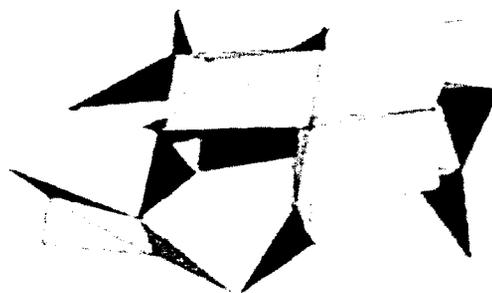


CHAPTER 3



*Polyvinyl alcohol supported
12-tungstocobaltate (II) as a novel
promising heterogeneous catalyst for
the oxidation of benzylic alcohols.*

3.0 Poly(vinyl) alcohol supported 12-tungstocobaltate (II) as a novel promising heterogeneous catalyst for the oxidation of benzylic alcohols.

3.1 Introduction

3.2 Experimental

3.3 Present Work

3.4 Results and Discussion

3.5 Conclusions

3.6 References

3.1 Introduction

A. Catalysis

During recent years, increasingly demanding legislation as well as public and economic pressure led to increased interest in new, “clean” methods for the production of chemical compounds [1,2]. Today, catalysis-based chemical synthesis accounts for 60% of the chemical products and 90% of current chemical processes [3]. These numbers tend to veil the fact that while bulk chemicals are usually produced in highly efficient processes with low amounts of by-products and waste, many of the intermediates still use synthesis routes that were developed at a time when “ecological responsibility” was not part of the public vocabulary, particularly in oxidation processes [4]. The development of heterogeneous catalyst for fine chemicals synthesis has recently become a major area of research due to

the advantages of these materials over the homogeneous systems like simplified recovery and reusability [5,6].

B. Immobilization

One of the major problems of most homogeneously catalyzed reactions is the difficulty in recovering the catalyst. The same reasons that account for high activity in a homogeneous reaction—good distribution of the catalyst and high reactivity—lead to inhibited separation of the catalyst from reaction solution. Quite often, the result is the destruction of the catalyst in the work-up procedure.

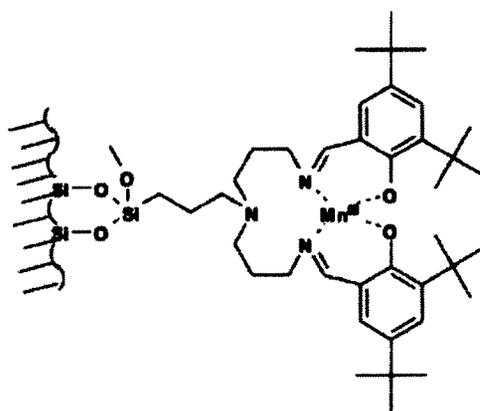
Generally, the recyclability of homogeneous catalysts is deplorably low. Another important drawback is the generation of high amounts of waste effluent, usually saline waste and contaminated solvents. By replacing the homogeneous catalyst with a heterogeneous one, these problems can be eliminated and the process can be changed to a more desirable and clean one [7–9]. For years, research in the field of heterogeneous catalysis has concentrated on complex crystalline solids, such as zeolites [10–12] because of their added feature of shape selectivity. These catalysts have been proven very useful in many reactions but are often incompatible with the production plants already existing for the same application. For many industrial processes, a simple exchange of a well known homogeneous catalyst against a heterogeneous one, working in the same conditions but eliminating extensive work-up procedures, would be interesting. This demand can be met by the so-called “heterogenization” of homogeneous catalysts. This method leads to heterogeneous catalysts that display most of the characteristics of their homogeneous counterparts but are easier to handle and can show increased re-usability.

C. OXIDATION REACTIONS

The oxidation of organic substrates leads to a wide variety of functionalized molecules, many of which are of fundamental importance for the chemical industry. The number of publications on heterogenized catalysts in oxidation reactions emphasizes the interest in replacing the homogeneous catalysts [13] and cited literature therein, [14]. The oxidants used in heterogeneously catalyzed reactions tend to differ from the standard oxidants of homogeneous reactions. Classic sources of oxygen are peroxyacids, peroxides, and stoichiometric metal oxidants e.g., chromates, permanganates, periodides, and hypochloride. These can lead to high amounts of hazardous or toxic by-products and waste. In heterogeneously catalyzed reactions, the oxidants of choice are pure oxygen, air, hydrogen peroxide, ozone, and in a few cases N_2O . Their advantages are comparatively low prices and the lower amounts of hazardous by-products obtained [4,15]. The conventional method for immobilizing metal catalysts is the incorporation of redox metal centers into the surface of an oxide support [16,17]. By incorporating metal centers or complexes into the structure of zeolites or other molecular sieves, it is possible to combine the redox activity with the shape selective properties of the support material. Metal complex oxidation catalysts can be bound to the surface of solids via the metal center or one of the ligands, or by encapsulation in the framework. We will focus on metal complexes containing a ligand that has been grafted onto the surface.

A second possibility is the use of supported oxidants. A lot of oxidation reactions rely on the use of "sacrificial aldehydes" or peroxyacids. Usually, these results in stoichiometric amounts of carboxylic acids that have to be considered waste or recycled after reduction to the aldehyde. Immobilization would facilitate

separation and recovery of these sacrificial molecules and might allow their recycling. In 1996, Sutra and Brunel reported the preparation of a MCM-41-bonded manganese(III) Schiff base complex [18] (Scheme 1).



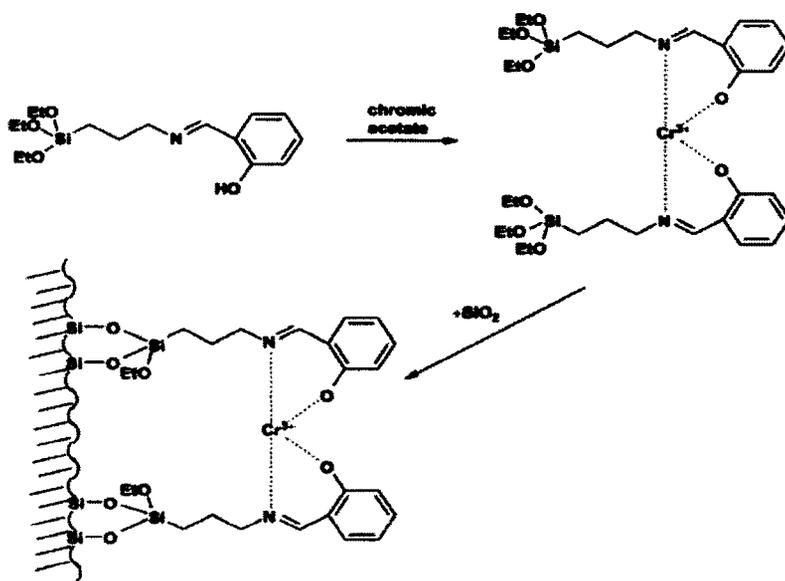
Scheme 1. Manganese (III) Schiff base complex bonded to MCM-41.

Such homogeneous complexes are well known as Jacobson catalysts, used in stereoselective oxidation reactions. The product was synthesized in five steps, starting with the grafting of a chloropropylsilyl group, this being the first time that the successful immobilization of such a complex was reported. Activity and stability of the catalyst were investigated in the epoxidation of styrene using various oxygen donors [19]. The best results were achieved using iodosylbenzene as oxidant, with turnover frequencies (TOFs) of 0.8–0.9 hr⁻¹ and selectivities of up to 58%.

Lau et al. found that an Mn(III)-Schiff base complex, when supported on MCM-41 by grafting, gave poorer catalytic activity for the oxidation of cyclohexene than its homogeneous counterpart [20]. This was explained by interaction between anchored

complexes at high surface coverage. By replacing the phenoxy groups of the Schiff base with pyridine groups, this interaction was avoided and high catalytic activities (99.8% yield after 10 hr at 50°C) could be achieved.

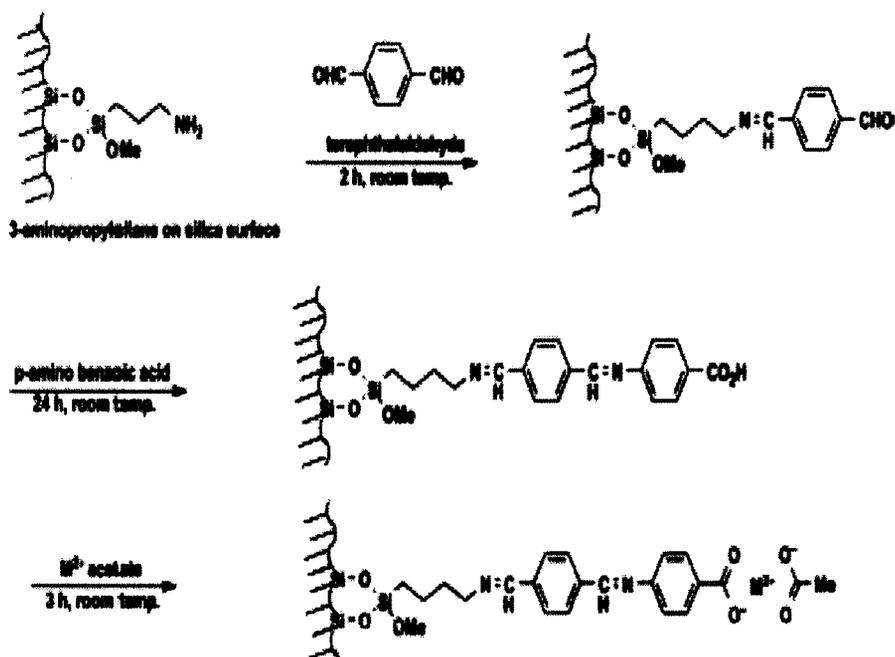
Che and co-workers reported the preparation of a chromium-Schiff base complex for the asymmetric epoxidation of alkenes via grafted aminopropylsilyl functionalities [21]. The yields obtained increased with higher content of Schiff base until it reached 1.8 wt%, while a further increase in the content of the Schiff base resulted in a slight decrease of yield. This catalyst featured significantly higher enantioselectivity (73%) than the homogeneous counterpart (54%), which was explained by the spatial environment formed by Schiff base ligand and surface of the support. The immobilization of a chromium(III)-Schiff base complex on amorphous silica reported by Clark's Green Chemistry Group is quite unusual, as it is one of the few cases where a complex was completely formed before the grafting step took place [22] (Scheme 2).



Scheme 2. A silica-supported chromium(III) Schiff base complex

The catalyst proved to be active in the oxidation of ethylbenzene to acetophenone using air as a source of oxygen, reaching a TOF of 1225 turnovers hr^{-1} during the first five hours. The catalyst was recyclable, even though in all cases deactivation could be observed after ca. 5 hr of reaction time, probably caused by inefficient removal of water from the reaction system. It could be shown that the catalyst was by far superior to catalysts prepared by simple physisorption of Cr (III). Similarly, a catalyst prepared by grafting the ligands followed by addition of Cr(III) showed little catalytic activity above that of a control reaction without catalyst, probably due to the less favorable spatial orientation of the ligands on the surface.

A catalyst which is reportedly able to catalyze both the epoxidation of cyclohexene to cyclohexene oxide and the oxidation of ethylbenzene to acetophenone is shown [23,24] (Scheme 3).



Scheme 3. Functionalization of the silica surface and addition of the active metal species

This catalyst was prepared by Chisem et al. and tested with different metal species. The most active metals in the epoxidation reaction proved to be Cr, Ni, and Cu, the Ni-complex giving 85% conversion after 6 hr, while for the oxidation of ethylbenzene only the results for the Cr-catalyst are given. Here, 35% conversion after 8 hr was achieved.

The majority of catalysts are based on silicas, since its stability (chemical and thermal), 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 conditions and it cannot easily be formed into membranes or into other forms, which could be attached to novel reactors for use in intensive processing applications.

Versatile polystyrene-based resins have been used as solid phase catalyst support, polymer support for organic synthesis, absorption and separation of chemicals [25,26]. Polystyrene resins are rather hydrophobic and thus some of their applications in aqueous media are limited where as hydrophilic polymers have better swellability in water. The choice of a hydrophilic polymer support becomes crucial, especially when the catalyst is water soluble. Polyvinyl alcohol (PVA), a hydrophilic and low cost polymer would be a good candidate in making such solid supports. PVA can be made in hydrogel form, after appropriate physical cross-linking by electron beam or γ - rays irradiation [27] and freeze thaw treatment of PVA solutions or by chemical cross-linking using reagents such as boric acid, dialdehydes and epichlorohydrin [28,29].

Oxidation of alcohols to aldehydes and ketones is a highly desirable and much sought after transformation both in industrial process as well as in organic synthesis due to the wide ranging utility of these products as important

precursors and intermediates for many drugs, vitamins and fragrances [30,31]. In industrial chemistry, heterogeneous catalyst systems are preferred over homogeneous system due to easy recyclability and separability. Therefore, development of an active and recyclable heterogeneous catalyst for alcohol oxidation is a highly attractive research area.

3.2 Experimental

The catalyst 12-tungstocobaltate (II) was prepared by the previously reported in Chapter 2 and standardized spectrophotometrically. FT-IR was recorded as KBr pellet on a IR Spectrum GX series 49387. TGA-DTA was recorded on a SDT-2960, TA Instruments USA at the rate 10°C/min under nitrogen atmosphere. SEM of the membrane was recorded on a LEO 1430VP instrument. Polyvinyl alcohol (Mol Wt. 1,25,000 approx) was purchased from S D Fine chemicals (Mumbai India). All alcohols are commercial materials and were purchased from Lancaster. Potassium peroxomonosulphate was purchased from Across Chemicals. Acetonitrile, dichloromethane purchased from S D fine chemicals (Mumbai India) and were used without further purification. All the products are known compounds and were identified by comparison of their physical & spectral data with those of authentic samples. Melting points were determined in open capillaries and are uncorrected.

Preparation of Polyvinyl alcohol supported 12-tungstocobaltate (II)

1 gm of PVA was dissolved in 25 ml distilled water. To this viscous solution about 6ml of glutraldehyde was added as a crosslinking agent.. The mixture was stirred vigorously. Then, a solution of 12-tungstocobaltate (II) (0.5 gm in 15 ml of distilled water) was added with continuous stirring. The stirring was

stopped after pre-crosslinking and 250 ml paraffin oil was added to the viscous mixture, which was first stirred with a relatively high speed for about 5 min followed by the addition of 2 ml of Tween 80 surfactant. The PVA supported POM beads were formed during the reverse suspension. At the end of the reaction, the beads were washed by a mixture of toluene and petroleum ether (1:1, 3x 200 ml) and by methanol (100 ml) to extract the oil from the beads. They were subsequently washed by large amounts of deionised water (5 x 100 ml). Finally the beads were filtered and dried. The beads having mesh size no.300 were used for catalytic runs.

3.3 Present Work

We have reported the homogeneous 12-tungstocobaltate (II) catalysed oxidation of aliphatic and benzylic alcohols in Chapter 2 [32]. In view to heterogenize the homogeneous POM catalyst, 12-tungstocobaltate (II) we now report the work on the catalytic activity of PVA supported polyoxometalate, 12-tungstocobaltate (II) for the oxidations of benzylic alcohols with Oxone®.

To optimize the reactions we studied the oxidation of 4-nitrobenzyl alcohol was studied. In a typical experiment 4-nitrobenzyl alcohol (2.2 mmol) and Oxone® (1mmol) were taken in 50:50 % aqueous acetonitrile mixture in a round-bottomed flask followed by the addition of PVA-POM Catalyst (0.10 g). The reaction mixture was stirred at ambient temperature. The progress of the reaction was monitored by TLC. After the completion of the reaction, the supported catalyst was filtered off and the resulting filtrate solution was extracted with dichloromethane (20ml x2). The combined organic layer was washed with a solution of NaHCO₃ and dried over MgSO₄, and the solution was concentrated to afford the crude 4-nitrobenzaldehyde, which was further purified by column chromatography

(petroleum ether-ethyl acetate, 9:1). Oxidation of aliphatic alcohols were also attempted but the reaction was slow hardly the conversion of alcohols to carbonyl compounds took place at ambient. So the benzylic substrates were chosen for further study.

3.4 Results and Discussion

Preparation and analysis of catalyst

FTIR spectra of pure 12-tungstocobaltate (II), polyvinyl alcohol (PVA) and supported 12-tungstocobaltate onto PVA are shown in Fig 6.a-c respectively. The spectrum of catalyst (Figure 6a) shows fundamental bands at 933, 862, and 756 cm^{-1} corresponding to W-O_a , $\text{W-O}_b\text{-W}$ and $\text{W-O}_c\text{-W}$ stretching motion of the Keggin structure. The broad peak centered at 3392 cm^{-1} and sharp peak at 1619 cm^{-1} indicate the water associated with the Keggin structure of the catalyst as either in the lattice or in the co-ordinated form. The spectrum of pure PVA (Figure 6b) 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} have been found to be retained in the FTIR spectra of the supported catalyst (Figure 6c) indicating no change in the nature of the catalyst after supporting it on to the polymer network [33,34]. This retainment of the catalyst basic structure helps to use it as an efficient heterogeneous catalyst for the present study. The peaks due to the water associated with the pure catalyst are also retained in the supported catalyst as evidenced by the broad peak at 3397 and a sharp peak at 1657 cm^{-1} (Figure 6c). Therefore, it becomes difficult to conclude quantitatively about the number of water molecules associated with 12-

tungstocobaltate of the supported catalyst in comparison with that of the pure catalyst.

The spectroscopic examination of the supported catalyst has shown that the Keggin structure of the pure catalyst is retained. It has been also 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. Therefore, binding of the catalyst to the polymeric network might be through replacement of one or more coordinated water molecules of the catalyst by the -OH group of the PVA. In order to know the coordinated water molecules in the pure and supported catalyst the TGA and DTA analysis was carried out and are shown in Fig.2a-c. The TGA of pure PVA (Figure 7a) shows endothermic weight loss due to decomposition between 250 to 400°C. Where as pure catalyst loses its coordinated water molecules (Figure7b) between 50 to 180°C. From the percentage weight loss the number of water molecules were calculated to be eight. The TGA of the supported catalyst (Figure 7c) also shows weight loss between 50 to 180°C and the number of water molecules lost accounts to five molecules. While calculating the number of water molecules from the supported catalyst the contribution from that of pure PVA was subtracted. Therefore, our assumption that the supported catalyst will 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 (Figure 8). The tentative illustrative structure of the supported may be represented as below (Figure 4).

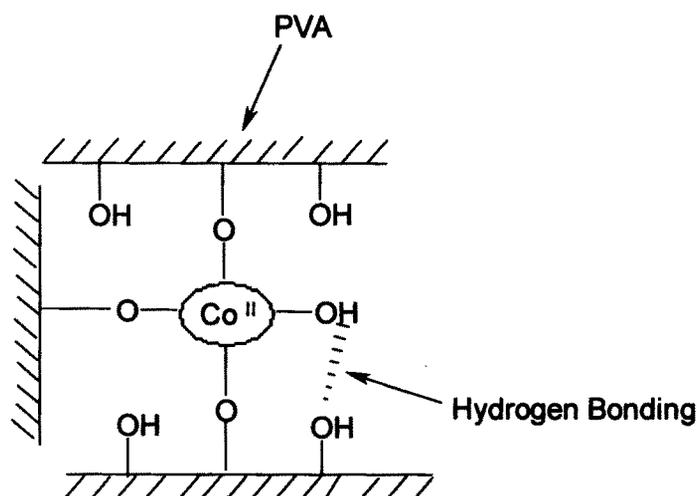
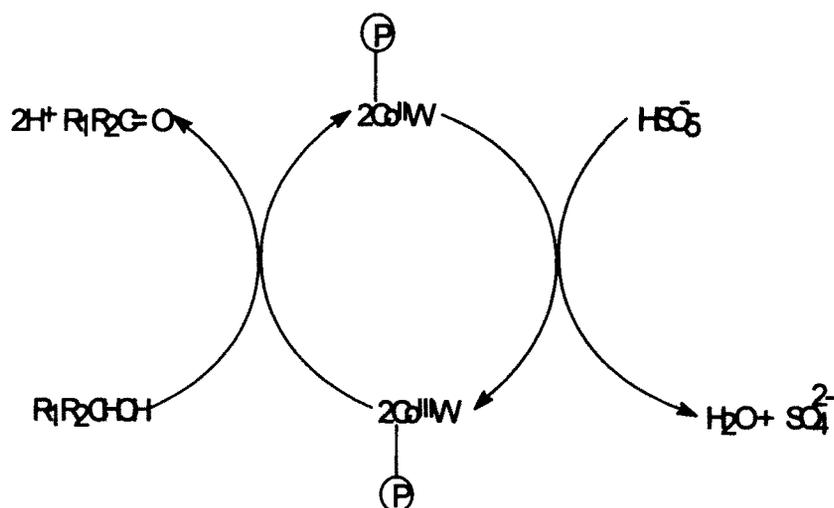


Figure 4. Tentative Illustrative Structure of PVA supported 12-Tungstocobaltate (II)

Catalytic study:

In the present study, a method for efficient oxidation of alcohols by oxone in presence of PVA supported of 12-tungstocobaltate (II) is described. The uncatalyzed oxidation of alcohols occurred at a negligible rate under the experimental conditions. The results of this study are shown in Table 1 for various alcohols which shows that aldehyde is the only product obtained in comparatively high yields without further conversion of aldehyde to carboxylic acid. Therefore, the reaction is initiated by the oxidation of 12-tungstocobaltate (II) by oxone and converting it into 12-tungstocobaltate (III), an outer-sphere oxidant. This oxidant generated in situ will react with the alcohol in a rate-determining step. Therefore, the catalysed path of the reaction can be represented as in Scheme 1.



Scheme 4: Proposed catalysed path of the reaction.

The possible Transition State, between PVA-supported 12-tungstocobaltate (III) and the alcohol is shown in the Figure 5

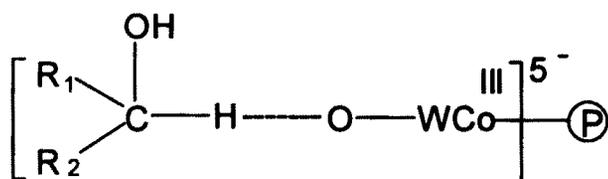


Figure. 5

which involves the development of negative charge. Such transition state is more stabilized by electron-withdrawing substrates and makes the reaction to occur faster. In the present study also the 4-nitro and 4-chloro benzyl alcohols reacts at a faster rate than that of the benzyl alcohol. After the first run the catalyst was filtered and added to a second run. In this case the conversion was 63%. Isolation of the catalyst after this run and recycling in the subsequent runs, conversion was low. Hence the catalyst is easy to prepare and can readily be separated from the

reaction mixture by simple filtration and the catalyst reuse is possible without any significant loss of activity and selectivity (Fig. 6) up to three cycles.

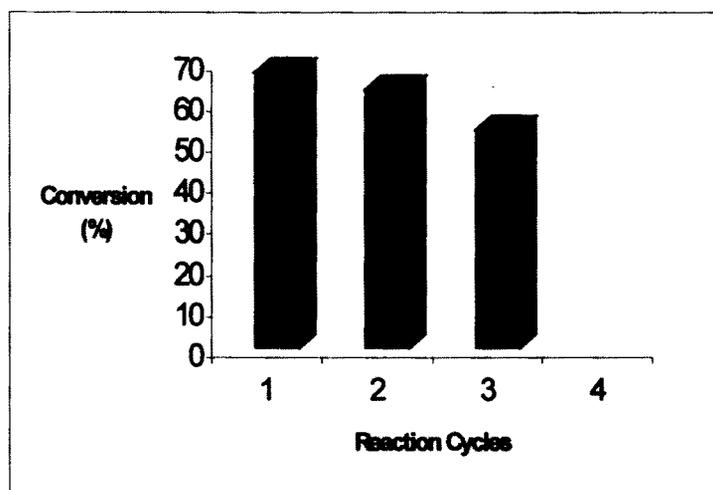


Figure 6 : Recyclability of PVA supported 12-tungstocobaltate (II) for the oxidation of 4-Nitro benzyl alcohol (reaction conditions: 0.10 g catalyst, 40hr, stir)

3.5 Conclusions

In conclusion, the Keggin-type polyoxometalate 12-tungstocobaltate (II) $\{[\text{Co}^{\text{II}}(\text{W}_{12}\text{O}_{40})]^{6-}\}$ supported on to polyvinyl alcohol is an efficient catalyst for the heterogeneous liquid phase peroxomonosulphate (Oxone®) oxidation of benzylic alcohols 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.

Table 1: Oxidation of alcohols to carbonyl compounds catalysed by PVA supported $[\text{Co}^{\text{II}}(\text{W}_{12}\text{O}_{40})]^{6-}$ /Oxone®

Srl No	Reactant	Product	Time hr	Yield (%) Isolated	M.P/B.P of carbonyl compound T ^o C	M.P of 2,4-DNP derivative T ^o C
1	Benzyl alcohol	Benzaldehyde	45	58	179	235
2	2-Nitro Benzyl alcohol	2-Nitro benzaldehyde	40	65	43-45	264
3	4-Nitro benzyl alcohol	4-Nitro benzaldehyde	40	67	104	>300
4	4-Methoxy benzyl alcohol	4-Methoxy benzaldehyde	43	63	248	254
5	4-Chloro benzyl alcohol	4-Chloro benzaldehyde	40	69	47	263
6	4-Methyl benzyl alcohol	4-Methyl benzaldehyde	48	48	201-204	231

Figure 6. FT-IR spectra of A) 12-tungstocobaltate (II), B) pure polyvinyl alcohol (PVA), and C) 12-tungstocobaltate (II) supported on to PVA.

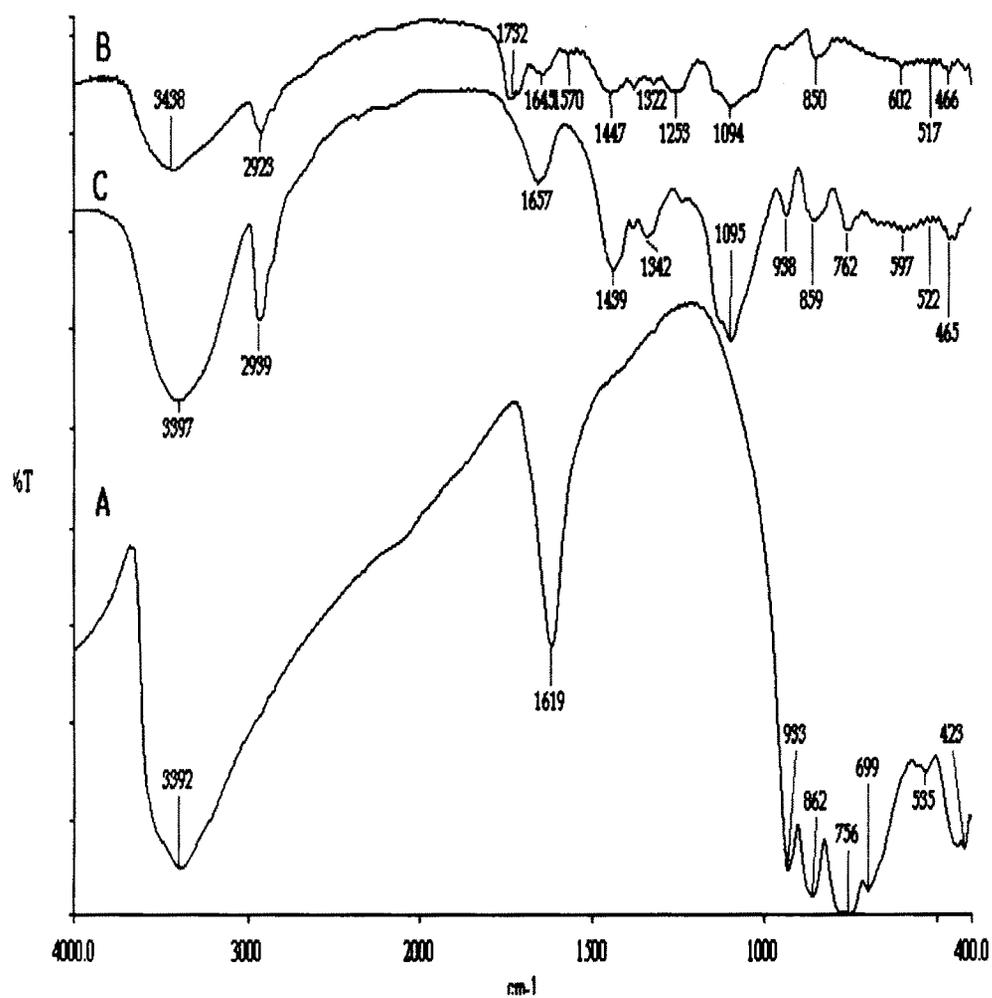


Figure 7(A)- TGA of PVA

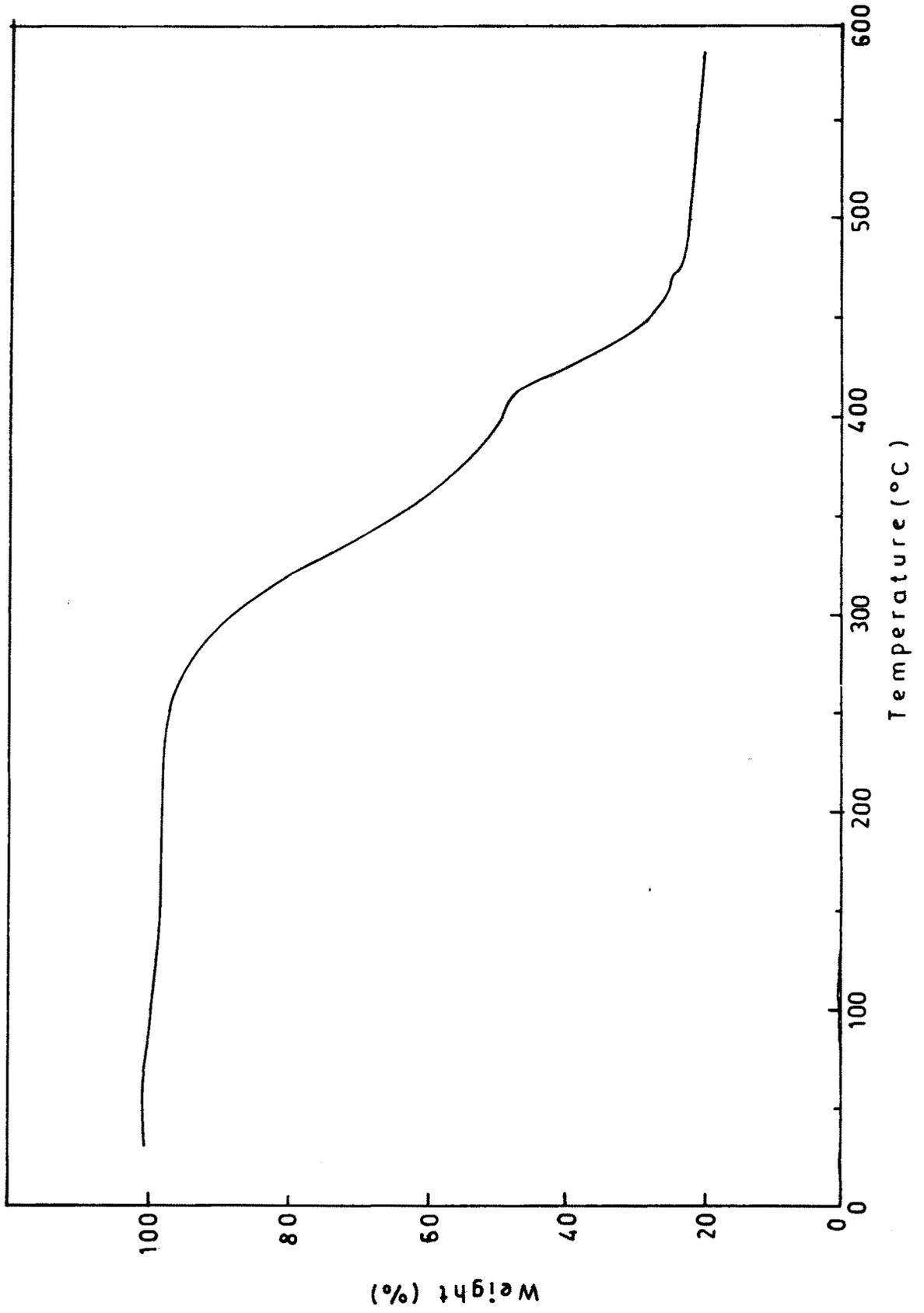


Figure 7(B) 12 – Tungstocobaltate (II)

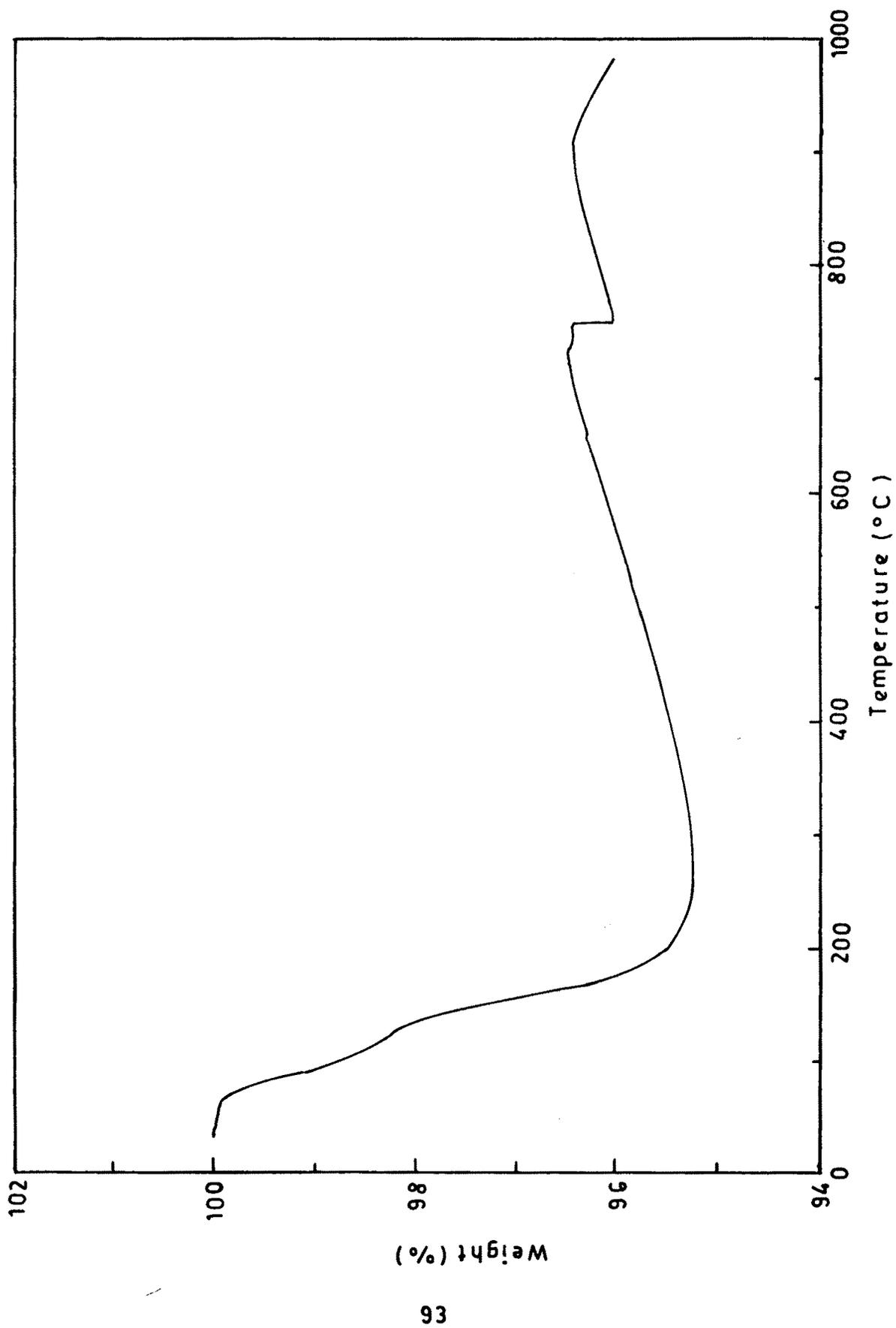


Figure 7 (C)- PVA-supported 12-tungstocobaltate

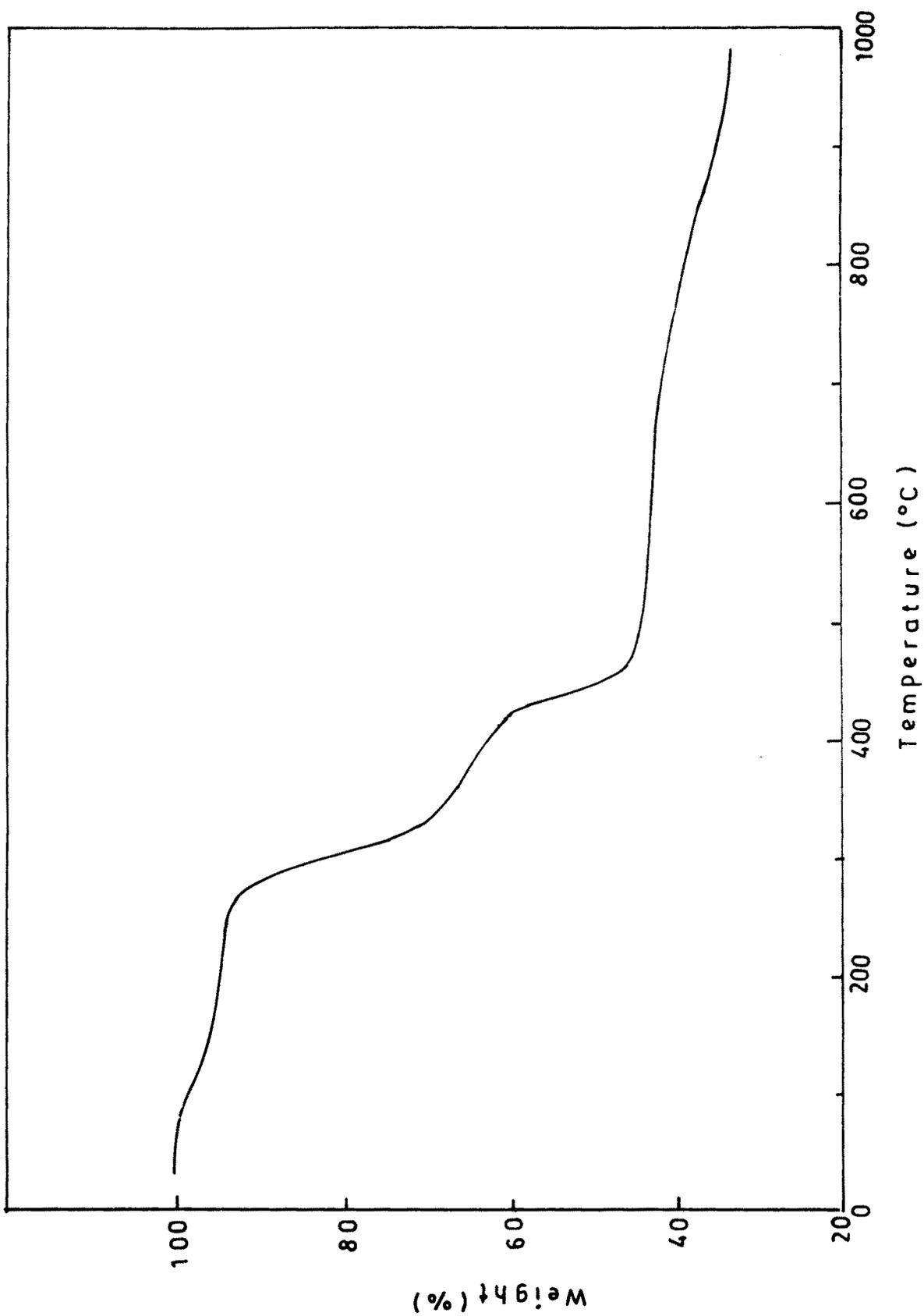
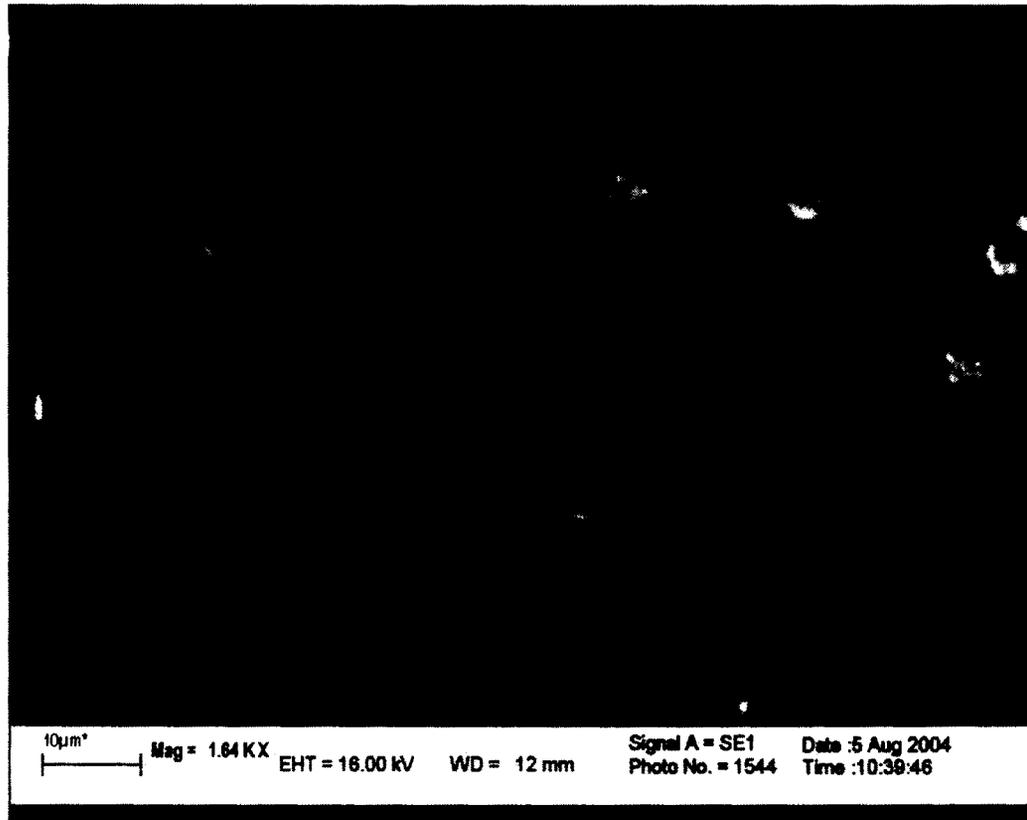


Figure 8: Surface Electron Micrograph of PVA supported 12-tungstocobaltate



3.6 References:

1. P. T. Anastas.; L.B. Bartlett.; M.M. Kirchhoff.; T.C. Williamson. *Catal. Today*. 55 (2000) 11.
2. P.T. Anastas.; J.C. Warner. *Green Chemistry: Theory and Practice*. Oxford University Press: New York, (1998).
3. ACS I&ES Division. access.
4. W.F. Hölderich.; F. Kollmer. *Pure Appl. Chem.* 72 (2000) 1273.
5. J. H. Clark and D. J. Macquarrie, *Hand Book of Green Chemistry and Technology ed*, Blackwell Oxford, (2002).
6. P. T. Anastas, M. M. Kirchoff and T. C. Williamson, *App. Catal. A: Gen*, 221 (2001) 3.
7. J. N. Armor. *Appl. Catal. A:Gen.* 189 (1999) 153.
8. K. Tanabe.; Hölderich, W.F. *Appl. Catal. A:Gen.* 181(1999)399.
9. J.H. Clark.; P.M. Price.; K.Martin.; D.J. Macquarrie.; T.W. Bastock. *J. Chem Res.(S)* (1997) 430.
10. W.F. Hölderich.; J. Röseler.; G. Heitmann.; A.T. Liebens. *Catal. Today* 37 (1997) 353.
11. C.E. Fowler.; S.L. Burkett.; S. Mann. *Chem. Commun.* (1997) 1769.
12. D.J. Macquarrie.; D.B. Jackson.; J.E.G. Mdoe.; J.H. Clark. *New J. Chem.* 23 (1999) 539.
13. J.S. Rafelt.; J.H.Clark. *Catal. Today* 57 (2000) 33.
14. R.A. Sheldon.; I.W.C.E. Arends.; H.E.B. Lempers. *Catal. Today* 41 (1998) 387.
15. R.A. Sheldon.; M. Wallau.; I.W.C.E. Arends.; U. Schuchardt. *Acc. Chem. Res.* 31 (1998) 485.
16. P. Sutra.; D. Brunel. *Chem. Commun.* (1996) 2485.
17. D. Brunel. *Micropor. Mesopor. Mat.* 27 (1999) 329.
18. S.-H. Lau.; V. Caps.; K.-W.Yeung.; K.-Y. Wong.; S.C. Tsang,. *Micropor. Mesopor. Mat.* 32 (1999) 279.

19. X.-G. Zhou.; X.-Q. Yu.; J.-S. Huang.; S.-G. Li.; L.-S. Li.; C.-M. Che. *Chem. Commun.* (1999) 1789.
20. I.C. Chisem.; J. Rafelt.; M.T. Shieh.; J. Chisem.; J.H. Clark.; R. Jachuk.; D.J. Macquarrie.; K. Scott. *Chem. Commun.* (1998) 1949.
21. J. Chisem.; I.C. Chisem.; J.S. Rafelt.; D.J. Macquarrie.; J.H. Clark. *Chem. Commun.* (1997) 2203.
22. I.C. Chisem.; J.Chisem.; J.H. Clark. *New J. Chem.* 22 (1998) 81.
23. R. B. Merrifield. *J. Am. Chem. Soc.* 85 (1963) 2149.
24. K. Takigawa.; Y. Inaki.; R. M. Ottenbrite. *Functional Monomers and Polymers*, New York, Marcel Dekkar, (1987).
25. N. A. Peppas.; E. W. Merrill. *J. App. Polym. Sci*, 21 (1977) 1763.
26. T. Takigawa, H. Kasibara and T. Masuda, *Polym. Bull.* 24 (1990) 613.
27. G. Ketla and A. Ricard, *Polym. Bull.* 24 (1990) 627.
28. N. A. Peppas and R. E. Berner, *Biomaterials.* 1 (1980) 158.
29. M. Dimonic.; H. D. Schell.; G. Huba.; M. A. Mateescu.; C. G. Opreseu.; S. Todireanu.; O. Maior.; M. Iosif. *J. Macromol. Sci. Chem*, A22 (1985) 729.
30. R. A. Sheldon.; J. K. Kochi. *Metal Catalysed Oxidation of Organic Compounds*, Academic Press, New York, (1981).
31. M. Hudlicky, *Oxidations in Organic Chemistry*, American Chemical Society, Washington DC, (1990).
32. S. P. Maradur, S. B. Halligudi and G. S. Gokavi, *Catal Lett.* 96 (2004) 165.
33. J. C. Edwards, C. Y. Thiel, B. Benac and J. Kniffon, *Catal. Lett.*, 51 (1998) 77.
34. C. Rocchiccioli-Dehcheff, M. Fournier, R. Franek and R. Thouvenot, *Inorg. Chem.*, 22 (1983) 207.