**EFFICIENT AND SELECTIVE POLYMER SUPPORTED Mo(VI) CATALYST FOR ALKENE EPOXIDATION IN BATCH AND CONTINUOUS REACTORS**

**Misbahu L. Mohammed, Rene Mbeleck and Basudeb Saha\***

*Centre for Green Process Engineering, School of Engineering,*

*London South Bank University, 103 Borough Road, London, SE1 0AA, UK*

*\*b.saha@lsbu.ac.uk*

**ABSTRACT**

A polystyrene 2-(aminomethyl)pyridine supported Mo(VI) i.e., Ps.AMP.Mo complex has been successfully prepared, characterised and used as a catalyst for alkene epoxidation in batch and continuous reactors. The catalytic activity of the polymer supported Mo(VI) catalyst has been tested for the epoxidation of 4-vinyl-1-cyclohexene in a batch reactor. Batch experiments were conducted to study the effect of catalyst loading, feed molar ratio (FMR) of alkene to TBHP and reaction temperature on the yield of 4-vinyl-1-cyclohexane 1,2-epoxide. The long-term stability of Ps.AMP.Mo catalyst was evaluated by recycling the catalyst several times in batch reactions using conditions that forms the basis for continuous epoxidation in a FlowSyn continuous flow reactor. The loss of Mo from polymer support has also been investigated by isolating any residue from reaction supernatant solutions, following removal of the heterogeneous catalyst, and then using the residues as potential catalyst in epoxidation reactions. The efficiency of Ps.AMP.Mo catalyst has been assessed for continuous epoxidation of 4-vinyl-1-cyclohexne 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 substrate 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.

**1. INTRODUCTION**

Epoxides are used as raw materials or intermediates for the production of commercially important products for flavours, fragrances, paints and pharmaceuticals.1-10 The production of epoxides often uses peracids including peracetic acid and *m*-chloroperbenzoic11 or chlorohydrin12 as oxidising reagents in liquid phase batch reactions. However, such processes are not environmentally benign as the former produces equivalent amount of acid waste, while the latter yields chlorinated by-products and calcium chloride waste. Hence, there is a strong need for cleaner catalytic epoxidation methods that employ safer oxidants and produce little waste. Soluble compounds of transition metals have been used to catalyse alkene epoxidation with good activity and increased product selectivity.13-15 A notable industrial implementation of homogenous catalysed epoxidation was the Halcon process described by Kollar (1967).16 This process uses homogenous molybdenum(VI) to catalyse liquid phase epoxidation of propylene with *tert*-butylhydroperoxide for the production of 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.17

 Consequently, researchers have been focusing on developing stable heterogeneous catalysts for epoxidation by immobilisation of catalytically active metal species on organic or inorganic materials.18-20 Polymers have gained attention as suitable support for transition metal catalysts as they are inert, non-toxic, insoluble and often recyclable.21 A number of chelating functional molybdenum-containing copolymers have been prepared and used as catalysts for the epoxidation of alkenes in the presence of TBHP as an oxidant. 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.22-25

In this work, an efficient and selective polystyrene 2-(aminomethyl)pyridine supported molybdenum(VI) complex (Ps.AMP.Mo) has been used as a catalyst for epoxidation of
4-vinyl-1-cyclohexene using batch and continuous reactors. This process is atom efficient, solvent-free and uses environmentally benign *tert*-butyl hydroperoxide (TBHP) as an oxidant.

**2. EXPERIMENTAL**

**2.1. 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%), divinylbenzene (DVB) (80%), ethanol (≥99.5), 2-ethylhexanol (≥99.6%), molybdenyl acetylacetonate (MoO2(acac)2), styrene (≥99%), toluene (anhydrous, 99.8%) and vinylbenzyl chloride (VBC) (97%). Ps.AMP.Mo catalyst was washed with 1,2-dichloroethane (anhydrous, 99.8%) after each successive 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 concentration of the resulting TBHP solution was determined by iodometric titration.26 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.

**2.2. Catalyst preparation and characterisation**

Cross-linked polystyrene 2-(aminomethyl)pyridine (Ps.AMP) was prepared by suspension polymerisation of known mixtures of divinylbenzene (DVB), vinylbenzyl chloride (VBC) and styrene in the presence of 2-ethylhexanol as a porogen. This was followed by amination of the formed resin with an excess of 2-aminomethyl pyridine in ethanol. The crosslinked resin beads are commonly used as catalyst support due to their high porosity, large surface area and robust spherical particles with uniform size distribution.27 Ps.AMP resins were loaded with Mo by reaction with an excess of molybdenyl acetylacetonate, (MoO2(acac)2), relative to polymer bound ligand under reflux in toluene for four days. The excess MoO2(acac)2 was removed by exhaustive extraction with acetone in a Soxhlet. Fresh acetone was replaced at regular time intervals until the refluxing solvent remained colourless. Molybdenum in the prepared catalyst was found to be homogeneously distributed in the polymer. The particle size distribution of Ps.AMP.Mo catalyst was assayed using a Malvern Mastersizer. BET surface area was determined by nitrogen adsorption and desorption method using Micromeritics ASAP (accelerated surface area and porosimetry) 2010. Molybdenum content of the supported catalyst was assayed using atomic absorption spectrophotometric (AAS) method.

**2.3. Batch epoxidation studies**

Batch epoxidation of a 4-vinyl-1-cyclohexene 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 4-vinyl-1-cyclohexene 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 ±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 a Shimadzu GC-2014 gas chromatography (GC).

**2.4. Continuous alkene epoxidation in a FlowSyn reactor**

Continuous epoxidation of 4-vinyl-1-cyclohexene (4-VCH) was 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±0.02 g) and enclosed in an electronically controlled column heater.

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 ± 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. 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.

**2.5. 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 of1 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.

**3. RESULTS**

Batch and continuous epoxidation of 4-VCH with TBHP as an oxidant in the presence of Ps.AMP.Mo catalyst was found to be selective in the formation of 4-VCH 1, 2-epoxide. The GC analysis of the reaction mixture showed no evidence of either terminal or diepoxides products.

**3.1. Batch epoxidation results**

Epoxidation of 4-VCH with TBHP as an oxidant in the presence of Ps.AMP.Mo catalyst was carried out in a batch reactor to study the effect of various parameters such as reaction temperature, feed molar ratio of 4-VCH to TBHP and catalyst loading on the yield of 4-VCH 1, 2-epoxide. The catalyst reusability and supernatant studies were carried out to assess the long term stability of Ps.AMP.Mo catalyst and leaching of Mo from the polymer support. The results of batch epoxidation form the basis for continuous experiment in FlowSyn reactor. The analytical error was within ±3% for all the experiments

**3.1.1. Effect of reaction temperature**

Epoxidation of 4-vinyl-1-cyclohexene 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. The results are shown in Figure 1.

● 333 K ⯁ 343 K ■ 353 K

Figure 1. Effect of reaction temperature on the yield of 4-VCH 1,2-epoxide for epoxidation of 4-vinyl-1-cyclohexene catalysed by Ps.AMP.Mo at catalyst loading: 0.3 mol% Mo; feed molar ratio of alkene to TBHP: 5:1; stirrer speed: 400 rpm.

**3.1.2. Effect of feed molar ratio**

In most of the catalysed epoxidation processes, reactions are conducted with a substantial excess of alkene in order to avoid over oxidation and to achieve high conversion of the oxidant and high yield of epoxide. Hence, batch experiments were carried out using 2:5:1, 5:1 and 10:1 feed molar ratio of 4-VCH to TBHP to study the effect of feed molar ratio of 4-VCH to TBHP on the yield of 4-VCH 1, 2-epoxide. The results are presented in Figure 2.

Figure 2. Effect of feed molar ratio on the yield of 4-VCH 1,2-epoxide for epoxidation of
4-vinyl-1-cyclohexene catalysed by Ps.AMP.Mo at reaction temperature: 343 K; catalyst loading: 0.3 mol% Mo; stirrer speed: 400 rpm.

**3.1.3. Effect of catalyst loading**

The effect of catalyst loading (i.e., mole ratio of Mo to TBHP x 100%) was investigated by conducting batch experiments using 0.15 mol% Mo, 0.3 mol% Mo and 0.6 mol% Mo catalyst loading. The catalyst loading was defined based on the active Mo component instead of total mass of Ps.AMP.Mo catalyst in order to take into account the slight differences in Mo content obtained from different batches of the prepared Ps.AMP.Mo catalyst. However, all batch and continuous epoxidation studies in this work were conducted from one batch of the prepared catalyst. The results are shown in Figure 3.

Figure 3. Effect of catalyst loading on the yield of 4-VCH 1,2-epoxide for epoxidation of
4-vinyl-1-cyclohexene catalysed by Ps.AMP.Mo at reaction temperature: 343 K; feed molar ratio of alkene to TBHP: 5:1; stirrer speed: 400 rpm.

**3.1.4. Catalyst reusability and supernatant studies**

The reusability potentials of Ps.AMP.Mo catalyst for 4-VCH epoxidation have been investigated by recycling the catalyst several times in batch experiments. The results are presented in Figure 4. 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 Figure 5. 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 Figure 5 for comparison with the experiments carried out in the presence of residue.

■ Run 1 ⯁ Run 2 ● Run 3 ▲ Run 4 ▬ Run 5 **🞪** Run 6 **🞵** Uncatalysed

Figure 4. Catalyst reusability studies for epoxidation of 4-vinyl-1-cyclohexene (4-VCH) catalysed by Ps.AMP.Mo at reaction temperature: 343 K; catalyst loading: 0.3 mol% Mo; feed molar ratio of alkene to TBHP: 5:1, stirrer speed: 400 rpm.

■ Run 1 ⯁ Run 2 ● Run 3 ▲ Run 4 **🞵** Uncatalysed

Figure 5. Supernatant studies for epoxidation of 4-VCH catalysed by residue isolated from supernatant solutions where Ps.AMP.Mo catalyst is reused at reaction temperature: 343 K; feed molar ratio of alkene to TBHP: 5:1; stirrer speed: 400 rpm.

**3.2. 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. Figure 6 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.

Figure 6. Mole fractions of the various constituents in the reaction mixture for continuous epoxidation of 4-vinyl-1-cyclohexene (4-VCH) with TBHP as an oxidant.

**3.2.1. Effect of reaction temperature**

Continuous epoxidation of 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 results are presented in Figure 7.

Conversion of TBHP Yield of epoxide

Figure 7. Effect of reaction temperature on the conversion of TBHP and the yield of 4-VCH 1,2-epoxide at steady state for continuous epoxidation of 4-VCH with TBHP using a FlowSyn continuous flow reactor in the presence of Ps.AMP.Mo catalyst (~1.5 g) at feed flow rate: 0.1 mL/min; feed molar ratio of alkene to TBHP: 5:1.

**3.2.2. 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 (Figure 8).

Conversion of TBHP Yield of epoxide

Figure 8. Effect of feed flow rate on the conversion of TBHP and the yield of 4-VCH 1,2-epoxide at steady state for continuous epoxidation of 4-VCH with TBHP using a FlowSyn continuous flow reactor in the presence of Ps.AMP.Mo catalyst (~1.5 g) at reaction temperature: 353 K; feed molar ratio of alkene to TBHP: 5:1.

**3.2.3. 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. The results are illustrated in Figure 9.

Conversion of TBHP Yield of epoxide

Figure 9. Effect of feed molar ratio on the conversion of TBHP and the yield of 4-VCH 1,2-epoxide at steady state for continuous epoxidation of 4-VCH with TBHP using a FlowSyn continuous flow reactor in the presence of Ps.AMP.Mo catalyst (~1.5 g) at reaction temperature: 353 K; feed flow rate: 0.1 mL/min.

**4. DISCUSSION**

**4.1. Batch epoxidation studies**

As expected, higher reaction temperatures gave higher yield of 4-VCH 1,2-epoxide at a fixed reaction time. It can be seen from Figure 1, the reaction reached equilibrium within the first 5 min for experiments carried out at 353 K due to distinct exothermic effect observed during first 5 min of the reaction i.e. the temperature of the reaction mixture overshoots the desired temperature, which was controlled immediately to maintain the reaction mixture at 353 K. This effect, however, was not significant when the experiments were conducted at 333 K and 343 K. The experiments were replicated twice for all three temperatures i.e. 333 K, 343 K and 353 K and the same behaviour was observed in all cases. On the other hand, the trends for the yield of 4-VCH 1,2-epoxide for experiments conducted at 333 K and 343 K were quite similar. A significantly higher yield of 4-VCH 1,2-epoxide obtained at 353 K as compared to the experiments conducted at 333 K and 343 K. The yield of 4-VCH 1,2-epoxide after 5 min at 333 K, 343 K and 353 K was ~18%, ~28% and ~94%, respectively. On the other hand, the yield of 4-VCH 1,2-epoxide at 260 min was ~95% for all three temperature ranges. Ambroziak et al.28 observed similar exothermic effect while studying the effect of reaction temperature on cyclohexene epoxidation with TBHP catalysed by polymer-supported Mo(VI) complex. It is evident from Figure 1 that ~95% yield of 4-VCH 1,2-epoxide was achieved at 10 min for reactions at 353 K, hence 353 K was considered to be the optimum reaction temperature for this process.

The efficiency in the use of oxidant and its conversion to the desired product is a major criterion for assessing the proficiency of alkene epoxidation with alkyl hydroperoxide. No significant effect in the rate of formation of epoxides was found when feed molar ratio (FMR) of 4-VCH to TBHP was increased beyond 2.5:1 as shown in Figure 2. For instance, the yield of 4-VCH 1,2-epoxide obtained at 260 min for 2.5:1, 5:1 and 10:1 FMR of 4-VCH to TBHP was ~92%, ~96% and ~98%, respectively. However, the reaction reached equilibrium at 80 min for FMR of 4-VCH to TBHP of 10:1, and this is considered as the optimum FMR for this study.

An increase in catalyst loading increases the number of active sites per unit volume of reactor leading to an increase in the yield of 4-VCH 1,2-epoxide. The rate of epoxide formation for experiments carried out with 0.6 mol% Mo recorded a significantly high yield of 4-VCH 1,2-epoxide compared to 0.15 mol% Mo and 0.3 mol% Mo as shown in Figure 3. On the other hand, despite the equilibrium was reached within the first 20 min for catalyst loading of 0.6 mol% Mo and within 100 min for 0.3 mol% Mo catalyst loading, the yield of 4-VCH 1,2-epoxide at 260 min for catalyst loading of 0.3 mol% Mo and 0.6 mol% Mo was found to be similar i.e., ~95%. It should be noted that 92% yield of epoxide was achieved at 20 min for catalyst loading 0.6 mol% Mo and this is regarded as the preferred catalyst loading for epoxidation of 4-VCH with TBHP using Ps.AMP.Mo catalyst.

Figure 4 shows that high rate of epoxide formation was observed in Run 1 as compared to the subsequent runs. This is due to the availability of sufficient active sites in fresh catalyst that are available for adsorption by the reacting species as compared to subsequent runs. The yield of 4-VCH 1,2-epoxide for Run 2 and Run 3 was quite similar as both reached equilibrium at 160 min. However, a gradual decrease in rate of epoxidation was observed in the subsequent experimental runs (Runs 4-6). The yield of 4-VCH 1,2-epoxide for Runs 4, 5 and 6 at 260 min was ~90%, ~81% and ~74%, respectively. Supernatant studies of Ps.AMP.Mo revealed that some catalytically active Mo species are present in the residues isolated from Run 1 to Run 3, but it became negligible ‘After Run 4’ (Figure 5). The leaching of molybdenum could either be soluble leached complexes or as traces of Mo containing microgel released as a result of mechanical attrition of the beads or both.

**4.2. Continuous epoxidation studies**

It can be seen from Figure 7 that 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 7). 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 7). Hence, 353 K was selected for further optimisation studies of 4-VCH epoxidation in a FlowSyn reactor.

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. For instance, 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 8). However, when the residence time of the feed was increased to ~4 min by reducing the flow rate to 0.13 mL/min, the conversion of TBHP and the yield of 4-VCH 1,2-epoxide increased to ~90% and ~77%, respectively (Figure 8). 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 4-VCH 1,2-epoxides in the continuous flow epoxidation.

Figure 9 illustrates that both TBHP conversion and the yield of epoxide increase with an increase in feed molar ratio of alkene to TBHP. 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 9). 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 9). Therefore, it can be concluded that 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.

Reusability studies of Ps.AMP.Mo catalyst in batch epoxidation of 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 Figure 4 and 5). In continuous epoxidation of 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 4-VCH 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. 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±3% and 82±3%, respectively for all four experimental runs. 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.

**5. Conclusions**

Ps.AMP.Mo catalyst has been proved to be long lived, stable and suitable for batch and continuous alkene epoxidation. The optimum reaction condition for batch epoxidation experiment was found at 353 K, 0.6 mol% Mo catalyst loading and 10:1 feed molar ratio of
4-VCH to TBHP, which gave ~98% yield of 4-VCH 1, 2-epoxide. However, reusability studies of Ps.AMP.Mo catalyst carried out in a batch reactor showed a decrease in the yield of 4-VCH 1, 2-epoxide. Furthermore, supernatant studies confirmed the presence of some catalytically active molybdenum that may have contributed to homogenous catalysis during batch epoxidation. It was established that in batch epoxidation studies, Mo leaching 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.

**Acknowledgements**

The financial supports from EPSRC (grant no. EP/H027653/1) and The Royal Society Brian Mercer Feasibility award are gratefully acknowledged. One of the authors, M. L. Mohammed is thankful to London South Bank University, UK and Tertiary Education Trust Fund (TETFund), Nigeria for the PhD scholarships.

**Nomenclature**

AAS atomic absorption spectrophotometric

AMP 2-(aminomethyl)pyridine

ASAP accelerated surface area and porosimetry

BET Brunauer-Emmett-Teller

DVB divinylbenzene

ECTM-5 Econo-CapTM-5

FID flame ionisation detector

FMR feed molar ratio

GC gas chromatography

Mo molybdenum

MoO2(acac)2 molybdenyl acetylacetonate

Ps.AMP polystyrene 2-(aminomethyl)pyridine

Ps.AMP.Mo polystyrene 2-(aminomethyl)pyridine supported Mo(VI) complex

TBHP *tert*-butyl hydroperoxide

VBC vinylbenzyl chloride

4-VCH 4-vinyl-1-cyclohexene

4-VCH 1,2-epoxide 4-vinyl-1-cyclohexane 1,2-epoxide

**REFERENCES**

(1) Sienel G, Rieth R, Rowbottom KT, Epoxides, *Ullmann’s encyclopedia of industrial chemistry*, Weinheim, Wiley-VCH, (2000).

(2) Bauer K, Garbe D, Surburg H, *Common Fragrance and Flavour Materials*, 4th ed. Weinheim, Wiley-VCH, (2001).

(3) Yudin AK, *Aziridines and Epoxides in Organic Synthesis*, Weinheim, Wiley-VCH, (2006).

(4) Mbeleck R, Mohammed ML, Ambroziak K, Sherrington DC, Saha B, Efficient epoxidation of cyclododecene and dodecene catalysed by polybenzimidazole supported Mo(VI) complex, *Catal. Today*, **256**, 287-293, (2015).

(5) Saha B, Ambroziak K, Sherrington DC, Mbeleck R, Liquid phase epoxidation process, US Patent 8759522 B2, (2014).

(6) Ambroziak K, Mbeleck R, Saha B, Sherrington D, Greener and Sustainable Method for Alkene Epoxidations by Polymer-Supported Mo(VI) Catalysts, *Int. J. Chem. React*. Eng., **8**, A125, (2010).

(7) Mohammed ML, Mbeleck R, Patel D, Niyogi D, Sherrington DC, Saha B, Greener and efficient epoxidation of 4-vinyl-1-cyclohexene with polystyrene 2-(aminomethyl)pyridine supported Mo(VI) catalyst in batch and continuous reactors, *Chem. Eng. Res. Des.,* **94**, 194-**203**, (2015).

(8) Mohammed ML, Mbeleck R, Patel D, Sherrington DC, Saha B, Greener route to 4-vinyl-1-cyclohexane 1,2-epoxide synthesis using batch and continuous reactors, *Green Process Synth*., **3**, 411–418, (2014).

(9) Mohammed ML, Patel D, Mbeleck R, Sherrington DC, Saha, B., A safer and scalable continuous alkene epoxidation process, 21st International Congress of Chemical and Process Engineering CHISA, Prague, August 2014, [CD-ROM].

(10) Mohammed ML, Patel D, Mbeleck R, Niyogi D, Sherrington DC, Saha B, Optimisation of alkene epoxidation catalysed by polymer supported Mo(VI) complexes and application of artificial neural network for the prediction of catalytic performances, *Appl. Catal., A*, **466**, 142-152, (2013).

(11) Swern D editor. *Organic Peroxides*. New York, Wiley Interscience, (1971).

(12) Bezzo F, Bertucco A, Forlin A, Barolo M. Steady-state analysis of an industrial reactive distillation column. *Sep. Purif. Technol.* **16**, 251-260, (1999).

(13) Hauser SA, Cokoja M, Kuehn FE, Epoxidation of olefins with homogeneous catalysts - quo vadis? *Catal. Sci. Tech.,* **3**, 552-561, (2013).

(14) Oyama ST, *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*, Amsterdam, Elsevier, (2008).

(15) Xia Q, Ge H, Ye C, Liu Z, Su K, Advances in homogeneous and heterogeneous catalytic asymmetric epoxidation, *Chem. Rev*. **105,** 1603-1662, (2005).

(16) Kollar J, Epoxidation process, USA patent US Patent 3351635, (1967).

(17) Salavati-Niasari M, Esmaeili E, Seyghalkar H, Bazarganipour M, Cobalt(II) Schiff base complex on multi-wall carbon nanotubes (MWNTs) by covalently grafted method: Synthesis, characterization and liquid phase epoxidation of cyclohexene by air, *Inorg. Chim. Acta*, **375,** 11-19, (2011).

(18) Arnold U, Habicht W, Doring M, Metal-doped epoxy resins - New catalysts for the epoxidation of alkenes with high long-term activities, *Adv. Synth. Catal*., **348,** 142-150, (2006).

(19) Nath GR, Rajesh K, Transition Metal Complexed Crosslinked Pyrazole Functionalized Resin-Use as Polymeric Catalysts for Epoxidation of Olefins, *Asian J. Chem.,* **24,** 4548-4550, (2012).

(20) Angelescu E, Pavel OD, Ionescu R, Birjega R, Badea M, Zavoianu R, Transition metal coordination polymers MeX2(4,4 ' bipyridine) (Me = Co, Ni, Cu; X = Cl-, CH3OCO-, acetylacetonate) selective catalysts for cyclohexene epoxidation with molecular oxygen and isobutyraldehyde, *J. Mol. Catal. A: Chem*., **352,** 21-30, (2012).

(21) Gupta KC, Sutar AK, Catalytic activities of polymer-supported metal complexes in oxidation of phenol and epoxidation of cyclohexene, *Polym. Adv. Technol*. **19**, 186-200, (2008).

(22) Tangestaninejad S, Moghadam M, Mirkhani V, Mohammadpoor-Baltork I, Ghani K, Alkene epoxidation catalyzed by molybdenum supported on functionalized MCM-41 containing N-S chelating Schiff base ligand, *Catal. Commun*., **10**, 853-858, (2009).

(23) Grivani G, Tangestaninejad S, Halili A, A readily prepared, highly reusable and active polymer-supported molybdenum carbonyl Schiff base complex as epoxidation catalyst, *Inorg. Chem. Commun.,* **10**, 914-917, (2007).

(24) Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I, Mirbagheri NS. Molybdenum hexacarbonyl supported on functionalized multi-wall carbon nanotubes: Efficient and highly reusable catalysts for epoxidation of alkenes with *tert*-butyl hydroperoxide*, J. Organomet. Chem*., **695**, 2014-2021, (2010).

(25) Nooraeipour M, Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I, Nabavizadeh SM, Highly efficient epoxidation of alkenes with hydrogen peroxide catalyzed by tungsten hexacarbonyl supported on multi-wall carbon nanotubes, *Transit. Metal Chem*., **36**, 861-866, (2011).

(26) Sharpless KB, Verhoeven TR, Metal-Catalyzed, Highly Selective Oxygenations of Olefins and Acetalynes with *tert*-Butyl Hydroperoxide, Practical Condiderations and Mechanisms, *Aldrichim. Acta*, **12**, 63-82, (1979).

(27) Sherrington DC, Preparation, structure and morphology of polymer supports, Chem. Commun., **21**, 2275-2286, (1998).

(28) Ambroziak K, Mbeleck R, He Y, Saha B, Sherrington DC, Investigation of Batch Alkene Epoxidations Catalyzed by Polymer-Supported Mo(VI) Complexes, *Ind. Eng. Chem. Res*. **48**, 3293-3302, (2009).