

SUMMARY AND CONCLUSIONS

SUMMARY

A novel class of heteropoly compounds has attracted world-wide attention as potential catalysts for organic reactions. The synthesis of this class of compounds can be tailored in a fashion suited for application in a particular reaction. Heteropoly compounds containing protons as the counter cations are known to be very strong acids having Bronsted type of acidity. Their acid strength is found to be greater than that of the mineral acids. Special properties associated with them like thermal stability, ease in synthesis and handling, high selectivity and good solubility facilitate their use in acid catalyzed reactions. The substitution of one or more metal atoms by another transition metal provides oxidation property to these compounds. The solubility of these transition metal substituted polyoxometalates, (T.M.S.P as they are called), can be controlled by selecting an appropriate counter cation. The most common counter cations include protons, alkali metals, alkyl ammonium groups, transition metals, etc. These compounds can be used under both homogeneous and heterogeneous reaction conditions with a wide variety of oxidants.

In the present work we have studied the oxidation as well as acid properties of the Keggin/ Anderson Compounds and utilized them as catalysts. We have also utilized transition metal complex and polymeric resin for fine chemical synthesis. The study has been conveniently divided into seven chapters.

Chapter-1 : Introduction

A brief information about the different types of heteropoly compounds and an account of the history of heteropolyoxometalates is given. This is followed by the nomenclature, structural details and general properties of polyoxometalates.

The general methods of synthesis of these compounds are also described in this chapter. The catalytic behavior of Keggin heteropoly compounds with special emphasis being laid on the oxidation properties is discussed thereafter. An outline of the proposed work is also mentioned.

Chapter-2 : Oxidation of aliphatic and benzylic alcohols by Oxone[®], catalysed by 12-tungstocobaltate (II).

In this chapter we discuss the oxidation of aliphatic and benzylic alcohols by Oxone[®], catalyzed by 12-tungstocobaltate (II). The uncatalyzed oxidation of alcohols did not occur under the experimental conditions. Various alcohols were oxidized to their corresponding carbonyl compounds with comparatively high yields. The reduced POM formed in the oxidation of alcohols is re-oxidized by Oxone[®] (potassium peroxomonopersulphate). We also did not noticed the further oxidation of the products to the corresponding acids. The catalytic method: 12-tungstocobaltate (II)/ Oxone[®] demonstrated in this chapter will be effective for the oxidation of alcohols. This work is published in *Catalysis Letters*, 96 (2004) 165-167.

Chapter-3 : Poly(Vinyl alcohol) supported 12-tungstocobaltate (II) as a novel heterogeneous catalyst for oxidation of benzylic alcohols.

This chapter describes the work on the catalytic activity of PVA supported polyoxometalate (POM), 12-tungstocobaltate(II) as an active heterogenised and recyclable catalyst for the oxidations of benzylic alcohols with Oxone[®]. The POM, 12-tungstocobaltate(II) was chosen because of its stability towards oxidative and hydrolytic decompositions. The supported catalyst was characterized by FT-IR spectra and thermo-gravimetric analysis. The spectroscopic examination of the supported catalyst has shown that the Keggin structure of the pure catalyst is

retained. It has also been found that the catalyst was not released even after swelling the supported catalyst in water for three to four days, as there was no significant weight loss. Since, there was no leaching of the catalyst, simple adsorption on to polymeric network is ruled out. Based on the thermo gravimetric results, our assumption that the supported catalyst was bound to the polymer matrix through the replacement of some of the coordinated water molecules by the -OH group of the PVA is justified. The surface electron microscopic analysis of the membranes of the PVA supported catalyst prepared by solution casting technique revealed that the catalyst is dispersed on to the polymer network. A variety of benzylic alcohols were oxidized to the corresponding carbonyl compounds. The low cost, ease of handling and with increasing environmental concern in the present method makes it useful for industrial applications. The catalyst reported here can be regarded as an important step toward simple systems with the potential for commercial application of heterogeneous catalysis in organic oxidation reactions.

Chapter-4 : Catalytic activity of Anderson-type: Sodium hexamolybdochromate (III) in alcohol oxidations by hydrogen peroxide

In this chapter, we have utilized an Anderson-type polyoxometalate; sodium hexamolybdochromate (III) $[\text{Na}_3[\text{CrMo}_6\text{O}_{24}\text{H}_6]\cdot 8\text{H}_2\text{O}]$ as a catalyst for the oxidation of aliphatic and benzylic alcohols to the corresponding carbonyl compounds. The reduced polyoxometalate formed in the oxidation of alcohols is re-oxidized by Hydrogen peroxide. The oxidation of organic substrates by aqueous hydrogen peroxide is very attractive from a synthetic and industrial viewpoint since this reagent is relatively inexpensive, of low equivalent weight, environmentally clean, and easy to handle. In some applications however, the

oxidizing power of hydrogen peroxide is insufficient. The presence of a metal catalyst is often required and in recent years a considerable effort has been devoted to the search for new efficient metal derivatives suited to this purpose. Hence the catalytic system: sodium hexamolybdochromate (III)/ H_2O_2 is effective in the oxidation of aliphatic and benzylic alcohols to the corresponding aldehydes and ketones. To the best of our knowledge this is the first report on alcohol oxidations by hydrogen peroxide catalyzed by an Anderson-type polyoxometalate; sodium hexamolybdochromate(III). The catalyst was synthesized according to established procedure and was characterized by FT-IR and Atomic absorption spectroscopy. A variety of alcohols underwent oxidation smoothly to their corresponding carbonyl compounds. Even the heterocyclic alcohols and olefinic alcohols underwent oxidation to their corresponding carbonyls without forming any side products attesting the mildness and effectiveness of the catalytic system.

Chapter-5 :Multi Component Reactions (MCRs): Biginelli 3,4-Dihydropyrimidin-2(1*H*)-ones synthesis catalyzed by 11-molybdo-1-vanadophosphoric acid ($\text{H}_4\text{PMo}_{11}\text{VO}_{40}$)

In this chapter we shift the attention to the use of vanadium substituted Phosphomolybdic acid as efficient acid catalyst under homogeneous reaction conditions. Here we discuss an efficient and high-yielding protocol for the synthesis of biologically potent aryl 3,4-dihydropyrimidin-2(1*H*)-ones by means of MCR's three-component condensation in a one-pot operation catalyzed by heteropolyacid, 11-molybdo-1-vanadophosphoric acid ($\text{H}_4\text{PMo}_{11}\text{VO}_{40}$) as a novel and environmentally benign, acid catalyst. This method is applicable to a wide range of substrates, including aromatic, aliphatic, α , β -unsaturated, and heterocyclic aldehydes, and provides a variety of biologically relevant

dihydropyrimidinones in quantitative yields with short reaction times. Compared with the classical Biginelli reaction conditions, this new method has an advantage of excellent yields (81–95%).

Chapter-6 : (Salen)chromium(III) complex catalysed oxidation benzylic alcohols by Oxone®

In this chapter we continued our work on explorations of Oxone® oxidations, we report on the selective oxidation of a series of benzylic alcohols to the corresponding acids with Oxone® as the oxygen source catalyzed by (Salen)chromium(III). The in-situ generated (salen)oxochromium(V) complex is proposed as the actual oxidant. Such (salen)oxochromium(V) complexes have been previously isolated and subsequently used for the epoxidation of olefins by Kochi's group. The ligand salen and (Salen)chromium(III) complex were synthesized using established procedure. In the presence of the catalyst, the oxidation of 4-Nitrobenzyl alcohol was examined with Oxone® in aqueous acetonitrile under reflux. We found that the alcohol was oxidized to the corresponding acid within three hours in 89% yield. The oxidations of other benzylic alcohols were then examined using the optimized reaction conditions yielding the corresponding acids.

Chapter-7 Synthesis of β -hydroxyl ketones in water: A green protocol under metal-free conditions

Though our main interest was in polyoxometalates, we shifted slightly to utilize Amberlite IRA 400 (basic) resin as an efficient catalyst for the aldol reactions of unmodified ketones and reactive aldehydes in pure water at ambient temperature. The current method is very attractive and appealing synthetic process for β -hydroxyl ketones because of the following advantages: (1) Utilization of unprotected ketones, (2) Very high yield, (3) Simplicity of product isolation, (4)

Usage of water as environmentally benign reaction medium and (5) Catalytic usage of Amberlite IRA 400 (basic) as a reusable catalyst. The protocol reported in this paper can be easily developed into large-scale preparation of β -hydroxyl ketones

Conclusion

POM catalysis is a rapidly expanding field. As environmentally harmful methods become more and more restricted, these new green catalysts will flourish. New catalysts are being discovered daily, and old ones are being optimized. The primary focus of current research has been creating new catalysts for fine chemical synthesis. The thesis briefly mentions the major findings of the study followed by logical conclusions derived from it. This study mainly includes the utilization of polyoxometalates as a catalysts for fine chemical synthesis, attempts were also made to utilize transition metal complexes and polymeric resins for the purpose. We have laid emphasis on the reaction mechanism, which is aptly supported by spectroscopic evidence. Thus the successful utilization of these compounds as catalysts promises a bright and a promising future for this class of compounds.

List of Publications

- 1). S. P. Maradur, S. B. Halligudi and G. S. Gokavi; "*Oxidation of aliphatic and benzylic alcohols by Oxone[®], catalysed by 12-tungstocobaltate (II)*". **Catalysis Letters**. **96 (2004) 165-167**.
- 2). S. P. Maradur, T. M. Aminabhavi and G. S. Gokavi; "*Polyvinyl alcohol supported 12-tungstocobaltate (II), A novel promising heterogenised catalyst for the oxidation of benzylic alcohols*". (Communicated).
- 3). S. P. Maradur, and G. S. Gokavi; "*(Salen)chromium (III) complex catalysed oxidation of benzylic alcohols to Corresponding Acids by Oxone[®]*" (Communicated).
- 4). S. P. Maradur, and G. S. Gokavi; "*Multi Component Reactions (MCRs): Biginelli 3,4-Dihydropyrimidin-2(1H)-ones synthesis catalyzed by 11-molybdo-1-vanadophosphoric acid (H₄PMo₁₁VO₄₀)*". (Communicated).
- 5). S. P. Maradur, and G. S. Gokavi; "*Catalytic activity of Anderson-type: sodium hexamolybdochromate (III) in alcohol oxidations by hydrogen peroxide.*" (Communicated).
- 6). S. P. Maradur, and G. S. Gokavi "*Synthesis of β -hydroxyl ketones in water: A green protocol under metal-free conditions*". (Communicated).

Published contributions to academic conferences:

1. S. P. Maradur and G. S. Gokavi (2005). "*Organic-Inorganic Hybrids: Polyvinyl alcohol supported 12-tungstocobaltate (II), A novel promising heterogenised catalyst for the oxidation of benzylic alcohols.*" International Conference on Advances in Polymer Blends, Composites, IPNS and Gels: Macro to Nano Scales. Mahatma Gandhi University, Kottayam, India, 21st-23rd March 2005.
2. S. P. Maradur and G. S. Gokavi (2005). "*Synthesis of β -hydroxyl ketones in water: A green protocol under metal-free conditions.*" UGC-SAP National Seminar on Recent Trends in Synthetic and Polymer Chemistry Department of Chemistry, Himachal Pradesh University, Shimla 5th-6th December 2005.