Poly(Vinyl Alcohol) Supported 12-Tungstocobaltate (II) as a Novel Heterogeneous Catalyst for Oxidation of Benzyl Alcohols

Sanjeev P. Maradur[†] **and Gavisiddappa S. Gokavi**[*]

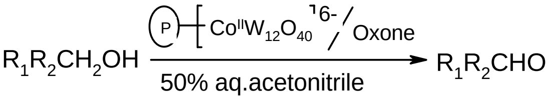
Kinetics and Catalysis Laboratory, Department of Chemistry,
Shivaji University, Kolhapur 416 004

Parasuraman Selvam[‡]

National Centre for Catalysis Research, Department of Chemistry,
Indian Institute of Technology–Madras, Chennai 400 076

[Received 14th January 2007]

Abstract: In this paper, selective oxidation of alcohols to the corresponding carbonyl products using Oxone® has been investigated on poly(vinyl alcohol) supported 12-tungstocobaltate (II), a heterogeneous catalyst. Variety of activated and non-activated alcohols has been effectively oxidized under relatively mild reaction conditions.



$$R_1R_2CH_2OH \xrightarrow[\text{50\% aq.acetonitrile}]{\text{(P)}-[Co^{II}W_{12}O_{40}]^{6-}/\text{Oxone}} R_1R_2CHO$$

1. INTRODUCTION

Organic-inorganic hybrid materials have many distinct advantages over the conventional materials. Development of heterogeneous catalysts for the fine chemicals synthesis has recently become a major area of research in view of the advantages like simplified recovery and reusability of these materials over the homogeneous systems [1,2]. Majority of catalysts are based on silica, since its (chemical and thermal) stability, high surface area, good accessibility and organic groups can be robustly anchored to the surface to provide catalytic centers. However, it has limited stability in aqueous media since it cannot easily form membranes. Variety of polystyrene-based resins has been used as solid phase catalyst supports for organic synthesis, absorption and separation of chemicals [3,4]. Polystyrene resins are rather hydrophobic and hence, their applications in aqueous media are limited, whereas hydrophilic polymers possess

---

[*] Corresponding author e-mail: gsgokavi@indiatimes.com

[†] Present address: Solid State and Catalysis Laboratory, Department of Chemistry,
Indian Institute of Technology-Bombay, Powai, Mumabi 400 076.

[‡] On lien from Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumabi 400 076.
E-mail: selvam@iitb.ac.in; selvam@iitm.ac.in

better swell ability in water. Poly (vinyl alcohol) (PVA), a hydrophilic and a low cost polymer, would be a good choice in making such solid supports.

Oxidation of alcohols to aldehydes and ketones has several industrial applications as well as in organic synthesis due to wide ranging utility of these products. Traditional alcohol oxidations use toxic, corrosive and expensive oxidants such as chromium (VI) and manganese complexes under stringent conditions such as high pressure or temperatures or use of strong mineral acids [5-8]. Other methods use molecular oxygen in the presence of stoichiometric amount of a reactive aldehyde, producing peracid as the actual oxidizing agent [9]. However, due to increasing environmental concerns, oxidations use environmentally benign oxidants such as molecular oxygen or hydrogen peroxide. Oxidation with hydrogen peroxide is relatively less economical due to its cost and comparatively poor efficiency [10]. Oxone®, used in the present study, is convenient because it is readily available and has been used for various transformations in organic synthesis [11-16]. Recently, we have studied the homogeneous 12-tungstocobaltate (II) as a highly effective catalyst for the oxidation of aliphatic and benzylic alcohols [17].An interesting modification of the above described catalytic system would be the heterogenization of the 12-tungstocobaltate (II) onto a polymer such as poly (vinyl alcohol) (PVA). In the present paper, we report the results on catalytic activity of PVA supported polyoxometalate (POM), 12-tungstocobaltate (II) as an active heterogenized and recyclable catalyst for the oxidation of benzylic alcohols with Oxone®. The POM, 12-tungstocobaltate (II) was selected due to its stability towards oxidative and hydrolytic decompositions.

2. EXPERIMENTAL

The catalyst 12-tungstocobaltate (II) was prepared as reported before [18] and was standardized spectrophotometrically. FTIR was recorded as KBr pellet on IR Spectrum GX series 49387. TGA-DTA was recorded on SDT-2960, TA Instruments, USA at the heating rate of 10°C/min under nitrogen atmosphere. SEM of the film was recorded on a LEO 143OVP instrument. Polyvinyl alcohol (Mol Wt. 1,25,000) was purchased from s.d. fine chemicals, Mumbai, India. The alcohols were of commercial grade samples, purchased from Lancaster, Mumbai. Potassium peroxomonosulfate was purchased from Across Chemicals. Acetonitrile and dichloromethane were purchased from s.d. fine chemicals (Mumbai) and were used without purification. Comparing their physical and spectral property data identified all raw materials used. Melting points were determined in open capillaries and are uncorrected.

2.1.Preparation of polyvinyl alcohol supported 12-tungstocobaltate (II)

About 1 g of PVA was dissolved in 25 mL distilled water. To this viscous solution, about 6 mL of glutaraldehyde was added as a crosslinking agent, and the mixture was stirred vigorously. To this, a solution of 12-tungstocobaltate (II) (0.5 g taken in 15 mL distilled water) was added with continuous stirring. Stirring was stopped after pre-crosslinking; then after adding 250 mL paraffin oil, the viscous mixture was stirred at a high speed for about 5 min followed by the addition of 2 mL Tween 80 surfactant. PVA supported POM beads were formed during the reverse suspension. At the end of the reaction, beads were washed with a mixture of toluene and petroleum ether (1:1, 3x200 mL) and then by methanol (100 mL) to extract the oil from the beads. The beads were subsequently washed with deionized water (500 mL), filtered and dried. Beads having the mesh size of 300 were used for catalytic runs.

2.2. General procedure

Alcohol (2.2 mmol) and Oxone® (1 mmol) were taken in 50:50 % aqueous acetonitrile mixture in a round-bottom flask followed by adding PVA-POM catalyst (0.10 g). The reaction mixture was stirred at room temperature and TLC monitored the progress of reaction. After completion of the reaction, supported catalyst was filtered and the resulting filtrate was extracted with dichloromethane (40 mL). The combined organic layer was washed with a solution of $NaHCO_3$ and dried over $MgSO_4$. The solution was then concentrated to obtain the crude carbonyl compound, which was purified by crystallization or distillation.

3. RESULTS AND DISCUSSION

FTIR spectra of pure 12-tungstocobaltate (II), PVA and the supported 12-tungstocobaltate onto PVA are shown in Fig. 1(A-C). Spectrum of the catalyst (Fig. 1A) shows fundamental bands at 933, 862 and 756 cm^{-1} corresponding to W-O_d, W-O_b-W and W-O_c-W stretching modes of the Keggin structure. A broad peak at 3392 cm^{-1} and a sharp peak at 1619 cm^{-1} indicate the water associated with Keggin structure of the catalyst as either in the lattice or in the coordinated form. The spectrum of pure PVA (Fig. 1B) shows characteristic OH and CH_2 stretching frequencies at 3458 and 2923 cm^{-1} along with smaller peaks at lower frequencies. The characteristic bands of the Keggin unit between 900 to 700 cm^{-1} were retained in the FTIR spectra of the supported catalyst (Fig. 1C), indicating no change in the nature of the catalyst after supporting it onto polymer network.[19,20] This retainment of basic structure of the catalyst helped to use it as an efficient heterogeneous catalyst in the present study. The peaks due to water associated with the pure catalyst were also retained in the supported catalyst as evidenced by the broad peak at 3397 cm^{-1} and a sharp peak at 1657 cm^{-1} (Fig. 1C). Therefore, it becomes difficult to conclude quantitatively about the number of water molecules associated with 12-tungstocobaltate of the supported catalyst as compared to pure catalyst.

Spectroscopic examination of the supported catalyst indicated that Keggin structure of the pure catalyst is retained. Note that catalyst was not released even after swelling the supported catalyst in water for 3-4 days since there was no significant weight loss. There was no leaching of the catalyst, which rules out the adsorption onto polymeric network. Therefore, binding of the catalyst to the polymer network might be by replacing of one or more of the coordinated water molecules of the catalyst by the -OH group of PVA. In order to know the coordinated water molecules in pure and supported catalyst, TGA and DTA analyses were performed (see Fig. 2). The TGA of pure PVA (Fig. 2A) shows an endothermic weight loss due to decomposition between 250° to 400°C. On the other hand, pure catalyst looses its coordinated water molecules (Fig. 2B) between 50° to and 180°C. From the % weight loss data, number of water molecules was calculated to be eight. The TGA of the supported catalyst (Fig. 2C) also shows weight loss between 50° and 180°C; here, number of water molecules lost accounts for five. While calculating the number of water molecules from the supported catalyst, contribution from pure PVA was subtracted. Therefore, the assumption that supported catalyst is bound to the polymer matrix through the replacement of some of the coordinated water molecules by the -OH group of PVA is justified

The surface electron microscopic analysis of the films (see Fig. 3) of PVA-supported catalyst prepared by solution casting method revealed that catalyst is dispersed onto the polymer matrix.

The present study addresses a method for efficient oxidation of alcohols by Oxone® in the presence of PVA supported of 12-tungstocobaltate (II). The uncatalyzed

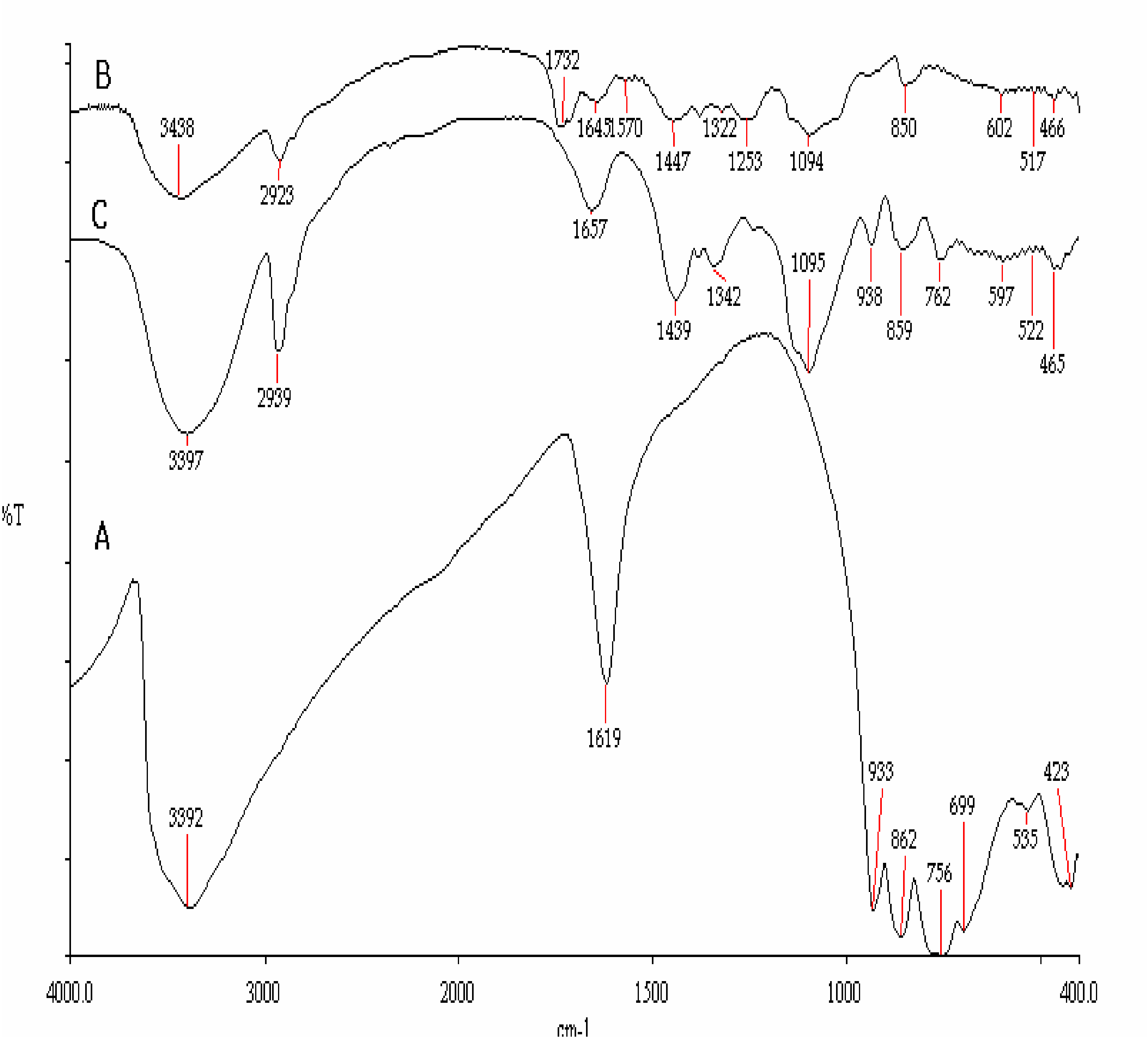


Fig. 1. FT-IR spectra of (A) 12-tungstocobaltate (II), (B) poly(vinyl alcohol) and (C).

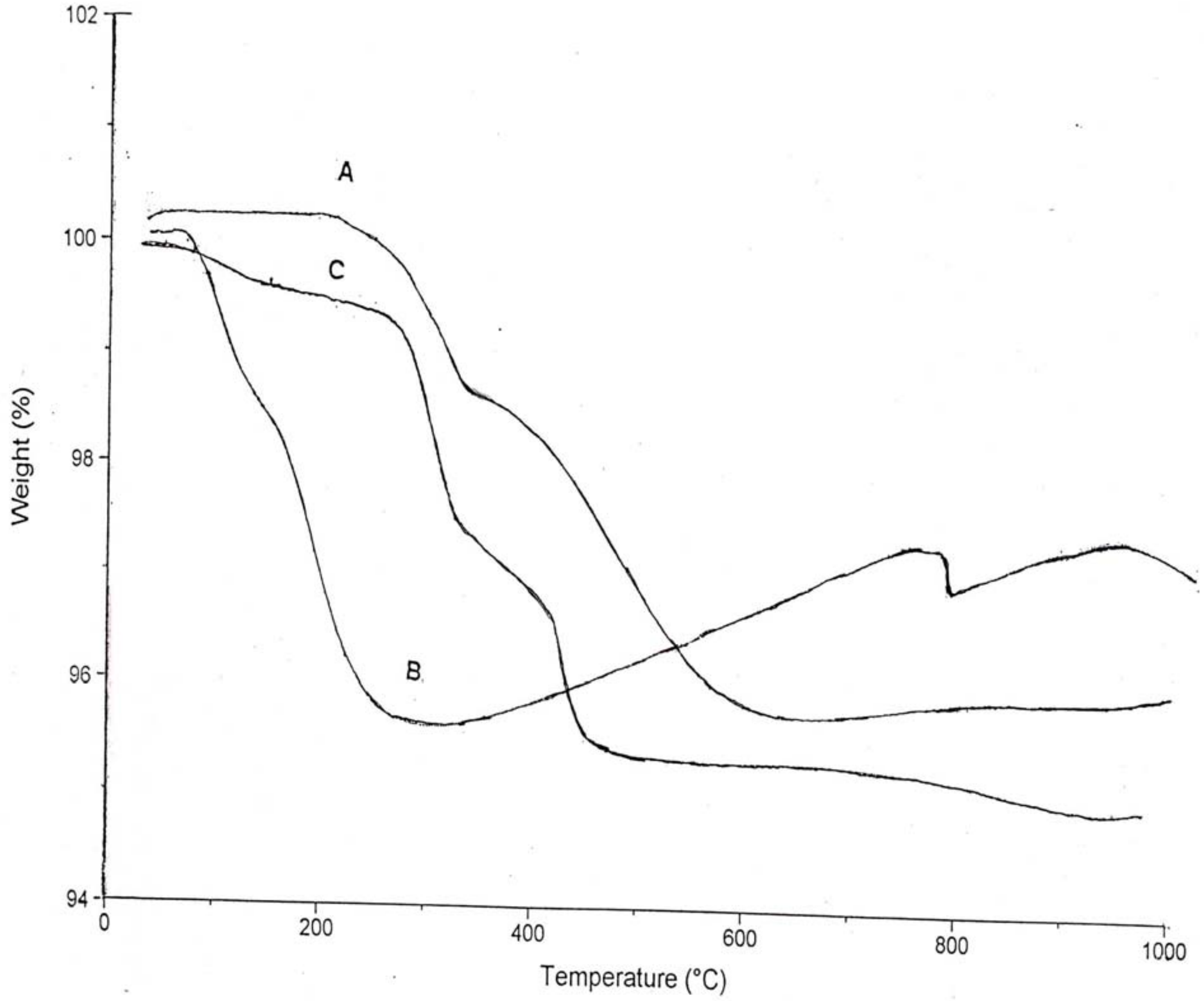


Fig. 2. TGA of (A) PVA, (B) 12-Tungstocobaltate (II) and (C) PVA-supported 12-tungstocobaltate.

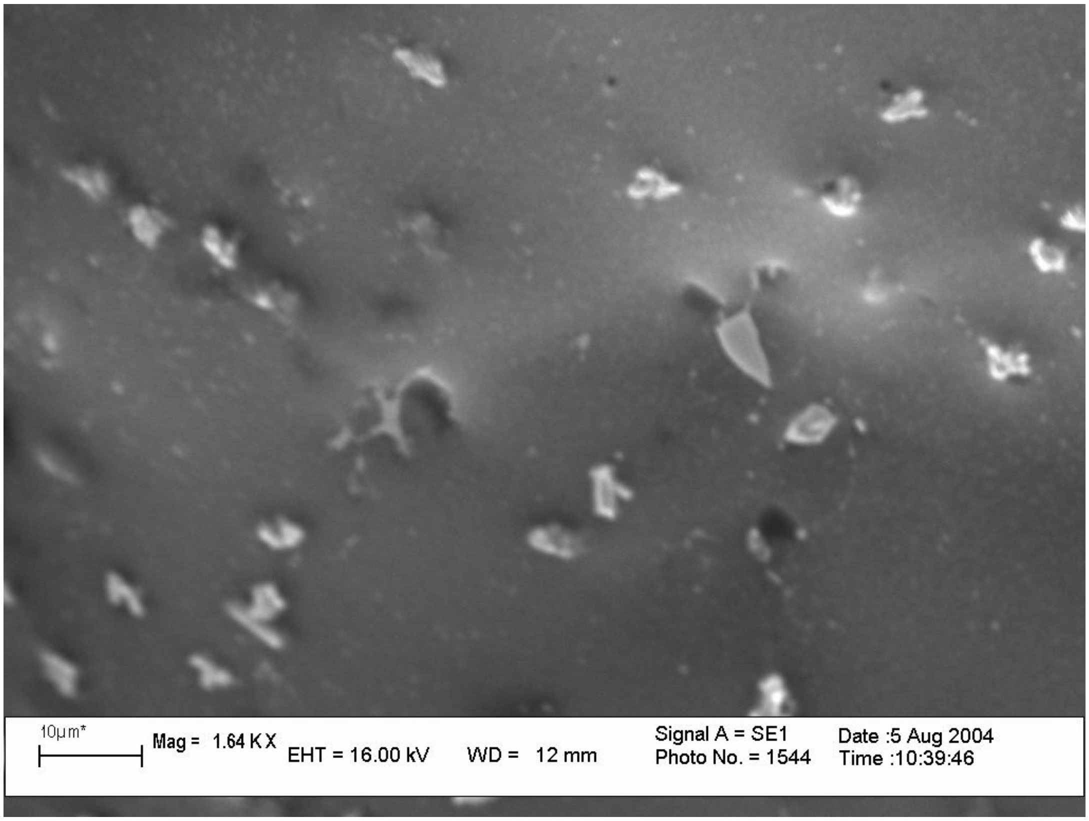


Fig. 3. SEM of PVA-supported 12-tungstocobaltate.

Table 1: Oxidation of Alcohols to Carbonyl Compounds Catalyzed by PVA Supported $[Co^{II}(W_{12}O_{40}]^{6-}$/Oxone®.

Reactant	Product	Time (h)	Yield (%)	M.P/B.P of carbonyl compound (°C)	M.P of 2,4-DNP derivative (°C)
Benzyl alcohol	Benzaldehyde	45	58	179	235
2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	40	65	43-45	264
4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	40	67	104	>300
4-Methoxybenzyl alcohol	4-Methoxy benzaldehyde	43	63	248	254
4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	40	69	47	263
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	48	48	201-204	231

oxidation of alcohols occurred at a negligible rate under the experimental conditions. Results of this study (see Table 1) for various alcohols indicated that aldehyde is the only product obtained in comparatively high yields without further conversion to carboxylic acid. Thus, the reaction is initiated by oxidation of 12-tungstocobaltate (II) by Oxone® and converting it to 12-tungstocobaltate (III), an outer- sphere oxidant [17]. This oxidant generated *in situ* will react with alcohol in a rate-determining step,

which involves the creation of negative charge. Such a transition state is more stabilized by electron-withdrawing substrate and makes the reaction to occur faster. In the present study, 4-nitro and 4-chlorobenzyl alcohols react at a faster rate than benzyl alcohol. After the first run, catalyst was filtered and added to a second run. In this case, conversion was 63 %. However, for the isolation of catalyst after this run, and recycling in the subsequent runs, the

conversion was low. Hence, the catalyst is easy to prepare and can be readily separated from the reaction mixture by filtration. Also, the catalyst reuse is possible without any significant loss of activity and selectivity up to three cycles.

4. CONCLUSIONS

Keggin-type polyoxometalate12-tungstocobaltate (II) $[\{Co^{II}(W_{12}O_{40})^{6-}\}]$ catalyst supported on PVA is efficient for heterogeneous liquid phase peroxomonosulfate (Oxone®) oxidation of benzyl alcohols to the corresponding carbonyl compounds. The reduced reactivity in the heterogeneous *vs*. homogeneous is probably related to the more limited interaction of the catalyst-substrate upon heterogenization which limits contact and /or diffusion of the reacting species. The low cost, ease of handling and environmental concern makes this method useful for industrial applications. The catalyst reported here is important with the potential for commercial exploitation in organic oxidation reactions.

Acknowledgements: G.S.G and S.M. thank the University Grants Commission (UGC) (F.12-29/2003[SR]) New Delhi for financial support.

REFERENCES

[1] J. H Clark, D.J. Macqarrie, Hand Book of Green Chemistry and Technology Ed., Blackwell: Oxford, 2002.

[2] P. T. Anastas, M. M. Kirchoff, T. C. Williamson., Appl. Catal. A: Gen, **221**(2001) 3.

[3] R. B. Merrifield., J. Am. Chem. Soc. **85** (1963) 2149.

[4] K. Takigawa, Y. Inaki, R. M. Ottenbrite., Functional Monomers and Polymers, Marcel Dekkar: New York, 1987.

[5] R. A. Sheldon, and J. K. Kochi, Metal Catalyzed Oxidation of Organic Compounds, Academic Press: New York, 1981.

[6] M. Hudlicky, Oxidations in Organic Chemistry, American Chemical Society: Washington DC, 1990.

[7] R. A. Sheldon, I. W. C. E. Arends, A. Dijksman., Catal. Today **57** (2000) 157.

[8] W. P. Griffith, J. M. Joliffe., Dioxygen Activation and Homogeneous Catalytic Oxidation, Ed., Simandi, I. I. Elsevier: Amsterdam, 1991.

[9] S. J. Murahashi, T. Naota, J. J. Hirai., Org. Chem. **58** (1993) 7318; T. Inokuchii, K. Nakagawa, S. Torii, Tetrahedron. Lett. **36** (1995) 3223; T. Iwaharna, S. Sakaguchi, Y. Nishiyama, Y. Ishii, Tetrahedron. Lett. **36** (1995) 6923.

[10] U. R. Pillai, E. Shale-Denessie., Appl. Catal. A: Gen. **245** (2002) 103.

[11] L. A. Wozniak, W. J. Stec, Tetrahedron. Lett. **40** (1999) 2637.

[12] L. A. Wozniak, M. Koziolkiewicz, A. Kobylanska, W. J. Stec., Bio. Org. Med. Chem. Lett. **8** (1998) 2641.

[13] K. S. Webb, D. Levy., Tetrahedron. Lett. **36** (1995) 5117.

[14] K. S. Webb, S. J. Ruszkay., Tetrahedron. **54** (1998) 401.

[15] B. M. Trost, D. P. Curran, Tetrahedron. Lett. **22** (1981) 1287.

[16] L. Baumstark, M. Beeson, P. C. Vasquez, Tetrahedron. Lett. **30** (1989) 5567.

[17] S. P. Maradur, S. B. Halligudi, G. S. Gokavi., Catal. Lett. **96** (2004) 165.

[18] S. E. Denmark, D. C. Forbes, D. S. Hays, J.-S. Depue, R. G. Wilde., J. Org. Chem. **60** (1995) 1391.

[19] C. Edwards, C. Y. Thiel, B. Benac, J. Kniffton., Catal. Lett. **51** (1998) 77.

[20] C. Rocchiccioli-Dehcheff, M. Fournier, R. Franek, R. Thouvenot., Inorg. Chem. **22** 207 (1983).