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Epoxidation of Limonene by *Tert*-butyl Hydroperoxide Catalyzed by Polybenzimidazole-supported Mo(VI) Complex

Krzysztof Ambroziak and *Basu Saha

Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

Rene Mbeleck and David C. Sherrington

WestChem Graduate School, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK

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Abstract

A polybenzimidazole supported Mo(VI) (PBI.Mo) catalyst has been prepared and characterised. The catalytic activities of the PBI.Mo catalyst in epoxidation of limonene with *tert*-butyl hydroperoxide (TBHP) as oxidant have been studied under different reaction conditions in a batch reactor. The batch experimental data provided useful information for conducting continuous experiments in a reactive distillation column (RDC).

Key words: Polymer supported molybdenum catalyst, limonene, limonene epoxidation, 1,2-limonene oxide.

1 Introduction

Monoterpenes, present in most essential oils, are considered to be the main agents responsible for the flavour characteristics of many fruits, spices and vegetables. Limonene, which is the main component of the orange essential oil, has a low price, and is thus a particularly important substrate for the production of much higher value products [1-3]. One of the limonene oxidation products is limonene oxide, which is a key raw material in the synthesis of pharmaceuticals, fragrances, perfumes and food additives and also have great importance in organic synthesis [4]. Conventionally, it is manufactured by oxidation of limonene with stoichiometric amounts of peracids. As this process is not environmental friendly due to the formation of stoichiometric amounts of the corresponding acid, there are many attempts in progress to develop more suitable solid catalysts for this reaction [5-11]. Most of the known solid catalysts e.g. Ti-MCM-41 [5], carbon-anchored Co(acac)₂ [7], and supported Keggin heteropoly compounds [8,11], show significantly low limonene conversions and epoxide selectivities (20-30%); carveol, carvone and polymeric products are also formed in large quantities.

There has been a considerable amount of academic work published on polymer-supported metal complex alkene epoxidation catalysts with a number of Mo(VI) based systems looking particularly attractive for scale-up and commercial exploitation [12]. Despite this there appears to have been no significant attempt to move the chemistry on

from being a useful small-scale laboratory procedure to being a viable medium to large-scale production technology. We are now involved in a chemistry/chemical engineering collaboration aimed at addressing both of these shortcomings and have selected a highly active and selective polymer-supported Mo(VI) alkene epoxidation catalyst (PBI.Mo), employing *t*-butyl hydroperoxide as the oxidant, which one of us developed for use in small batch reactions some time ago. The most attractive support is a highly thermo-oxidatively stable polybenzimidazole (PBI) available in a bead form from Hoechst-Celanese which has been loaded with Mo(VI) simply by treatment with excess MoO₂acac₂ followed by exhaustive washing to yield the PBI.Mo catalyst **1** [13].

We are currently re-visiting the use of this catalyst in small batch epoxidations of cyclohexene and have confirmed the remarkable catalytic performance. Very recently, the stability and recycling of polymer-supported Mo(VI) alkene epoxidation catalysts have been reported by Mbeleck et al. [14]. We are also developing a detailed knowledge of the repeated use of this catalyst to provide experimental parameters to aid in the design of a reactive distillation column (RDC). Reactive distillation (RD) is an emerging technology that has extremely attractive potential as a process alternative for carrying out liquid phase chemical reactions [15-18]. It is a unit operation which combines simultaneous chemical reaction and multi-component distillation in the same vessel in a single step. RD technology has particular benefit for equilibrium limited reactions. RD processes require the use of a stable heterogeneous catalyst that can be packed into an appropriate column, and for this purpose polybenzimidazole-supported Mo species (PBI.Mo) seemed to be an excellent candidate.

In this paper we will highlight some batch experimental studies for epoxidation of limonene catalyzed by polymer supported Mo(VI) complex. This information will be useful for performing the continuous experiments in RD rig, which is currently being designed and constructed in our laboratory.

2 Experimental

2.1 Preparation of Mo(VI) polymer supported catalyst (PBI.Mo)

Polybenzimidazole supported Mo(VI) (PBI.Mo) catalyst preparation and Mo determination have been reported elsewhere [14, 19].

2.2 Batch epoxidation studies

The experiments were conducted in a 250 ml jacketed batch reactor at temperatures from 333 to 353 K and at molar ratios of limonene to *tert*-butyl hydroperoxide from 2.5:1 to 10:1. Catalyst loading varied from 0.15 to 0.6 mol% (ratio of moles of Mo to moles of TBHP x 100%) and the stirrer speed was set at 400 rpm.

Fig. 1. Studied epoxidation reaction of limonene catalyzed by PBI Mo complex.

3 Results and discussion

Oxidation of limonene, in general, yields a variety of products. Generally, epoxides are the selective products if the oxidation occurs at olefinic positions. If the oxidation takes place at allylic positions, the products will be carveol and carvone. In addition, limonene has two olefinic bonds (1,2 and 8,9) and the oxidation can take place at either or both of these sites. Further, two types of diastereomers (*cis* and *trans*) are expected for each epoxide product [10]. Wentzel *et. al.* [20] studied the use of PBI.Mo catalyst in aerobic epoxidation of limonene, however no reaction was observed. In our studies using the same catalyst, we employed *tert*-butyl hydroperoxide as an oxidant and it was found that the main product for limonene epoxidation was in all cases 1,2-limonene epoxide. GC analysis showed the 1,2-epoxide to be 50:50 mixture of *cis* and *trans* diastereoisomers. 8,9-Limonene epoxide was found to be the by-product present in all conducted epoxidations. It is to be noted that neither diepoxide nor any other by-products were formed during the present study. Regardless of reaction conditions the selectivity of 1,2-limonene oxide reached 94% after 60 min of the reaction and remained constant at higher conversion levels (until the end of experiment). Only trace amount of 1,2-limonene oxide (~2% yield) was detected when the reaction was carried out without catalyst under standard experimental conditions.

The effect of temperature, catalyst loading, feed mole ratio and catalyst reusability was studied for the epoxidation of limonene with TBHP to synthesise 1,2-limonene oxide.

3.1 Effect of reaction temperature

Reactions were carried out at 333, 343 and 353 K in order to study the effect of temperature on the reaction rate and conversion of TBHP towards 1,2-limonene oxide formation, further in the text which is referred to as yield of 1,2-limonene oxide. The yield of the reaction was expressed as $Y = (C_{\text{epox}}/C_{\text{TBHP}}) \times 100\%$, where C_{epox} and C_{TBHP} are the molar concentration of 1,2-limonene oxide and the initial concentration of TBHP, respectively. The obtained information is also useful for calculating the activation energy for this reaction. Moreover, the intrinsic rate constants are strong functions of temperatures. Fig. 2 presents the variation of 1,2-limonene oxide yield with time for different reaction temperatures. As expected, it shows that the higher temperature gives the greater yield of 1,2-limonene oxide at a fixed reaction time.

Epoxidation of limonene at 353 K catalyzed by the PBI. Mo complex was not as fast as cyclohexene epoxidation catalyzed by the same catalyst when nearly 100% yield was achieved after only 50 min [14]. However, after 120 minutes of the reaction, nearly 90% yield of 1,2-limonene oxide was achieved. After the same reaction time, 86% yield was obtained at 343 K whilst at 333 K, 66% yield of 1,2-limonene oxide was achieved. Reaction rate for epoxidations carried out at 353 K and 343 K is very similar whilst significant drop of reaction rate at 333 K was recorded. However at the end of experiment (after 350 min) at 353 343 and 333 K similar yields of 95%, 95% and 89% was achieved, respectively. The reaction was completed after 240 minutes at 353 K and after 290 minutes at 343K.

Fig. 2. Effect of temperature on the yield of 1,2-limonene oxide and reaction rate at 5:1 molar ratio of limonene to TBHP, catalyst loading 0.3 mol%.

It is worth noting that temperature should be controlled carefully as an exothermic effect of the reaction could be observed especially when carrying out the reaction at 353 K. The temperature of the reaction mixture can increase up to 363 K. Therefore, a higher yield of 1,2-limonene oxide can be achieved in a shorter time.

The effect of temperature for batch studies provides us information about the optimum temperature required for obtaining high yield and reaction rate for limonene epoxidation. This information will be very useful for conducting continuous experiments in a RDC.

3.2 Effect of water content on the limonene epoxidation

Since the commercially supplied TBHP is “wet” (contains ~ 30 wt% of water), it was thought worthwhile to examine the use of this oxidant without removing the water. Fig. 2 (x) shows the obtained yield of 1,2-limonene oxide under the standard experimental condition (353 K, 5:1 molar ratio of limonene to TBHP, catalyst loading 0.3 mol%, 400 rpm agitation speed.) catalyzed by PBI.Mo, but using “wet” TBHP instead of the anhydrous material. The corresponding results obtained using PBI.Mo and dry TBHP are also shown in Fig. 2 (♦).

From these data it can be seen that initial reaction was slightly faster using “wet” TBHP but the amount of 1,2-limonene oxide formed reached a maximum of 50% (after 100 minutes) and then slowly decreased to about 42% at the end of experiment.

Even though there was no formation of limonene epoxide after 100 minutes, TBHP conversion was still increasing during the course of reaction, reaching 81% at the end of the experiment and TBHP consumed after 100 minutes was converted to *tert*-butanol, the by product of the epoxidation reaction where TBHP is used as an oxidant. Another interesting feature which was observed during the “wet” epoxidation of limonene was the diastereoselectivity. In reactions when dry TBHP was employed as an oxidant, 50:50 mixture of *cis* and *trans* diastereoisomers of 1,2-limonene oxide was obtained, whilst when using “wet” TBHP, 50:50 mixture was obtained only for the first 60 minutes, and after this reaction time the diastereoisomeric ratio started to change to give 25:75 mixture (*cis:trans*) at the end of the experiment. This is probably because the epoxide(s) formed undergo hydrolysis to diols, and possibly the reaction of one epoxide is faster than the other on steric grounds. Epoxide(s) continue to be formed and hydrolysed after ~60 minutes but the total amount present does not change much but the composition drifts in favour of the lesser reactive diastereomer. Some further control reactions are planned to shed more light on these results. The explanation for the loss of epoxide and increase of diastereoselectivity are currently being investigated.

3.3 Effect of catalyst loading

The effect of the catalyst loading on the reaction rate and yield of 1,2- limonene oxide was investigated with catalyst loading 0.15, 0.3 and 0.6 mol% (i.e. the ratio of moles of Mo to moles of TBHP x 100%) and for these loadings the molar ratio of Mo to TBHP was $1.5 \times 10^{-3}:1$, $3 \times 10^{-3}:1$, $6 \times 10^{-3}:1$, respectively. With an increase in catalyst loading, the number of active sites per volume of the reactor increases in direct proportion leading to an increase in the rate of the reaction and yield of 1,2- limonene oxide (Fig. 3).

Fig. 3. Effect of catalyst loading on the yield of 1,2-limonene oxide and reaction rate at 353 K, 5:1 molar ratio of limonene to TBHP.

For the catalyst loading 0.15 mol%, 90% yield of 1,2-limonene oxide was achieved after 240 minutes whilst with catalyst loading 0.3 mol%, 90% yield was achieved after 120 minutes. However, reaction rate was very high when 0.6 mol% of the catalyst was used, in this case 90% yield of 1,2-limonene oxide was obtained after 60 minutes, and the reaction was completed after 100 minutes. The obtained results clearly shows the reaction rate - catalyst loading dependence in epoxidation of limonene, increasing the catalyst loading leads to increase in reaction rate. It is also worth noting that very low catalyst loading was used in the epoxidation of limonene compared to other heterogeneous catalyzed reactions. This study demonstrates very high efficiency of PBI.Mo catalyst for limonene epoxidation reaction.

3.4 Effect of reactants molar ratio

In most of the catalyzed epoxidation processes a substantial excess of alkene is generally employed in order to achieve higher conversion of hydroperoxide and higher selectivity towards the epoxide. For limonene epoxidation catalyzed by PBI. Mo catalyst, regardless of feed mole ratio, the selectivity towards 1,2-limonene oxide has not changed in all three experiments and remained at the same value of 94% at the end of the reaction. The excess of alkene might also help in achieving higher reaction rate or product yield. It can be seen from Fig. 4 that variation of reactants molar ratio has not affected product yield significantly. After 120 minutes, reaction yield reached above 90% for all three molar ratio studied. This information would be very useful for carrying out continuous operation in RD rig. Unexpectedly, the slightly higher reaction rate obtained for 2.5:1 limonene to TBHP ratio might be explained by temperature increase of the reaction mixture due to the exothermic effect that was observed when the fresh catalyst was used for the reaction. It is therefore recommended that a feed mole ratio of 2.5:1 (limonene to TBHP) would be suitable for carrying out the reaction continuously in an RDC.

3.5 Effect of catalyst reusability

In the RD rig, the catalytic section of the column will be filled with PBI.Mo catalyst, packed in structured packing materials and the catalyst will be reused for several times. In order to check the reusability of the catalyst for continuous RD studies, it is essential to study the catalyst reusability. As it is shown in Fig. 5, the polymer supported catalyst remain active over many cycles. For all the runs more than 90% yield of 1,2-limonene oxide was achieved at the end of experiment after 350 minutes.

The rate of epoxide formation seems to decrease for the first 3 runs, however the results for "Run 3" and

Fig. 4. Effect of reactants molar ratio on yield of 1,2-limonene oxide and reaction rate at 353 K, catalyst loading 0.3 mol%.

Fig. 5. Effect of catalyst reusability on the yield of 1,2-limonene oxide and reaction rate at 353 K, 5:1 molar ratio of limonene to TBHP, catalyst loading 0.3 mol%.

“Run 4” are nearly identical for limonene epoxidation. For all the runs selectivity towards 1,2-limonene oxide remained constant during the course of reaction and found to be 94% at the end of experiment. Although the rate of reaction was slower when the catalyst was reused for more than two times, but the rate could be improved if the reaction could be conducted at a slightly higher temperature (it was proved that 10 K increase in the reaction temperature enhance the reaction rate). Some attrition of catalyst particles was noticed when they have been reused for more than three times under agitated condition in the batch reactor but this effect will be absent in the RDC as the catalyst will be packed within the structured packing materials in the reactive section of the column.

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References

- 1) M. Gomes Jr., O.A.C. Antunes, *Catalysis Commun.*, **2**, 225-227, (2001).
- 2) M.F.T. Gomes, O.A.C. Antunes, *J. Mol. Catal. A: Chemical*, **121**, 145-155, (1997).
- 3) National Industrial Chemical Notification and Assessment Scheme “Limonene: Priority Existing Chemical Assessment: Report No 22”, Australia, 1-130, (2002), ISBN 0 642 50190 4
- 4) B.D. Mookherjee, R.A. Wilson, “Encyclopedia of Chemical Technology Kirk-Orthmer, vol. 17 , 4th ed.”, Wiley, New York (1996), pp. 603–674.
- 5) R. Hutter, T. Mallat, A. Baiker, *J. Catal.*, **153**, 177-189, (1995).
- 6) M.V. Cagnoli, S.G. Casuscelli, A.M. Alvarez, J.F. Bengoa, N.G. Gallegos, N.M. Samaniego, M.E. Crivello, G.E. Ghione, C.F. Pe´rez, E.R. Herrero, S.G. Marchetti, *Appl. Catal. A: Gen.*, **287**, 227-235, (2005).
- 7) P. Oliveira, A.M. Ramos, I. Fonseca, A. Botelho do Rego, J. Vital, *Catal.Today*, **102/103**, 67-77, (2005).
- 8) P.A.L. Villa, A.F. Taborda, C. Monte de Correa, *J. Mol. Catal. A: Chem.*, **185**, 269-277, (2002).
- 9) P.A. Robles-Dutenhefner, M.J. da Silva, L.S. Sales, E.M.B. Sousa, E.V. Gusevskaya, *J. Mol. Catal. A: Chem.*, **217**, 139-144, (2004).
- 10) J. Bussi, A. López, F. Peña, P. Timbal, D. Paz, D. Lorenzo, E. Dellacasa, *Appl. Catal. A: Gen.*, **253**, 177-189, (2003).
- 11) N.K. Kala Raj, V.G. Puranik, C. Gopinathan, A.V. Ramaswamy, *Appl. Catal. A: Gen.*, **256**, 265-273, (2003).
- 12) D.C. Sherrington, *Catalysis Today*, **57**, 87-104, (2000).
- 13) S. Leinonen, D.C. Sherrington, A. Sneddon, D. McLoughlin, J. Corker, C. Canevali, F. Morazzoni, G. van Alba, J. Reedijk, S.B.D. Spratt, *J. Catal.*, **183**, 251-266, (1999).
- 14) R. Mbeleck, K. Ambroziak, B. Saha and D.C. Sherrington, *React. Funct. Polym.*, (2007), accepted.
- 15) B. Saha, M.M. Sharma, *React. Funct. Polym.*, **28**, 263-278, (1996).
- 16) B. Saha, S.P. Chopade, S.M. Mahajani, *Catal. Today*, **60**, 147-157, (2000).
- 17) B. Saha, H.T.R. Teo, A. Alqahtani, *Intl. J. Chem. Reactor Engng.*, **3** (A11), 1-14, (2005).
- 18) K. Sundmacher, A. Kienle, “Reactive Distillation Status and Future Directions”, Wiley-VCH Verlag gmbH, Weinheim, Germany (2003).
- 19) M.M. Miller, D.C. Sherrington, *J. Catal.*, **152**, 368-376, (1995).
- 20) B.B. Wentzel, S-M. Leinonen, S. Thompson, D.C. Sherrington, M.C. Feiters, R.J.M. Nolte, *J. Chem. Soc., Perkin Trans.*, **1**, 3428-3431, (2000).