**A CONTINUOUS-FLOW APPROACH TO ALKENE EPOXIDATION CATALYSED BY POLYSTYRENE 2-(AMINOMETHYL)PYRIDINE SUPPORTED MO(VI) COMPLEX**

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

*Centre for Green Process Engineering, Department of Applied Sciences,*

*School of Engineering, London SouthBank University,*

*103 Borough Road, London SE1 0AA, UK*

*\*Corresponding author; e-mail: b.saha@lsbu.ac.uk, tel. +44(0)20 7815 7190,*

1. BACKGROUND

Epoxides are raw materials for a broad range of products, from pharmaceuticals to plastics and paints to adhesives (Sienel *et al*., 2000). The production of epoxides often uses peracids including peracetic acid and *m*-chloroperbenzoic acid in batch reactions (Andrei 2006). The employment of peracids is not an environmentally friendly synthetic procedure since equivalent amounts of acid wastes are produced. Hence, there is a strong need for cleaner catalytic epoxidation methods that employ safer oxidants and produces little waste. There have been considerable amount of research efforts on developing stable heterogeneous catalysts for epoxidation by immobilisation of catalytically active metal species on organic or inorganic materials such as polymers (Huang, 2011; Angelescu, 2012), ion-exchange resins (Arnold, 2006; Nath, 2012), alumina (Satyarthi, 2011; Mikolajska, 2012) zeolite (Liu, 2014; Linares, 2014) and silica.(Jin, 2011; Sharbatdaran, 2014). Polymers have gained attention as suitable supports for transition metal catalysts as they are inert, nontoxic, insoluble and often recyclable (Gupta and Sutar, 2008).

In this work, we report a new process which is considered to be clean as it employs an efficient and selective Polystyrene 2-(aminomethyl) pyridine supported molybdenum complex, i.e. Ps.AMP.Mo as a catalyst for epoxidation of 4-vinyl-1-cyclohexene. The process uses environmentally benign *tert*-butyl hydroperoxide (TBHP) as a terminal oxidant. Experiments have been carried out to study the effect of reaction temperature, catalyst loading and feed molar ratio of alkene to TBHP on the conversion of TBHP to 4-vinyl-1-cyclohexene 1,2-epoxide for optimisation of reaction conditions in a batch reactor. The long term stability of the heterogeneous catalyst has been evaluated by recycling a sample of the catalyst several times in batch experiments. The extent of Mo leaching from the polymer supported catalyst has been investigated by isolating any residue from reaction supernatant studies after removal of the heterogeneous catalyst and using the residue as potential catalyst for epoxidation reaction. Furthermore, the efficiency of the 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 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.

2. EXPERIMENTAL

*2.1 Materials*

1, 2-dichloroethane (anhydrous, 99.8%), *tert*-butyl hydroperoxide, (i.e., TBHP solution in water
(70% w/w), *iso*-propanol (99.5 %), toluene (anhydrous, 99.8%), 4-vinyl-1-cyclohexene (97%) and *iso*-octane (anhydrous, 99.8%) were purchased from Sigma-Aldrich Co. Ltd. TBHP was rendered anhydrous by Dean-Stark distillation from a toluene solution using the procedure reported by (Sharpless and Verhoeven, 1979). The molarity of TBHP in toluene was determined by iodometry (Ambroziak *et al*., 2009). 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%), ethanol (≥99.5),
2-ethylhexanol (≥99.6%), molybdenyl acetylacetonate (MoO2(acac)2), methanol (99.8%), silica gel for flash chromatography 223-400 mesh, sodium chloride (BioXtra, ≥99.5%), styrene (≥99%), sodium hydroxide (purum p.a. ≥98%), toluene (anhydrous, 99.8%) and vinylbenzyl chloride (VBC) (97%).

*2.2 Preparation and characterisation of polymer-supported Mo(VI) catalyst*

Polystyrene 2-(aminomethyl) pyridine supported Mo(VI) complex, i.e. Ps.AMP.Mo catalyst was prepared by suspension polymerisation of DVB (12% (w/w)), VBC (25% (w/w)) and styrene (63% (w/w)) with 2-ethylhexanol as a porogen. This was followed by amination of the formed resin with an excess of 2-(aminomethyl)pyridine in ethanol to form polystyrene 2-(aminomethyl)pyridine (Ps.AMP) resin. Crosslinked resin beads were selected as support for the catalyst due to their high porosity, large surface area and robust spherical particles with uniform size distribution (Sherrington, 1998). The molybdenum (Mo) was loaded onto the Ps.AMP resin by reaction with an excess of molybdenyl acetylacetonate (MoO2(acac)2) under reflux in toluene for four days. The final product (Ps.AMP.Mo) was recovered and dried under vacuum at 40°C. The molybdenum content of the prepared catalyst was determined using Perkin-Elmer AAnalyst 200 spectrophotometer. A sample of the catalyst
(~0.1 g) was grounded to fine powder and digested in 15 mL aqua regia. The resulting mixture was diluted to 100 mL with distilled water and Mo content was analysed using an atomic absorption spectrophotometer (AAS). The particle size distribution of the catalyst was measured using Malvern Mastersizer and the BET surface area was determined by nitrogen adsorption and desorption method using Micromeritics ASAP (accelerated surface area and porosimetry) 2010. The properties of the prepared Ps.AMP.Mo catalyst are given in Table 1.

Table 1: Physical and chemical properties of Ps.AMP.Mo catalyst

|  |  |
| --- | --- |
| Catalyst properties | Values |
| Average density (g cm-3) | 1.44 |
| BET surface area (m2 g-1) | 53.5 |
| Mo loading (mmol Mo g-1 resin)a | 0.74 |
| Ligand loading (mmol g-1 resin)b | 0.5 |
| Ligand to Mo ratio | 0.68:1 |
| Particle size (µm) | 119–153 |
| Total pore volume (cm3 g-1) | 0.08 |
| Average pore diameter (nm) | 6.0 |

aFrom AAS analysis of digested resin, bFrom N% elemental analysis of Mo loaded resins assuming ligand = 2-(aminomethyl) pyridine

*2.3 Batch epoxidation studies*

Epoxidation of 4-vinyl-1-cyclohexene with TBHP as an oxidant in the presence of Ps.AMP.Mo catalyst was carried out in a jacketed four necked glass reactor of 0.25 L capacity. The batch reactor was equipped with agitator, condenser, digital thermocouple and water bath. Known quantities of
4-vinyl-1-cyclohexene and TBHP were weighed out and charged into the reactor vessel, and agitation was started at the desired rate. Heating to the reaction mixture was supplied through water bath via the reactor jacket and monitored by digital thermocouple. A known amount of catalyst was weighed and added into the reactor when the reaction mixture achieved a constant desired temperature (i.e. steady state). 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. 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 Epoxidation studies in a FlowSyn continuous flow reactor*

Epoxidation of 4-vinyl-1-cyclcohexene with TBHP was carried out in a FlowSyn continuous flow reactor 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. The actual temperature inside the column was monitored using a SquirrelView data acquisition software. The experimental set-up of the FlowSyn continuous flow reactor is shown in Figure 1. Samples were collected from the reaction mixture at specific time intervals and analysed using a Shimadzu GC-2014 gas chromatography (GC).



C – Stainless steel column packed with Ps.AMP.Mo catalyst

CI – Control Interface

D – Data acquisition software (SquirrelView)

F – Fraction collector

R1 – Reagent (4-vinyl-1-cyclohexene)

R2 – Reagent (TBHP)

S – Solvent (*iso*-propanol)

Figure 1. Experimental set-up of a FlowSyn continuous flow reactor

3. METHOD OF ANALYSIS

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

4. RESULTS AND DISCUSSION

Batch experiments were conducted under different reaction conditions to study the effect of various parameters such as reaction temperature, feed mole ratio (FMR) of 4-vinyl-1-cyclohexene to TBHP and catalyst loading on the yield of 4-vinyl-1-cyclohexene 1, 2-epoxide. Reusability and supernatant studies were carried out to evaluate the long term stability of polymer supported catalyst for epoxidation reaction. The continuous epoxidation was carried out in a FlowSyn continuous reactor to study the effect of reaction temperature, feed mole ratio of 4-vinyl-1-cyclohexene to TBHP and feed flow rate on the yield of 4-vinyl-1-cyclohexene 1, 2-epoxide and conversion of TBHP. The analytical error was within ±3% in all the experiments for both batch and continuous epoxidation results.

*4.1 Batch epoxidation results*

*Effect of reaction temperature.* An increase in reaction temperature increases the rate of reaction. Hence, experiments were conducted to study the effect of different reaction temperature on the yield of epoxide. Reaction temperatures used for this study were 333 K, 343 K and 353 K. Figure 2a shows that the reaction reached equilibrium within the first 5 min for experiments carried out at 353 K. The yield of 4-vinyl-1-cyclohexene 1, 2-epoxide in the presence of Ps.AMP.Mo catalyst after 5 min at
333 K, 343 K and 353 K was ~18%, ~28% and ~95%, respectively. However, the yield of epoxide achieved after 260 min was ~95% for all three temperature ranges.

*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, 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. Batch experiments were carried out at 2.5:1, 5:1 and 10:1 molar ratio of 4-vinyl-1-cyclohexene to TBHP to study the effect of different FMR of alkene to TBHP on the yield of epoxide. Figure 2b shows that an increase in FMR of alkene to TBHP above 2.5:1 has no significant effect on the rate of formation of epoxides, all the three mole ratios studied gave similar results throughout the reaction and the yield achieved was >95% at 260 min.

 (a) (b)

Figure 2. (a) Effect of reaction temperature on the yield of epoxide at catalyst loading 0.3 mol% Mo and FMR of 4-vinyl-1-cyclohexene to TBHP: 5:1. (b) Effect of FMR of 4-vinyl-1-cyclohexene to TBHP on the yield of epoxide at reaction temperature 343 K and catalyst loading 0.3 mol% Mo.

*Reusability and supernatant studies.* The reusability potentials of Ps.AMP.Mo catalyst has been evaluated by recycling the catalyst several times for batch experiments. The extent of Mo leaching from polymer supported catalyst has been investigated by isolating any residue from reaction supernatant solutions after the removal of the heterogeneous catalyst and using the residue as potential catalyst for epoxidation reactions. Figure 3a 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.

Supernatant studies of Ps.AMP.Mo revealed that some catalytically active Mo species are present in the residues isolated from run 1 to run 5, but it became negligible after run 6 (Figure 3b). The leaching of the molybdenum could be due to attrition of catalyst particles, low ligand to Mo ratio and stirring of the reaction mixture.

 (a) (b)

Figure 3. (a) Catalyst reusability studies and (b) supernatant studies at reaction temperature: 343 K and FMR of 4-vinyl-1-cyclohexene to TBHP: 5:1)

*4.2 Epoxidation in a FlowSyn continuous flow reactor results*

*Effect of reaction temperature.* The effect of reaction temperature on the yield of
4-vinyl-1-cyclohexene 1, 2-epoxide and conversion of TBHP was investigated at 333 K, 343 K, and 353 K. As expected, increase in reaction temperature resulted in higher yield of epoxide and conversion of TBHP as shown in Figure 4a. About 50% conversion of TBHP was achieved when the reaction reached steady state at 353 K, whilst after the same period; the conversion of TBHP for the experiments carried out at 343 K and 333 K was 43% and 30%, respectively.

 (a) (b) (c)

⯀Yield of 4-vinyl-1-cyclohexene 1, 2-epoxide ⯀Conversion of TBHP

Figure 4. Yield of 4-vinyl-1-cyclohexene 1, 2-epoxide and conversion of TBHP. (a) Effect of reaction temperature at 1:1 molar ratio of 4-vinyl-1-cyclohexene to TBHP, feed flow rate: 0.1 mL/min. (b) Effect of feed molar ratio at 353 K, feed flow rate: 0.1 mL/min. (c) Effect of feed flow rate at 353 K, FMR of 4-vinyl-1-cyclohexene to TBHP: 1:1.

*Effect of feed molar ratio (FMR).* Epoxidation of 4-vinyl-1-cyclohexene with TBHP is an equilibrium limited reaction. Hence, the use of an excess of alkene in a continuous experiment should increase the rate of reaction. The effect of FMR was studied at 1:1, 2.5:1 and 5:1 molar ratios of
4-vinyl-1-cyclohexene to TBHP. Figure 4b illustrates that the experiment conducted at 5:1 molar ratio resulted in ~82% yield of epoxide and 94% conversion of TBHP as compared to the experiments carried out at 2.5:1 and 1:1 molar ratios which gave 70% and 43% yield of epoxide, respectively.

*Effect of feed flow rate.* The effect of feed flow rate was investigated at feed flow rates of 0.1 mL/min, 0.13 mL/min and 0.16 mL/min. Increase in feed flow rate usually results in reduction in feed residence time in the reaction zone (packed column). The yield of 4-vinyl-1-cyclohexene 1, 2-epoxide and conversion of TBHP decreased with an increase in feed flow rate from 0.1 mL/min to 0.13 mL/min as shown in Figure 4c.

*Catalyst reusability studies*. Reusability studies of Ps.AMP.Mo catalyst in batch epoxidation of 4-vinyl-1-cyclohexene 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 3a and b). In continuous epoxidation 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. 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.

5. CONCLUSIONS

Polymer supported Mo(VI) catalyst i.e. Ps.AMP.Mo has been successfully prepared and characterised. The performance of this catalyst has been assessed for the epoxidation of
4-vinyl-1-cyclohexene in batch and continuous reactors using TBHP as an oxidant. Ps.AMP.Mo catalyst has been proved to be long lived, stable and suitable for the epoxidation of
4-vinyl-1-cyclohexene. 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. In comparison with batch experiment, the continuous flow reaction in a FlowSyn reactor shows substantial benefits that include fast heat and mass transfer, short setup and reaction times, flexibility of scaling-up reactions, complete non attended operation, safer and more environmentally friendly operating procedures.

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