

*Chapter 6:*  
*Summary and Conclusion*

## 6.1 Introduction

Selective oxidation of olefins and alcohols to produce epoxides, aldehydes, and ketones is of great importance in the fine chemical and pharmaceutical industries. Traditionally, these catalytic procedures produce a great deal of environmentally undesirable wastes because inorganic oxidants and organic solvents are used. Replacing the conventional process by an environmentally benign procedure along with the use of environment friendly oxidants like molecular oxygen or hydrogen peroxide is highly desirable. However, it is known that both these eco friendly oxidants generally do not show any direct activity towards the organic substrates. There are various transition metal ions based catalyst systems that are known to activate molecular oxygen and hydrogen peroxide. Most of them are of metal-organic ligand in origin like the metal-salen complexes or metal-porphyrin complexes. The problem with these systems is that the organic part of the catalyst is vulnerable to oxidation thereby losing its activity. Thus, a catalyst system that activates both molecular oxygen and hydrogen peroxide for the selective oxidation reactions, without itself undergoing oxidative decomposition during the course of reaction is certainly desired. This thesis deals with the use of Polyoxometalates as catalysts for all such oxidation reactions. A detailed summary and conclusion derived from each chapter is explained below.

## 6.2 Selective oxidation of alkenes and alcohols over [SbW<sub>9</sub>O<sub>33</sub>] based catalyst system with *aq.* H<sub>2</sub>O<sub>2</sub>

This chapter deals with selective oxidation of alkenes and alcohols over Na<sub>9</sub>[SbW<sub>9</sub>O<sub>33</sub>] in conjunction with a phase transfer catalyst [MTCA]<sup>+</sup>Cl<sup>-</sup> catalytic system, with *aq.* H<sub>2</sub>O<sub>2</sub> as the oxidant. The system was found to be capable of selectively oxidizing a number of structurally different alkenes as well as a variety of secondary and allylic in high yields. In most of the cases the selectivity for epoxide (in the case of alkenes) or ketone (in the case of alcohols) was excellent. Importantly, there was no need of any solvent for the reaction (except when the substrate was a solid). It could be unambiguously shown from the controlled experiments that tungstate species are indeed the active centers and that the incorporated transition metal ions do not play any major role. Spectroscopic studies indicated the formation of a tungsten-peroxo intermediate on the interaction of polyoxotungstate with *aq.* H<sub>2</sub>O<sub>2</sub> in presence of [MTCA]<sup>+</sup>Cl<sup>-</sup>, and this intermediate was observed for both the

transition metal containing polyoxotungstate as well as the transition metal free precursor. Spectroscopic studies also revealed that the catalyst was stable in the presence of PTC when *aq.* H<sub>2</sub>O<sub>2</sub> was used as the oxidant.

### **6.3 Alkene epoxidation catalyzed by vanadium heteropoly acids heterogenized on amine functionalized SBA-15 materials**

This chapter deals with vanadium substituted molybdophosphoric acids (V<sub>x</sub>HPA) immobilized on amine functionalized SBA-15 as catalysts for epoxidation of alkenes, once again with the same oxidants of *aq.* H<sub>2</sub>O<sub>2</sub> as well as TBHP. The synthesized materials were characterized by using various techniques prior to testing of their catalytic activities. Small angle X-ray scattering analysis provided evidence for the structural integrity of the amine functionalized SBA even after immobilizing with molybdovanadophosphoric acid. The synthesized materials were also characterized by nitrogen sorption studies, UV-Visible, NMR, and IR studies provided evidence for the presence of V<sub>x</sub>HPA inside the NH<sub>2</sub>-SBA. The catalytic activity of the immobilized sample (NH<sub>2</sub>-SBA-V<sub>x</sub>HPA) were studied for few substrates with aqueous hydrogen peroxide at 60 °C and compared with the neat V<sub>x</sub>HPA catalyst. It was found that selectivity of the products is higher with the immobilized catalyst. The catalyst part can be separated after the epoxidation reactions and can be reused for few cycles without losing its further activity, especially with TBHP as the oxidant.

### **6.4 Alkene epoxidation catalyzed by vanadium heteropoly acids dispersed on hydrated titania**

This chapter deals with alkene epoxidation catalyzed by vanadium substituted molybdophosphoric acids (V<sub>x</sub>HPA) dispersed on hydrated titania, with organic solvent extracted TBHP as the oxidant, in a lipophilic solvent system. It was clearly demonstrated that divanadomolybdophosphoric acid wet-impregnated on hydrated titania (TiO<sub>2</sub>.xH<sub>2</sub>O) was an excellent catalyst system for alkene epoxidation, with TBHP extracted in dichloroethane as the oxidant. The catalysts could be recycled without much loss in activity at least three times by choosing appropriate solvent for the reaction. For all the alkenes studied here the major product was always the corresponding epoxide. The controlled experiments unambiguously indicated that the

vanadium substitutions in the heteropoly acid as well as the titanium species from the support had a role to play. Hence a simple catalytic system, which was free of high temperature calcination steps and tedious multi-step procedures, normally encountered in heterogenization of heteropoly acids, was thus demonstrated.

### 6.5 Selective oxidation of ethane to acetic acid over MoVAIO<sub>x</sub> based catalytic system with molecular oxygen

This chapter deals with selective oxidation of ethane to acetic acid over MoVAIO<sub>x</sub> catalysts in a fixed bed down flow reactor set up. Catalysts of general formula MoVAIO<sub>x</sub> were prepared with initial elemental composition of 1.00: 0.34: 0.167 (Mo: V: Al) at different pH conditions, showed pH dependent elemental compositions. While all of them found to be active for selective oxidation of ethane, catalysts prepared at pH 2 showed excellent activity with 23 % ethane conversion with 80 % combined selectivity to ethylene and acetic acid in equimolar ratio at optimum experimental conditions. From powder XRD and other spectroscopic studies, the high activity was attributed to the presence of MoV<sub>2</sub>O<sub>8</sub> and other reduced species like Mo<sub>4</sub>O<sub>11</sub> phases supported on MoO<sub>3</sub>. Although presence of any amorphous phase was not clear at present, presence of V and Mo ions in partially reduced form, as confirmed by Raman, UV-visible and EPR spectra, played a crucial role in the selective oxidation of ethane.

### 6.6 Overall Conclusion

In this thesis, [SbW<sub>9</sub>O<sub>33</sub>] based polyoxotungstate in conjunction with a phase transfer catalyst (methyl trioctyl ammonium chloride) was used as catalyst for the selective oxidation of alkenes and alcohols with *aq.* H<sub>2</sub>O<sub>2</sub> as the oxidant. This system does not require any solvent, except in the case of solid alkenes/alcohols. It was also demonstrated using FT-IR spectroscopy that the polyoxotungstate moiety is stable even in the presence of *aq.* H<sub>2</sub>O<sub>2</sub>, after extraction in organic medium under the virtue of PTC. The drawback of the system however, was difficulty in the separation of the epoxidized or ketonized product from the catalyst. High temperature distillation was required for the separation of the products, which is certainly not desired.

To overcome this problem of difficulty in separation of product from catalyst, two approaches were used; one was heterogenization of the polyoxometalate based catalyst on amine functionalized SBA-15 and the other approach was dispersion of

the same on hydrated titania, as we shall see one by one. The first approach was thus heterogenization of vanadium substituted molybdophosphoric acids on amine functionalized SBA-15. The presence of the heteropoly acids inside the pores of SBA-15 was neatly showed using various techniques. Recycling experiments were also carried out, to demonstrate the reusability of catalysts for successive runs. However, the only drawback of the system was multi-step and high temperature syntheses of the catalyst materials, thus consuming lot of time as well as energy, prior to the actual oxidation processes.

In order to overcome these problems the other approach was designed i.e. dispersion of vanadium substituted molybdophosphoric acids on hydrated titania, which was very easy to synthesize and did not require high temperature or multiple-steps for the catalyst syntheses. Here also recycling experiments were carried out to demonstrate the reusability of catalysts for successive runs. However, the disadvantage with this system was we had to restrict ourselves to lipophilic solvents like dichloroethane as well as hydrophobic oxidants like organic solvent extracted TBHP, which is normally less active and costlier than *aq.* H<sub>2</sub>O<sub>2</sub>.

In all the works seen till now we were in a position to carry out oxidation of alkenes or alcohols which are comparatively reactive as substrates and also, we have used either *aq.* H<sub>2</sub>O<sub>2</sub> or TBHP as the oxidants, which are fairly better, as far as their activation by the catalysts is concerned. Thus for the final chapter of the thesis we have carried out the selective oxidation of ethane, which shows a very low reactivity, as compared to the other substrates *viz.* alkenes or alcohols, was chosen. Further, the selective oxidation of ethane to acetic acid was carried out using molecular oxygen, which is somewhat difficult to activate, when compared to other oxidants like *aq.* H<sub>2</sub>O<sub>2</sub> or TBHP that were used in this thesis work. Normally, at high temperature and high pressure reaction conditions, the products are more reactive than the reactants itself and the easily end up in getting further oxidized to CO and CO<sub>2</sub>, which are not the actual targets. Despite all these odds, selective oxidation of ethane to acetic acid has been successfully demonstrated in the current work.