

Selective oxidation of alcohols catalysed by a cubane-like Co(III) oxo cluster immobilised on porous organomodified silica

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Abstract

A catalytically active tetrameric cubane-like complex $[\text{Co}^{\text{III}}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4]$ (**1**) has been prepared, structurally characterised by single crystal X-ray diffraction, and immobilised on a porous organomodified silica, which is amorphous in nature. The resulting supported reagent has been found to promote the efficient and selective oxidation of benzylic alcohols and cyclohexanols with TBHP as the oxidant. The catalyst can be reused without any significant loss of activity.

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Keywords: Co(III) cubane cluster; Organomodified silica; TBHP; Supported catalyst; Alcohol oxidation

1. Introduction

Oxidation of alcohols to the corresponding aldehydes and ketones remains one of the most important reactions both from fundamental research as well as synthetic points of view [1,2]. Traditional processes, however, employ stoichiometric amounts of metallic oxidants – notably chromium(VI) reagents [3], permanganates [4,5] and ruthenium(VIII) oxide [6], which produce environmentally unacceptable heavy metal wastes [7]. Thus developing an environmentally friendly, efficient and selective catalyst system is of paramount importance. Although various catalytic systems with catalytic amounts of transition metal salts or complexes have been developed [8–11], in most of these homogeneous processes separation of the catalyst from the reaction mixture and its subsequent recovery in active form is cumbersome. Thus considerable efforts are directed towards the development of heterogeneous catalysts for this kind of reaction [12]. In this regard, encapsulation and/or immobilisation of known homogeneous catalysts on the surface and in the cavities of suitable supports such as zeolites and structurally tailored sol–gel materials have received considerable attention in recent times [13,14]. Moreover, in addition to the ease of separation of the product, catalyst recovery and reusability, the

heterogenization of catalytically active transition metal complexes can often lead to catalysts with improved activity and selectivity induced by the support [15–17]. Various compounds of cobalt(II) such as CoCl_2 [18], $\text{Co}(\text{acac})_2$ [19], cobalt Schiff base complexes [20] are widely used as homogeneous catalysts in the oxidation of alcohols to its corresponding carbonyl compounds [21]. In connection with cobalt-catalysed oxidation of organic substrates, it is also to be noted that the use of cobalt(III) complexes stabilized by suitable ligand environments leads to greater catalyst stability owing to the relative substitutional inertness of Co(III) [22]. Since Co(III) peroxo/alkylperoxo complexes are regarded as the key intermediates in the catalytic cycle for such processes [23], direct use of catalytically active Co(III) may enhance the rates of reaction and thus be beneficial. Although oxo-centred trimeric complexes of cobalt and manganese have been reported as catalysts for oxidation [24,25], use of cubane-like cobalt(III)-oxo cluster complexes in such processes is not known, particularly under heterogeneous condition. We have found that the cubane-like clusters of cobalt(III), viz. $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(4\text{-CNpy})_4]$ and $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(4\text{-CNpy})_4]$ display very good homogeneous catalytic activity and selectivity in the epoxidation of α -pinene [26] and in the oxidation of *p*-xylene in aqueous medium to produce 4-methylbenzoic acid along with traces of terephthalic acid [27], respectively. Herein we describe the immobilisation of a related complex, $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4]$ (**1**), on chemically modified silica (CMS)

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having $-(\text{CH}_2)_2\text{CO}_2\text{H}$ groups on its surface [28] and the activity of the resulting supported reagent in the oxidation of alcohols to corresponding carbonyl compounds in excellent yields with TBHP as the oxidant.

2. Experimental

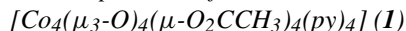
2.1. Materials

All materials used in this work were obtained from commercial sources and used without further purification. Cobalt(II) nitrate hexahydrate, sodium acetate trihydrate, hydrogen peroxide (30%, v/v), benzyl alcohol, 4-methoxy benzyl alcohol, 1-phenyl ethanol were obtained from E. Merck (India). 2-Hydroxy-1,2-diphenyl-ethanone and cyclohexanol were purchased from Loba Chemie (India), while pyridine was procured from Qualigens (India). TBHP (80% solution in di-*tert*-butylperoxide) was obtained from Merck (Germany). (2-cyanoethyl)triethoxysilane and *n*-dodecylamine were purchased from Lancaster Synthesis Ltd. (UK). 4-Methyl benzyl alcohol and 4-*tert*-butyl cyclohexanol were purchased from Aldrich (USA). Solvents used were of reagent grade. 1-(4'-methyl)-phenyl ethanol was prepared by reduction of corresponding ketone, 4-methyl acetophenone by literature method [29].

2.2. Instrumental

Infrared spectra in the mid-IR region ($4000\text{--}450\text{ cm}^{-1}$) were recorded using a Perkin-Elmer RX1 FT-IR spectrophotometer for KBr pellets. Diffuse reflectance infrared spectra (DRIFTS) were recorded using a Bruker Equinox 55 FT-IR spectrophotometer with DRIFTS attachment. UV–vis spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer. Cyclic voltammetric measurements were performed using a BAS 100B electrochemical analyser equipped with a BAS C2 cell stand. Electrochemical data were collected and analysed using BAS 100 W version 2.3 software. CV was conducted using a three-electrode cell assembly consisting of platinum disk working, platinum wire auxiliary and Ag/AgCl reference electrodes. Electrochemical studies were carried out in acetonitrile at room temperature using tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. ^1H and ^{13}C NMR spectra were recorded on a JEOL 270 MHz instrument. Powder X-ray diffraction studies on the catalyst and its support were carried out using a Rigaku Miniflex diffractometer in the continuous scanning mode at $2\theta/\theta$ mode (30 kV/15 mA). Porosimetry experiments for the calculation of BET surface area and BJH pore volume were performed by the N_2 adsorption method using a Coulter SA 3100 surface area analyser. The scanning electron micrographs (SEM) were recorded on a LEO-1430 VP scanning electron microscope having EDS attachment for X-ray microanalysis. Thermogravimetric studies were carried out using a Mettler Toledo thermal analyser. The temperature in the range $25\text{--}600\text{ }^\circ\text{C}$ was raised at the rate of $10\text{ }^\circ\text{C min}^{-1}$ under a flow of nitrogen gas.

2.3. Preparation of the molecular catalyst:



$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.90 g, 10 mmol) and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (2.7 g, 20 mmol) were taken in methanol (30 mL) and the mixture was heated to refluxing temperature. Pyridine (0.08 mL, 10 mmol) was added to the stirred reaction mixture followed by the addition of 30% hydrogen peroxide (v/v, 5 mL, ~ 50 mmol) in small portions. The reaction mixture was stirred under reflux for 4 h and cooled. It was then concentrated to $\sim 50\%$ of its original volume and allowed to stand at room temperature to obtain dark green needle-like crystals of the desired product in ca. 40% yield. Anal. calcd. (%) for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{12}\text{Co}_4 \cdot 0.5\text{NaNO}_3 \cdot 8\text{H}_2\text{O}$: C, 32.36; H, 4.62; N, 6.07. Found (%): C, 31.48; H, 4.14; N, 6.31. ^1H NMR (270 MHz; D_2O ; δ , ppm): 8.16 (d, $J = 4.86$ Hz, 8H), 7.69 (t, $J = 8.26$ Hz, 4H), 7.18 (t, $J = 7.02$ Hz, 8H). ^{13}C NMR (67.93 MHz; D_2O ; δ , ppm): 189.31, 152.49, 139.43, 125.37, 26.14. UV–vis data (MeOH, λ_{max}): 617 nm ($\epsilon = 360\text{ M}^{-1}\text{ cm}^{-1}$), 330 nm ($\epsilon = 5900\text{ M}^{-1}\text{ cm}^{-1}$), 246 nm ($\epsilon = 21\text{ }285\text{ M}^{-1}\text{ cm}^{-1}$). IR (KBr, $\nu_{\text{max}}\text{ cm}^{-1}$): 3400(m), 3109(w), 3072(w), 2964(w), 2924(w), 1655(w), 1606(w), 1538(s), 1483(m), 1449(m), 1410(s), 1385(s), 1339(w), 1211(m), 1152(w), 1070(m), 1044(w), 1019(w), 880(w), 762(m), 694(m), 632(m), 575(m) and 454(w) [s, strong; m, medium; w, weak].

2.4. Single crystal X-ray structure determination

Dark olive green crystals of the compound, $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4] \cdot 0.5\text{NaNO}_3 \cdot 8\text{H}_2\text{O}$ [$\mathbf{1} \cdot 0.5\text{NaNO}_3 \cdot 8\text{H}_2\text{O}$] were obtained from the concentrated reaction mixture by allowing it to stand for several days at room temperature. The needle shaped crystals were suitable enough for structure analysis by the method of single crystal X-ray diffraction. X-ray diffraction measurements were made on a Bruker SMART-CCD diffractometer employing graphite monochromatized Mo- $\text{K}\alpha$ radiation ($\lambda = 0.7107\text{ \AA}$) at 100 K. Satisfactory results could not be obtained using intensity data collected at 293 K. Crystallographic data on $\mathbf{1}$ are: triclinic, $\text{P}\bar{1}$, $a = 10.122(1)\text{ \AA}$, $b = 11.177(1)\text{ \AA}$, $c = 36.620(3)\text{ \AA}$, $\alpha = 92.187(2)^\circ$, $\beta = 91.111(2)^\circ$, $\gamma = 103.145(2)^\circ$, $V = 4029.8(2)\text{ \AA}^3$, $Z = 4$, $\mu = 1.710\text{ mm}^{-1}$, $R(\text{int}) = 0.0677$, $R(\text{sigma}) = 0.0922$, $R1 = 0.1072$ for 12 046 [$F_o > 4\sigma(F_o)$] data and 0.1361 ($wR2 = 0.2126$) for all 15 780 data, $\text{Goof} = 1.240$, $(\text{shift/esd})_{\text{max}} = 0.000$. The crystal structure was solved by using the direct methods program of SHELXS-97 [30]. All hydrogen atoms bonded to carbon were assigned idealized positions and refined by full-matrix least-squares method using a 'riding' model incorporated in the crystal structure refinement program SHELXL-97 [30]. The other hydrogen atoms were not included in the refinement. While nine of the water molecules present as solvent of crystallization (*please note*: the asymmetric unit for which structure refinement has been performed consists of two molecules of complex $\mathbf{1}$, one formula unit of NaNO_3 and 16 molecules of water) could be refined anisotropically at full occupancy, the remaining seven were found to be in a disordered state. These disordered water molecules were included in the refinement in the form of 21

peaks of site occupation factors ranging from 0.2 to 0.5. The site occupancies assumed were based on acceptable isotropic atom displacement parameters. The strongest peak of $\sim 1.2 \text{ e}/\text{\AA}^3$ in the final difference Fourier synthesis was found to be $\sim 0.7 \text{ \AA}$ away from one of the partial atoms from the disordered region of water molecules.

2.5. Preparation of the catalyst support

The carboxylate functionalized silica support was synthesized by the method originally developed by Macquarrie et al. [31,32]. To a mixture of water (160 mL) and ethanol (180 mL), *n*-dodecylamine (15.3 g) was added and the resultant mixture stirred until a clear solution formed. Tetraethylorthosilicate (5 mL) was added to the solution and stirred for 2 min. To this solution, another lot of tetraethylorthosilicate (40 mL) and (2-cyanoethyl)triethoxysilane (15.54 mL) were added simultaneously whereupon the solution became turbid and consequently, gave a white precipitate. The reaction mixture was stirred for a further 18 h. The resulting precipitate was filtered and washed with ethanol and dried at 105°C . The template was then removed by 16 h soxhlet extraction with ethanol, the precipitate again filtered and washed with ethanol and dried at 105°C . The above precipitate of CMS-(CH₂)₂CN, where CMS stands for chemically modified silica, was then treated with aqueous H₂SO₄ (45 mL of 98% H₂SO₄ + 105 mL of H₂O) for 6 h at 150°C . The resulting CMS-(CH₂)₂CO₂H material was filtered, washed with water and ethanol and dried at 105°C .

2.6. Preparation of the catalyst

To a solution of complex **1** (0.319 g) in water (30 mL) CMS-(CH₂)₂CO₂H (1 g) was added and the mixture was stirred on an oil bath at refluxing temperature for 12 h. The resulting olive green material, to be called **Co-CMS1** in this paper, was filtered off, washed with water and methanol and dried at 105°C .

2.7. Oxidation of alcohols (typical procedure)

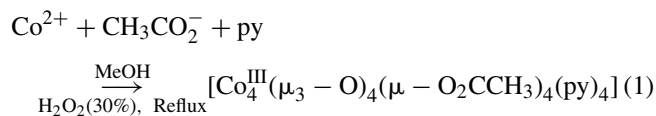
To a solution of benzyl alcohol (1 mL, 10 mmol) in acetonitrile (10 mL) 50 mg of Co-CMS1 was suspended and then 4 mL of *tert*-butyl hydroperoxide (80%) was added and the resultant mixture was stirred at 82°C . The reaction progress was monitored by TLC. After completion of the reaction, the catalyst was filtered off and excess TBHP was destroyed by adding sodium metabisulphite. After removal of solvent, the crude product was purified by flash chromatography.

3. Results and discussion

3.1. Isolation and characterization of the cubane cluster of Co(III)

The synthesis of the cluster compound [Co₄(μ₃-O)₄(μ-O₂CCH₃)₄(py)₄] (**1**), used in this paper as the catalytically active complex, was achieved by chemical (H₂O₂) oxidation of a mix-

ture of Co(II) nitrate, sodium acetate and pyridine in methanolic solution, as described in the following reaction, which proceeds via Co(III)-superoxo or binuclear μ-peroxo intermediates [33].



The pyridine ligand combined with the oxide ion (O²⁻) stabilises the +3 oxidation state of cobalt to facilitate the formation of complex **1**. Although a dark olive green product can be isolated from the concentrated reaction mixture, the isolated yield of the product is relatively low ($\sim 40\%$) due to its high solubility in the solvent system used. However, isolation of complex **1** via precipitation upon addition of petroleum ether to a CH₂Cl₂ extract of the reaction mixture leads to a much higher yield (74%) without affecting the purity of the product. No other cobalt complex could be isolated from the reaction mixture.

Of particular note is the solubility of **1**, which in a rather curious manner dissolves in such solvents of widely differing dielectric constants as water, DMF, DMSO, acetonitrile, ethanol, methanol acetone, diethyl ether and dichloromethane. The UV-vis spectra recorded in these solvents are all similar enough to suggest about the molecular stability of the complex in solution. The electronic spectrum for **1** (vide infra) in methanol shows a *d-d* band at 617 nm ($\epsilon = 360 \text{ M}^{-1} \text{ cm}^{-1}$) along with two stronger bands at 330 nm ($\epsilon = 5900 \text{ M}^{-1} \text{ cm}^{-1}$) and 246 nm ($\epsilon = 21\,285 \text{ M}^{-1} \text{ cm}^{-1}$) which are attributable to ligand to metal charge transfer (LMCT) transitions [34]. While the former LMCT band is likely to be due to a transition involving the μ₃-O-Co(III) moiety present in the complex [26], the latter is most likely to involve a molecular orbital from the other ligands. The ready solubility of complex **1** signifies the molecular nature of the compound which displays ligand field spectra as expected for a tetrameric coordination complex of cobalt(III) having a moderately high formula weight.

We have identified the metal complex conclusively by single crystal X-ray diffraction. Fig. 1 presents an ORTEP view of the complex part of [Co₄(μ₃-O)₄(μ-O₂CCH₃)₄(py)₄].0.5NaNO₃·8H₂O [1·0.5NaNO₃·8H₂O]. The crystal structure consists of two *molecules* of complex **1** in the asymmetric unit along with one unit of NaNO₃ and 16 water molecules. Molecular structure of complex **1** is similar to what was found by Beattie et al. in [Co₄(μ₃-O)₄(μ-O₂CCH₃)₄(py)₄].5CHCl₃ [35]. As shown by our single crystal structure analysis, complex **1** consists of four Co^{III} and O²⁻ ions present at alternate corners of a cube to form a [Co₄O₄]⁴⁺ core with acetato ligands bridging the Co³⁺ ions along four face diagonals of the Co₄O₄ cube. On the other hand, the four Co atoms form an approximate tetrahedron with Co...Co separations of $\sim 2.75 \text{ \AA}$. Pyridine ligands occupy the most outlying sites on the octahedral Co(III) centres. Inspection of the structural parameters shows that for the Co^{III} ions, the Co^{III}-O(oxide) and Co^{III}-O(carboxylate) bonds are in the ranges 1.843(3)–1.885(3) Å and 1.928(3)–1.982(3) Å, respectively to suggest the existence of partial double bond character in the Co^{III}-O(oxo) bonds. The average Co–N distance is $\sim 1.96 \text{ \AA}$.

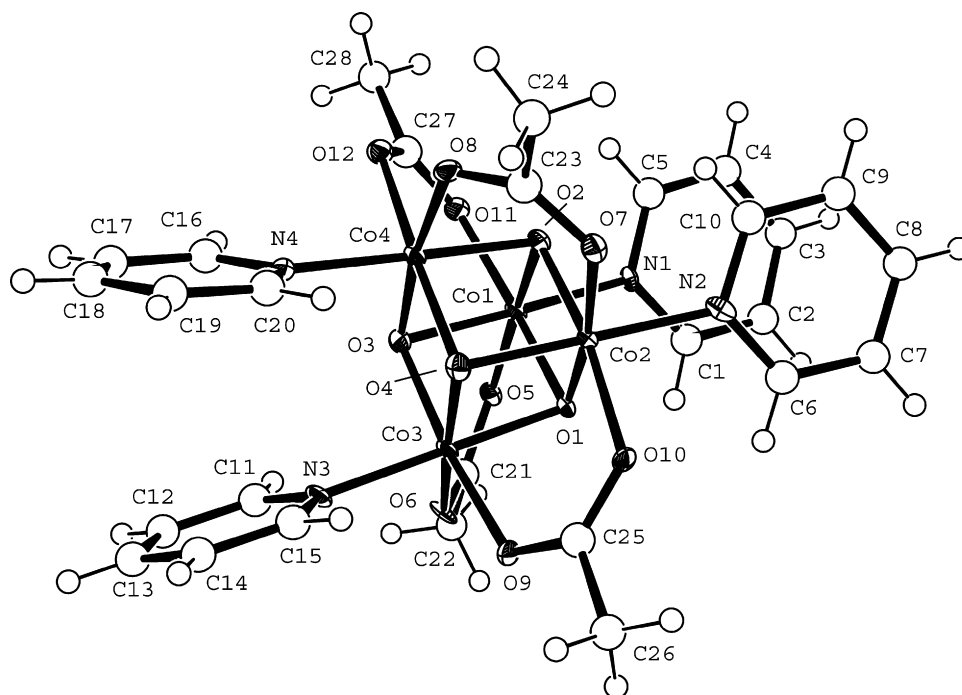


Fig. 1. A labelled ORTEP (30% probability) representation of the complex $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4]$ (**1**) present in $1\cdot 0.5\text{NaNO}_3\cdot 8\text{H}_2\text{O}$. Selected interatomic distances (\AA) are: Co(1)–O(1) 1.866(6), Co(1)–O(2) 1.843(6), Co(1)–O(3) 1.885(6), Co(1)–O(5) 1.947(6), Co(1)–O(11) 1.950(6), Co(1)–N(1) 1.949(7), Co(2)–O(1) 1.865(7), Co(2)–O(2) 1.862(6), Co(2)–O(4) 1.863(6), Co(2)–O(7) 1.962(6), Co(2)–O(10) 1.947(6), Co(2)–N(2) 1.959(8), Co(3)–O(1) 1.871(6), Co(3)–O(3) 1.871(6), Co(3)–O(4) 1.855(6), Co(3)–O(9) 1.942(6), Co(3)–O(6) 1.982(6), Co(3)–N(3) 1.971(7), Co(3)–Co(4) 2.8236(17), Co(4)–O(2) 1.866(6), Co(4)–O(3) 1.877(7), Co(4)–O(4) 1.850(6), Co(4)–O(8) 1.928(7), Co(4)–O(12) 1.965(6), and Co(4)–N(4) 1.968(7).

These values are consistent with a low spin d^6 configuration of Co(III).

^1H and ^{13}C NMR spectra of complex **1** have been recorded. Appearance of sharp signals in the NMR spectra is consistent with the expected diamagnetism of the complex. As shown by the ^1H NMR spectrum (Fig. 2) recorded in D_2O , all the char-

acteristic resonances due to the coordinated pyridine ligand and CH_3CO_2^- moiety appear at expected positions. A sharp singlet at 2.04 ppm indicates the presence of the acetate ligand, while protons of the pyridine ligand resonate at 8.16, 7.68 and 7.16 ppm in 2:1:2 integration ratio. The simplicity of the spectrum clearly indicates the presence of only one type of

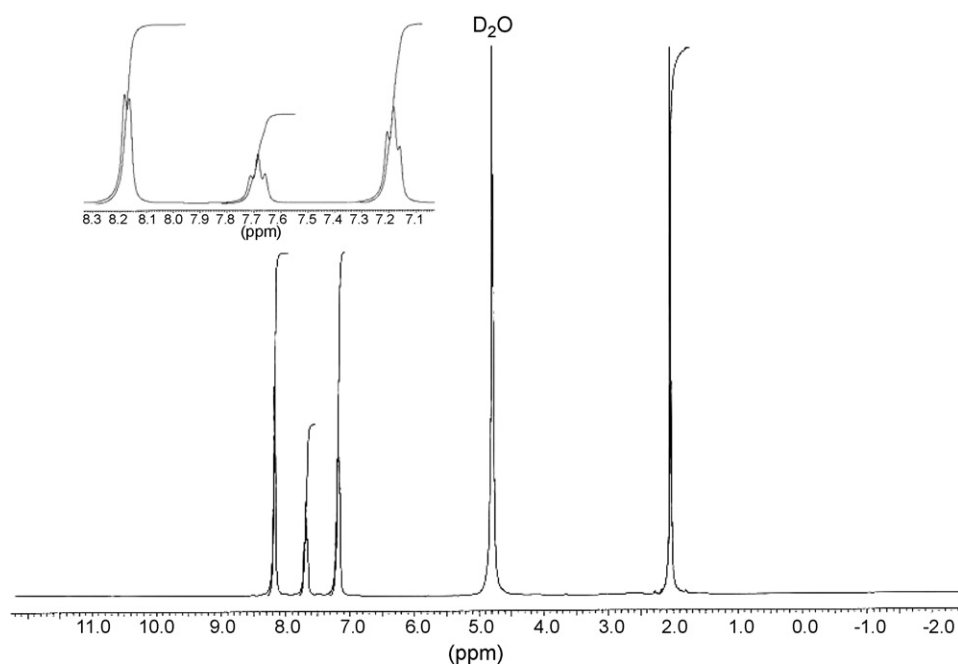


Fig. 2. ^1H NMR spectrum of $\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4$ (**1**) in D_2O .

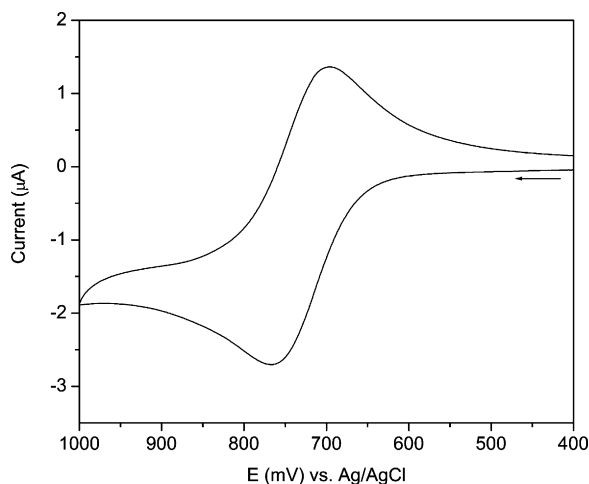


Fig. 3. Cyclic voltammogram for $\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4$ (**1**) in MeCN-0.2M TBAP at a scan rate 10 mVs^{-1} .

environment for pyridine and acetate ligands and is thus consistent with virtual T_d symmetry of the molecule in solution. This indicates the retention of the structure on dissolution. In ^{13}C NMR also peaks due to the carbon atoms of complex **1** appear at expected positions. The NMR spectra thus provide evidence for the bulk purity of the product as well as the substitutional inertness of the tetrameric Co(III) complex in water.

The cyclic voltammogram recorded for a 10^{-3} M solution of complex **1** in MeCN containing 0.2M TBAP as the supporting electrolyte (scan rate = 10 mV s^{-1}) using platinum electrode is shown in Fig. 3. The electrochemical study reveals a reversible oxidation at 0.73 V. It is imperative that the tetrameric $[\text{Co}_4(\mu_3\text{-O})_4]^{4+}$ core undergoes a one-electron oxidation to $[\text{Co}_4(\mu_3\text{-O})_4]^{5+}$ to form a mixed valence tetranuclear complex that contains three Co^{III} and one Co^{IV} ions, as had been observed for a related complex [36]. Such a favourable electrochemical redox potential for complex **1** makes it an interesting candidate for use as a catalyst for the oxidation of organic substrates.

The dehydration curve of complex **1** shows (Fig. 4) that loss of water molecules of crystallization (wt. loss = 11.4%) occurs in the temperature range 25–128 °C. The observed weight loss due to dehydration matches very well with the expected loss of all the water molecules present in

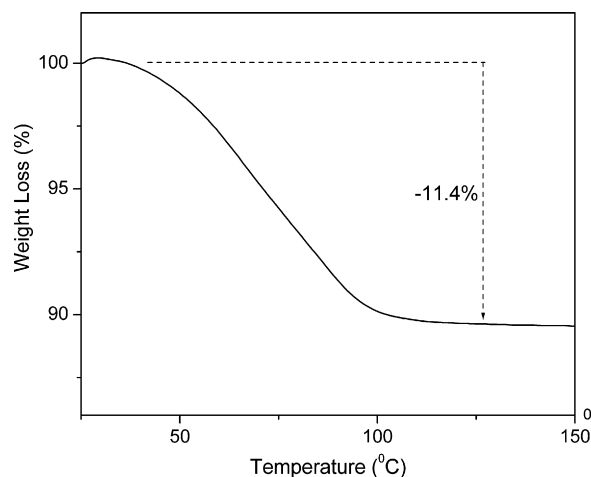


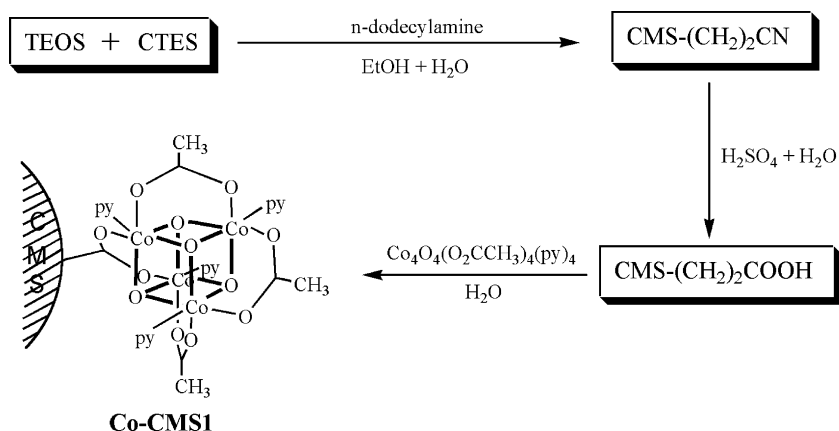
Fig. 4. Thermogravimetric dehydration curve for $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4] \cdot 0.5\text{NaNO}_3 \cdot 8\text{H}_2\text{O}$ [**1**· $0.5\text{NaNO}_3 \cdot 8\text{H}_2\text{O}$] in the temperature range 25–150 °C.

$[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4] \cdot 0.5\text{NaNO}_3 \cdot 8\text{H}_2\text{O}$ (calculated wt. loss = 11.5%). Therefore, the dehydration loss as given by TG data are consistent with the composition obtained from single crystal X-ray structure analysis as well as C,H,N data.

3.2. Preparation and characterization of catalyst (Co-CMS1)

The catalyst described in this paper is based on organomodified silica [30,31]. Cyanoethyl-silica – CMS-(CH_2) $_2$ CN – was prepared from the sol-gel reaction of tetraethylorthosilicate (TEOS) and (2-cyanoethyl)triethoxysilane (CTES) in aqueous ethanol in the presence of *n*-dodecylamine as the templating agent. CMS-(CH_2) $_2$ CN was converted to CMS-(CH_2) $_2$ CO $_2$ H and complex **1** was supported by carboxylate exchange reaction following a procedure reported in the literature [37] to obtain the olive green catalyst—Co-CMS1 (**2**). Scheme 1 shows the preparative procedure diagrammatically.

Co-CMS1 is stable over long periods of time in moist/dry air and against metal leaching upon suspension and/or dissolution in common solvents at room temperature. Powder X-ray diffraction analysis shows it to be nearly amorphous, as is the



Scheme 1.

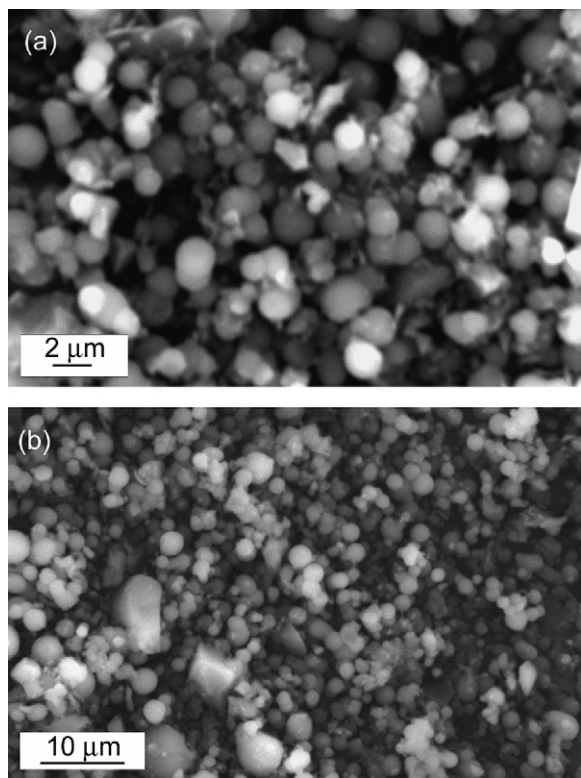


Fig. 5. Scanning electron micrographs of Co-CMS1 at two different magnifications.

case with its support – CMS-(CH₂)₂CO₂H, the only notable features of the powder diffraction patterns being two broad peaks centred at $2\theta = \sim 11.6^\circ$ and 23.1° of which the latter is stronger. This study thus indicates that even after anchoring complex **1** on CMS, the supported reagent remains by and large amorphous in nature. Atomic absorption spectral analysis of the digested material gives a cobalt loading of 0.86 mmol g^{-1} . Scanning electron micrographs (Fig. 5) recorded for Co-CMS1 show that the catalyst particles are predominantly of spherical morphology having an average diameter of $\sim 2 \mu\text{m}$ or less. Investigations by Energy dispersive spectroscopy (EDS) on randomly chosen catalyst particles show a consistent Co:Si ratio ca. 1:8 suggesting that the cobalt complex (**1**) is evenly distributed all over the support.

Adsorption isotherms of the support before and after the immobilisation (Fig. 6) are of similar shape and of Type IV

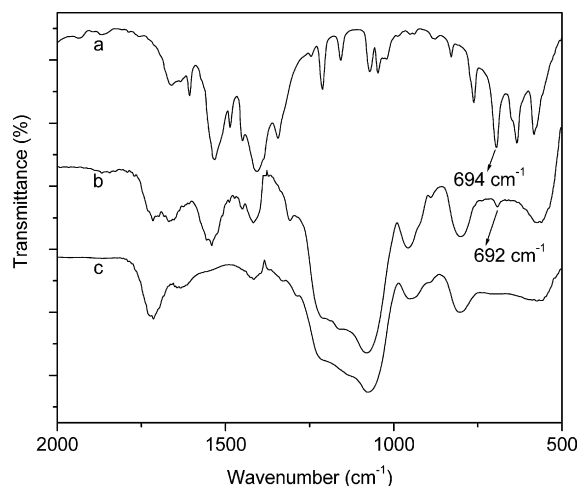


Fig. 7. Infrared spectra of [a] complex **1**; [b] Co-CMS1; [c] CMS-(CH₂)₂CO₂H.

according to IUPAC classification [38]. The BET surface area drops from $1041 \text{ m}^2 \text{ g}^{-1}$ for CMS-(CH₂)₂CO₂H to $426 \text{ m}^2 \text{ g}^{-1}$ in the olive green catalyst, Co-CMS1 (**2**). While the pore volume observed is 0.5100 mL/g , only 36% of the pores have diameters between 3.2 nm and 6.0 nm. On the other hand, nearly 84% pores of CMS-(CH₂)₂CO₂H have diameters in the same range, while the total pore volume is now 0.6876 mL/g . These results indicate that a metal complex has indeed been immobilised on the surface of CMS-(CH₂)₂CO₂H, with some of the complex molecules occupying sites inside the smaller pores. Assuming complex **1** to have a nearly spherical shape, the largest spatial dimension for the molecule will have a value under 20 \AA (2 nm), and thus the cubane complex (**1**) has the right size to enter the pores having diameters in the 3.2–6.0 nm range so as to remain anchored through covalent links with the carboxyl groups present at the inside walls of porous CMS support.

The vibration spectra of complex **1**, CMS-(CH₂)₂CO₂H and the catalyst, Co-CMS1 are shown in Fig. 7. In the KBr phase IR spectrum of complex **1**, it is possible to identify bands due to the bridging acetate ions as well as for the pyridine ligands. The carboxyl stretching vibrations $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ for the acetate groups appear as strong bands at 1538 cm^{-1} and 1410 cm^{-1} , respectively. The separation of the asymmetric and symmetric stretching vibrations ($\nu_{\text{asym}} - \nu_{\text{sym}} = \Delta\nu = 128 \text{ cm}^{-1}$) of the carboxyl group is consistent with this ligand bonding in

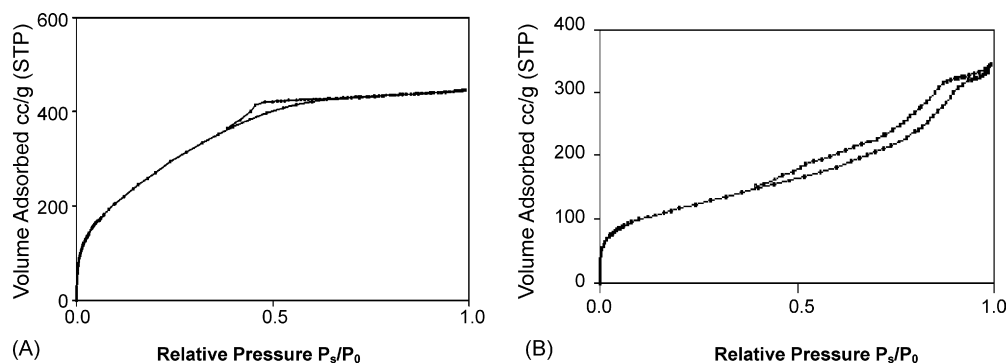


Fig. 6. N₂ adsorption isotherms for (A) CMS-(CH₂)₂COOH and (B) Co-CMS1.

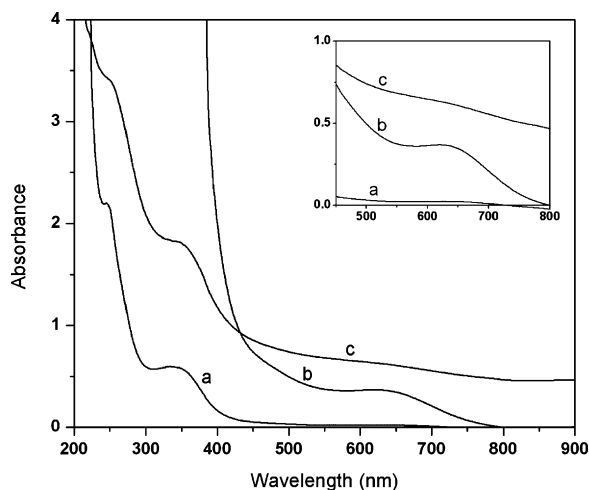


Fig. 8. UV-vis spectra of [a] complex **1** (10^{-4} M) in MeOH; [b] complex **1** (10^{-3} M) in MeOH; [c] Co-CMS1 in nujol mull.

a *syn-syn* bridging mode. The breathing vibration for the $(\mu_3\text{-O})\text{Co}_3$ groups present in $[\text{Co}_4(\mu_3\text{-O})_4(\mu\text{-O}_2\text{CCH}_3)_4(\text{py})_4]$ (**1**) shows up as a characteristic peak at 694 cm^{-1} [25]. Appearance of this vibration as a weak band at 692 cm^{-1} in the DRIFT spectrum of the supported reagent under study suggests the existence of a tetrameric cobalt(III) complex closely related to complex **1** in Co-CMS1 as well. The ν_{asym} and ν_{sym} vibrations of bridging carboxyl groups appear at 1540 and 1417 cm^{-1} , respectively in the spectrum of Co-CMS1. The conclusion to be drawn from the infrared spectral evidence is that we have successfully anchored complex **1** by replacing one of its μ -acetato ligands by the carboxylate anions derived from CMS- $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ as illustrated in the last step of Scheme 1.

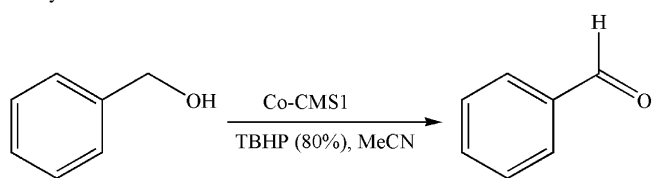
Fig. 8 shows the UV-vis spectra recorded for complex **1** and Co-CMS1. All three spectral bands of the cobalt complex are observed in the spectrum recorded for the supported catalyst as well. LMCT transitions for Co-CMS1 are observed at 251 and 354 nm while the band due to *d-d* transition appears at 620 nm. These positions and their relative intensities are comparable with the bands for complex **1**, which occur at 246, 330 and 617 nm, respectively. This close spectral similarity suggests that the nature of the complex present in Co-CMS1 is nearly the same as complex **1**.

3.3. Catalytic oxidation of alcohols

To begin with, a systematic study was carried out for catalytic evaluation of Co-CMS1 for the oxidation of benzyl alcohol (Table 1). In a typical reaction, benzyl alcohol (1.1 g; 10 mmol), 50 mg of catalyst, 4 mL of TBHP (80%) were mixed in 5 mL acetonitrile and refluxed (82°C) for an appropriate length of time. The progress of the reaction was monitored by TLC. After usual work up and chromatographic purification, the isolated yield of benzaldehyde was found to be 93%. However, the reaction is slow when carried out at room temperature with only 37% benzaldehyde obtained after 24 h. To optimize the catalyst requirement, catalyst concentration was varied between 30 mg and 70 mg per 10 mmol of benzyl alcohol. Increase in the yield

Table 1

Catalytic oxidation of benzyl alcohol by TBHP (80%) using Co-CMS1 as the catalyst under different conditions^a



Entry	Amount of catalyst (mg)	Amount of TBHP (mL)	Temp ($^\circ\text{C}$)	Time (h)	Yield (%) ^b
1	50	1.0	82	5.0	14
2	50	2.0	82	4.5	49
3	50	3.0	82	4.0	55
4	50	4.0	82	4.5	93
5	50	5.0	82	4.5	94
6	50	4.0	27	24	37
7	40	4.0	82	7.0	68
8	30	4.0	82	7.5	25
9	70	4.0	82	4.0	93
10 ^c	10	4.0	82	5.5	60
11 ^d	50	4.0	82	4.5	88
12 ^e	0	4.0	82	5.0	2

^a Reaction condition—benzyl alcohol: 1.1 g (10 mmol); acetonitrile: 5 mL.

^b Isolated yield of benzaldehyde.

^c Homogeneous phase reaction with complex **1**.

^d Recovered catalyst was reused.

^e Blank reaction.

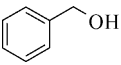
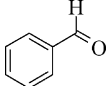
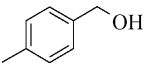
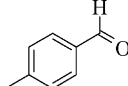
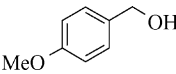
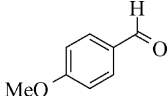
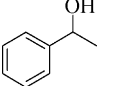
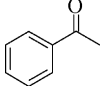
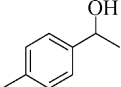
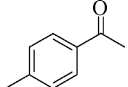
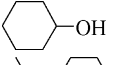
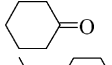
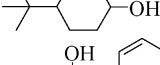
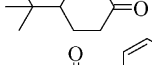
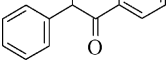
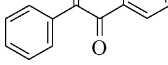
of benzaldehyde was observed when the amount of catalyst was increased from 30 mg to 50 mg but the yield remained same with further increment of catalyst amount up to 70 mg. Then the reaction was studied with varying amounts of TBHP. The yield of the aldehyde also significantly increases upon increasing the concentration of the oxidant, TBHP. An optimum of 50 mg of catalyst and 4 mL of TBHP (per 10 mmol of the substrate) in the reaction mixture is ideal for achieving the best yield. The essential role played by the catalyst is evident from the extremely low (2%) yield of benzaldehyde found in a blank reaction carried out in absence of the catalyst.

A comparative study of the catalytic activity of complex **1** in the oxidation of benzyl alcohol in homogeneous and in heterogeneous phase under similar conditions reveals that complex **1** in the immobilised state, i.e. Co-CMS1 is more active than the neat complex (Table 1, entry 9). The amount of complex **1** (10 mg) used in the homogeneous reaction was approximately the same as the amount of the cobalt complex estimated to be present in 50 mg of Co-CMS1. Benzaldehyde was the only product observed in both the cases.

At the end of the reaction, the catalyst was filtered and reused for benzyl alcohol oxidation. A slight decrease in the yield of benzaldehyde from 93% with fresh catalyst (first run) to about 88% in the second run is observed (Table 2, entry 9). No detectable leaching of cobalt was observed in the first as well as the second run of the reaction. Furthermore, the amount of cobalt estimated for the catalyst obtained after first use remained unchanged.

After optimizing the reaction conditions, we extended the process to other benzylic alcohols, which also underwent oxi-

Table 2
Oxidation of various alcohols by TBHP using Co-CMS1 as the catalyst^a

Entry	Substrate	Product	Time (h)	Yield ^b
1			4.5	93
2			1	69
3			4.5	89
4			1	78
5			2	86
6			5	64
7			3	73
8			12	89

^a Reaction condition: substrate, 10 mmol; amount of catalyst, 50 mg; acetonitrile, 5 mL; reaction temperature, 82 °C.

^b Isolated yields after chromatographic purification.

ation as summarized in Table 2. The present method thus works well for benzylic alcohols very efficiently to produce the corresponding carbonyl compound in excellent yield. After successful attempt for the catalytic oxidation of benzylic alcohols, we thought of applying the procedure for the oxidation of secondary alcohols such as cyclohexanol. As can be seen from the tabulated data, substrates like cyclohexanol, 4-*tert*-butyl cyclohexanol also could be oxidised successfully to the corresponding ketones using this heterogeneous catalyst.

4. Conclusions

A cobalt(III) cubane cluster has been prepared and characterised in detail. We have shown that the oxo-bridged cobalt cluster can be chemically immobilised on organomodified CMS to prepare an efficient heterogeneous catalyst for the highly selective oxidation of alcohols such as benzylic alcohols and cyclohexanols using TBHP as the oxidant. The catalyst could also be reused after simple filtration. No leaching of the immobilised complex was observed in the catalysed reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.11.042.

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