence, 353 K was selected for further optimisation studies of 1-hexene and 4-VCH epoxidation in a FlowSyn reactor.

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 Fig. 10a. 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 (Fig. 10b). 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 (Fig. 10a), 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 (Fig. 10b). 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.

Effect of feed molar ratio. 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. Fig. 11 illustrates that both TBHP conversion and the yield of epoxide increase 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 Fig. 11a. 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 (Fig. 11b). 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 (Fig. 11b). Therefore, it can be concluded that the feed molar ratio of 2.5:1 (1-hexene to TBHP) is an appropriate reactant ratio for continuous epoxidation experiments since the reactions carried out at 5:1 molar ratio of 1-hexene to TBHP gave negligible increase in the yield of epoxide (see Fig.11a). On the other hand, higher yield of 4-VCH 1,2-epoxide was obtained at 5:1 molar ratio of 4-VCH to TBHP (82%) compared

to reactions conducted at 2.5:1 and 1:1 molar ratio of 4-VCH to TBHP (Fig. 11b).

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 Fig. 6a and b). 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±4% and 82±4%, respectively for all four experimental runs. On the other hand, 1-hexene epoxidation under similar conditions gave 79±4% and 64±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.

Conclusions

The catalytic performance of polymer supported Mo(VI) complex, i.e. Ps.AMP.Mo has been assessed for alkene epoxidation using TBHP as an oxidant. The catalyst has demonstrated higher catalytic performance for the epoxidation of 4-VCH as compared to 1-hexene in both batch and continuous reactors. The supernatant studies confirmed the presence of some catalytically active Mo that might have contributed to homogenous catalysis. 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 from a small quantity of reactants under different 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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