Optimisation of Greener Alkene Epoxidation Catalysed by Polybenzimidazole Supported Mo(VI) Complex *via* Response Surface Methodology

Md Masud R. Bhuiyan[1], Basudeb Saha[1*]
[1]*School of Engineering, Lancaster University, Lancaster LA1 4YW, UK*
**corresponding author: b.saha@lancaster.ac.uk*

Introduction

Alkene epoxidation has been established as an important process for chemical synthesis as the resultant epoxide acts as a raw material or intermediate that can be transformed into many useful substances such as plasticizers, perfumes, and epoxy resins [1]. The conventional epoxidation process involves stoichiometric peracids as oxidising agents, but it is not environmentally friendly. In contrast, polymer-supported heterogeneous catalysts with *tert*-butyl hydroperoxide (TBHP) as an oxidant have demonstrated strong catalytic activity and product selectivity [1, 2].

In this study, an efficient and selective polybenzimidazole supported molybdenum (VI) complex (PBI.Mo) was used for the batch epoxidation of 1,5-hexadiene and 1,7-octadiene. Experiments were carried out to study the effect of reaction temperature, feed molar ratio of alkene to TBHP, catalyst loading and reaction temperature on the yield of epoxide to optimize the reaction conditions in a classical batch reactor. Response surface methodology (RSM) using Box-Behnken Design (BBD) was employed to study the interaction effect of different variables on the reaction response.

Materials and Methods

Polymer-supported Mo(VI) catalyst was prepared by reacting PBI resin with $MoO_2(acac)_2$ in the stoichiometric ratio of 2:1 in toluene for four days. The molybdenum content of the prepared catalysts was analysed using PerkinElmer NexION 350D spectrophotometer. Brunauer-Emmett-Teller (BET) surface area, pore volume and pore diameter were determined by nitrogen adsorption and desorption method using Micromeritics Gemini VII. The particle size measurement was performed with Malvern Mastersizer.

Response surface methodology (RSM) using Box-Behnken Design (BBD) was employed for designing experimental runs and studying the interaction effect of different variables including reaction feed molar ratio of 1,5-hexadiene to TBHP, reaction temperature, catalyst loading and reaction time on the reaction response. Batch epoxidation of 1,5-hexadiene and 1,7-octadiene with TBHP as an oxidant in the presence of polymer supported Mo(VI) catalyst was conducted in a 0.25 L jacketed four neck glass reactor. A specific quantity of internal standard (*iso*-octane) was added to samples with known concentrations of the components in the product mixture and analysed using Shimadzu GC-2014 gas chromatography. A quadratic regression model was developed representing empirical relationship between reaction variables and response. The yield of epoxide was selected as the response for this study.

Results and Discussion

The mathematical model was defined using the general quadratic model as shown in **equation (1).**

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j>1}^{n} b_{ij}\, x_i x_j + \varepsilon \qquad (1)$$

By fitting the experimental results, the generic quadratic equation shown in **equation (1)** was used to obtain a model of polynomial regression. The developed models demonstrated the effect of each independent variable, variables interactions and excess of each variable on the response. ANOVA was applied to examine the significance of the model parameters at 95% confidence level. The good estimate for the response values from the model was clearly concluded from the similarity between the predicted and actual experimental results. Moreover, the perturbation plot represents the effect of each variable on the reaction response.

Design Expert software was used to develop the numerical optimisation step by combining the desirability of each independent variable into single value and then search for optimum values for the response goals. The dependent response variable was set to be maximised to achieve the highest yield. The numerical optimisation technique concluded that the maximum yield of 1,2-epoxy-5-hexene is 64.2% at a feed molar ratio of 2.76:1, reaction temperature of 348 K, 0.56 mol% catalyst loading, and reaction time of 76 min. On the other hand, the maximum yield of 1,2-epoxy-7-octene was 66.22% at feed molar ratio of 7.97:1, reaction temperature 347 K, 0.417 mol% catalyst loading and reaction time of 218 min.

To validate the optimal response values of the predicted quadratic equation, experiments were performed at optimum condition. The experimental results showed a similar response value to the predicted optimal response with an error of 3.5% and 1.92 % for both 1,2-epoxy-5-hexene and 1,2-epoxy-7-octene respectively. The relative error can be affected by the temperature variation during the reaction.

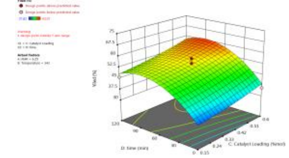

Figure 1. 3-D graph showing the effect of reaction time and catalyst loading on the yield of 1,2-epoxy-5-hexene.

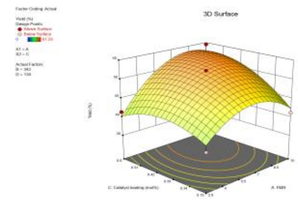

Figure 2. 3-D graph showing the effect of catalyst loading and FMR on the yield of 1,2-epoxy-7-octene.

Significance

The polymer-supported Mo(VI) (PBI.Mo complex) was prepared, characterized and assessed as a catalyst for the epoxidation of 1,5-hexadiene and 1,7-octadiene in a batch reactor using TBHP as an oxidant. Two quadratic polynomial model were developed demonstrating the yield of 1,2-epoxy-5-hexene and 1,2-epoxy-7-octene in four independent variables. The optimisation results observed for the maximum yield of 1,2-epoxy-5 hexene and 1,2-epoxy-7-octene were validated experimentally. The experimental results showed 62.03% yield of 1,2-epoxy-5 hexene and 64.97% yield of 1,2-epoxy-7-octene, which show the adequacy of the predicted optimum conditions from the experimental results. This study demonstrates that PBI.Mo complex could be used as an effective catalyst for a greener and more efficient epoxidation of 1,5-hexadiene and 1,7-octadiene with TBHP as an oxidising reagent.

References

1. Bhuiyan, M.M.R.; Mohammed, M.L.; Saha, B. Greener and Efficient Epoxidation of 1,5-Hexadiene with *tert*-Butyl Hydroperoxide (TBHP) as an Oxidising Reagent in the Presence of Polybenzimidazole Supported Mo(VI) Catalyst. *Reactions* **2022**, 3, 537–552.

2. Mbeleck, R.; Mohammed, M.L.; Ambroziak, K.; Sherrington, D.C.; Saha, B. Efficient epoxidation of cyclododecene and dodecene catalysed by polybenzimidazole supported Mo(VI) complex. *Catal. Today* **2015**, *256*, 287–293.