

Alkene epoxidation catalyzed by vanadomolybdophosphoric acids supported on hydrated titania

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Abstract

Vanadomolybdophosphoric acids wet-impregnated on hydrated titania ($\text{TiO}_2 \cdot x\text{H}_2\text{O}$), make an efficient catalytic system for the epoxidation of a variety of alkenes with organic solvent extracted TBHP as the oxidant. By an appropriate choice of solvent, the catalyst can be reused at least three times without much loss in the activity for subsequent runs. XRD shows that the heteropoly acid is uniformly dispersed over the support and up to 15 wt% loading of the heteropoly acid, no additional peak of the same can be seen in the XRD pattern of the catalyst. The reactivity varied with the nature of alkene but the major product was always the corresponding epoxide. The catalytic system is free of high temperature calcination steps and tedious multi-step procedures, normally encountered in the heterogenization of heteropoly acids.

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1. Introduction

Epoxides are the essential precursors in the synthesis of various important substances like plasticizers, perfumes, epoxy resins, etc., thus epoxidation reactions assume significant importance. Many catalytic systems containing transition metal ions have been exploited for the epoxidation of alkenes. In recent years, transition metal-substituted polyoxometalates based catalysts have gained considerable interest due to their multi versatilities for the oxidation of organic substrates [1–3]. Transition metal-substituted polyoxometalates (TMSP) generally provide higher conversion and better selectivity for epoxides [4–7]. Amongst the TMSP, vanadium-substituted polyoxometalates are the most studied ones that have attracted the attention as catalysts for a variety of catalytic oxidation reactions like

hydroxylation of benzene, oxidation of toluene and nitrobenzene with aqueous hydrogen peroxide, oxidation of isobutyric acid to methacrylic acid with molecular oxygen and so on [8–15].

Although, the activity of vanadomolybdophosphoric acids is well documented, most of the current examples demonstrate their catalytic applications as a homogenous catalyst [16–18]. Alternatively, they are heterogenized by anchoring them onto amine-functionalized SBA-15 and other mesoporous materials [19,20] or by impregnation on inert supports like silica, alumina or zirconia and further calcination at high temperatures [21–23]. The former strategy is generally applied for oxidation reactions while latter one is generally applied for acid catalyzed reactions. Both these methods have their own drawbacks like multi-step synthesis of catalyst materials and time as well as energy consuming calcination steps, respectively. So the simple strategy applied here was the wet-impregnation of vanadomolybdophosphoric acids on a support and carry out the reactions in non-polar or hydrophobic solvents, so as to minimize the dissolution of these polar molecules

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and maintain the heterogeneity of the catalyst. Thus, in the current system vanadomolybdophosphoric acids were wet-impregnated on $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ or $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ as the supports and after drying were tested for their activities in alkene epoxidation. Interestingly, amongst the two supports, titania supported vanadomolybdophosphoric acids showed a higher activity than the zirconia analogue. This, we think is due to synergistic effect between the heteropoly acids and titania support, as shall be seen further.

The mere wet-impregnation step of heteropoly acids on titania, however deprived us from using aq. hydrogen peroxide and aq. TBHP as oxidants, since the water component of these oxidants dissolves the heteropoly acids easily, hence losing the heterogeneous behavior of the catalysts. Thus the oxidant used here was TBHP extracted in dichloroethane, or other hydrophobic solvents. This has refrained in having a comparative data of the catalytic activity with different oxidants for our system. Although the use of hydrophilic solvent like acetonitrile increased the catalytic activity as compared to the activity in dichloroethane, most of the heteropoly acid was lost due to its dissolution in the former. As a result the subsequent catalytic activity reduced drastically in further runs for such hydrophilic solvent systems. The dissolution of heteropoly acids in hydrophilic solvents may be the reason behind the initial higher activity displayed in the same. Although the additives like TBHP dissolve the heteropoly acid to some extent even in the dichloroethane solvent system, it is observed that there is not much loss in activity for next two subsequent runs, as shall be seen further. Importantly, in all the cases the major product was always the corresponding epoxide.

2. Experimental

2.1. Sample preparation

Phosphomolybdic acid (PMA), phosphotungstic acid (PTA), titanium *t*-butoxide and zirconyl nitrate were purchased from Loba Chemie India Ltd. 1,2-Dichloroethane, acetonitrile, methanol, ether and other solvents were procured from Merck India Ltd. All the alkenes were obtained from Aldrich, while 70% aq. TBHP was obtained from Fluka. Sodium molybdate and sodium metavanadate were availed from S.D. fine chemicals India Ltd. All the chemicals were used as received without further purification.

Mono, di and tri vanadomolybdophosphoric acids (hereafter denoted by V_xPMA , where $x = 1, 2$ and 3 , respectively) were synthesized by known procedures [24] and their formation was checked by FTIR and elemental analysis. Hydrated titania ($\text{TiO}_2 \cdot x\text{H}_2\text{O}$) and hydrated zirconia ($\text{ZrO}_2 \cdot x\text{H}_2\text{O}$) were prepared by hydrolysis of titanium *t*-butoxide with distilled water and zirconyl nitrate solution with 1:1 ammonia, respectively and drying the same at 110 °C. 15 wt% HPA/ MO_2 samples (where HPA stands for heteropoly acid and MO_2 stand for titania or zirconia) were prepared by wet-impregnation method, using methanol for the dissolution of HPA. The samples were

dried at 110 °C prior to use. Thirty percent TBHP in 1,2-dichloroethane (henceforth TBHP/DCE) was prepared by shaking appropriate amounts of dichloroethane and commercially available 70% aq. TBHP. The exact strength of peroxide in TBHP/DCE was checked by iodometric titration [25].

2.2. Characterization

The room temperature powder X-ray diffraction patterns of the samples were collected on a Philips X'Pert Pro 3040/60 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), nickel filter and X'celerator as detector. Solid state UV–visible spectra were recorded on Perkin-Elmer lambda-350 UV–visible spectrophotometer. FTIR spectra were recorded on Shimadzu FTIR 8201 PC instrument. ICP analysis was done on Perkin-Elmer Plasma 1000 Emission Spectrometer.

2.3. Catalytic activity

The liquid phase epoxidation reactions were carried out in a two-necked 50 ml round bottom flask immersed in a thermostated oil bath maintained at desired temperature between 40 and 80 °C. A typical reaction mixture contained 0.1 g of catalyst, 10 mmol of substrate, 20 mmol of 30% TBHP and 10 ml of dichloroethane. The reaction mixture was stirred with a Teflon-coated magnetic bar. Progress of the reaction was monitored by drawing small aliquots of the reaction mixture at regular intervals and subjecting them to GC analysis (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m \times 0.32 mm 5% phenyl methylsilicone capillary column). The products were identified by GC–MS (Shimadzu gas chromatograph, G-17A fitted with QP-500 MS Mass spectrometer).

3. Results and discussion

3.1. Cyclooctene epoxidation with 15 wt% $\text{V}_2\text{PMA/TiO}_2$

Epoxidation of cyclooctene was performed with different 15 wt% HPA/ MO_2 catalysts. Amongst them 15 wt% $\text{V}_2\text{PMA/TiO}_2$ was a better catalyst for the reaction as can be seen in Table 1. In order to investigate its higher activity over other 15 wt% HPA/ MO_2 catalysts, an attempt was made to explore the role of vanadium, titanium and other transition metal ions in the system. So few controlled experiments were conducted with different 15 wt% HPA/ MO_2 catalysts using TBHP/DCE as the oxidant and dichloroethane as the solvent, and the results are presented in Table 1. It can be seen from the results (Table 1) that even 15 wt% PMA/ TiO_2 (where PMA stands for phosphomolybdic acid) was also active for this reaction but showed a poor activity. Thus for the same reaction with TBHP/DCE as the oxidant, only 32% cyclooctene conversion was seen with 15 wt% PMA/ TiO_2 as against 94% conversion observed for 15 wt% $\text{V}_2\text{PMA/TiO}_2$ at the same set

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