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Introduction

Oxidation reactions play a significant role in organic synthesis and presently there is a demand for more selective and efficient oxidation methods. Among oxidation reactions, the oxidation of alcohols to the corresponding carbonyl compounds is one of the most important and fundamental reactions in organic synthesis. Numerous oxidizing reagents have been exploited for this purpose. However, most of these reagents are required in stoichiometric quantities, which is not only expensive, but sometimes also toxic in nature. Therefore, from an environmental and economic perspective, catalytic oxidation processes are promising methods. In recent years there has been a significant growth in the field of aerobic oxidation catalysis.1 The use of molecular oxygen as the primary oxidant has several benefits, such as lower costs, improved safety, higher abundance and "green" methods with water as the sole by-product. Many transition metals such as vanadium,² cobalt,³ molybdenum,⁴ ruthenium,⁵ rhodium,⁶ palladium,7 nickel,8 osmium9 and polyoxometalates10 have been employed as catalysts for the oxidation of alcohols with

A mononuclear copper(II) complex immobilized in mesoporous silica: an efficient heterogeneous catalyst for the aerobic oxidation of benzylic alcohols[†]

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The diamide ligand 2,6-bis[(*N*-phenyl)amido]-4-methylphenol (HL) has been used to synthesize a mononuclear copper(II) complex, [CuL₂(DMF)₂] (1). The X-ray crystal structure of this complex reveals that the copper(II) center is coordinated to the two phenoxides and two amide carbonyl oxygens of the HL ligand and additionally to the amide carbonyl oxygens of two dimethylformamide molecules. This complex was also characterized using UV-Vis and EPR spectroscopy, along with thermal and electrochemical analysis. Complex 1 was then immobilized in a 2-D mesoporous silica matrix. This immobilized complex, 1a, has been characterized using UV-Vis and FT-IR spectroscopy, as well as small angle X-ray diffraction, N₂ sorption and TEM. The immobilized complex was found to heterogeneously catalyze the aerobic oxidation of benzylic alcohols to the corresponding aldehydes in the presence of TEMPO, with high turnover numbers and good recyclability for up to four cycles.

molecular oxygen as the oxidant. Recently, copper complexes have attracted significant attention for the catalytic oxidation of alcohols, since they are present in the active site of galactose oxidase (GO)¹¹ and several copper enzymes are also known to activate dioxygen for highly selective transformations under mild reaction conditions.¹¹

Copper-phenanthroline complexes were observed to react with methanol as early as 1966.¹² Since then, the copper complexes of 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) have been thoroughly investigated as catalysts in the oxidation of different alcohols.¹³ Markó *et al.* reported the efficient aerobic oxidation of alcohols to aldehydes and ketones in the presence of a copper catalyst comprised of CuCl, 1,10-phenanthroline and di*-tert*-butylhydrazine-1,2dicarboxylate (DBADH₂).¹⁴ Semmelhack *et al.* introduced a combined CuCl-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)– O₂ system for the oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds at room temperature.¹⁵ More recently, several other catalytic systems based on TEMPO and a copper complex for the aerobic oxidation of alcohols to aldehydes or ketones have also been reported.¹⁶

However, most of these catalytic processes are homogeneous and suffer from a serious limitation, namely, the separation and recovery of the catalyst. A catalyst with a high recycling capacity should require minimum effort for its separation and is the most desirable for industrial processes. Therefore, heterogeneous alternatives have attracted a lot of attention because heterogeneous catalysis permits the easy separation and reuse of the catalyst. This methodology

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[†] Electronic supplementary information (ESI) available: X-ray crystallographic file for compound 1 and Fig. S1–S6. CCDC reference number 912042. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c3ra41417e

represents a powerful tool in chemistry, allowing extremely complex chemical transformations to take place in a cleaner, more efficient, one-pot process.^{17–19} The immobilization of transition metal-based catalysts on different solid supports *e.g.*, silica,^{20,21} polymers,²² mesoporous materials,^{23–25} activated carbons,^{26,27} pillared clays²⁸ and zeolites,²⁹ has been achieved effectively. Recently, a Cu nanoparticle–polyacrylamide/SBA-15 (3-D hexagonal mesoporous silica) hybrid has been reported as a recyclable catalyst for the aerobic oxidation of alcohols.³⁰ Previously, the recovery of the catalysts in the above reactions have been achieved by using non-traditional perfluorinated solvents^{31a} and ionic liquids,^{31b} while coppersalen based catalysts have been recovered from aqueous media³² and heterogeneous Cu–Mn oxides.³³

We report here the synthesis and characterization of a mononuclear copper(II) complex (1) derived from a new amide based ligand 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL). This mononuclear copper(II) complex was immobilized in MCM-41 type 2D-hexagonal mesoporous silica (HMS). Absorption spectroscopy (UV-Vis-NIR), Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD), high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy studies have been used to characterize the material. The immobilized catalyst was employed for the catalytic aerobic oxidation of primary alcohols to the corresponding aldehydes using TEMPO as co-catalyst under heterogeneous conditions. The results show that the conversions of the primary alcohols occur in high yield and are totally selective towards the aldehydes. Our catalyst also offers an extra advantage as it does not require the use of any additives, which are necessary in most of the reported homogeneous methods. In addition, the separation and recovery of the catalyst in this heterogeneous catalytic system can be performed very easily by either centrifugation or filtration.

Experimental

Materials

Reagent grade chemicals were obtained from commercial sources and were used as received. The solvents were purified and dried according to standard protocols.³⁴ 2,6-Diformyl-4-methyl phenol,³⁵ 2,6-dicarboxylic-4-methyl phenol³⁶ and 4-hydroxymethylbenzaldehyde (HMB)³⁷ were prepared according to methods previously reported in the literature.

Physical measurements

Elemental (C, H, and N) analyses were performed using a Perkin-Elmer 2400 II elemental analyzer. FT-IR spectra were recorded using KBr disks with Shimadzu FT-IR 8400S and JASCO FTIR-460 Plus spectrophotometers. The electronic absorption spectra were measured at room temperature using an Agilent 8453 diode array spectrophotometer. ¹H NMR spectra were obtained using a Bruker Avance DPX spectrometer at 300 MHz with chemical shifts (δ , ppm) quoted relative to tetramethylsilane (TMS). Thermogravimetric analysis (TGA)

was performed using a Perkin Elmer Diamond TG thermal analyzer under a flow of nitrogen at a heating rate of 10 °C min⁻¹. Electrochemical measurements were carried out in N,N-dimethylformamide (DMF) at 25 °C under a nitrogen atmosphere using a Bioanalytical Systems BAS 100B electrochemical analyzer. The concentration of the supporting electrolyte, tetramethylammonium perchlorate (TEAP), was 0.1 M, while that of the complex was 1 mM. Cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out using a three-electrode assembly comprising either a glassy carbon or platinum working electrode, a platinum auxiliary electrode, and an aqueous Ag/AgCl reference electrode. Under the given experimental conditions, the potential of the external standard ferrocene/ferrocenium (Fc/Fc⁺) couple was measured at +0.390 V vs. Ag/AgCl. X-band EPR measurements were carried out using a JEOL JES-FA 200 instrument. Powder X-ray diffraction (XRD) patterns were obtained using a Philips PW 1140 parallel beam X-ray diffractometer with a Bragg-Bretano focusing geometry and monochromatic Cu-K α radiation (λ = 1.540598 Å). N₂-sorption isotherms were obtained using a Quantachrome Instruments analyzer at 77 K. Gas chromatographic analyses were conducted using an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary HP-5 column (30 m \times 0.32 mm) and a FID detector. The EDS spectra were obtained using a Horiba EDS analyzer attached to Hitachi S-3400 N scanning electron microscope (SEM). Transmission electron microscopy (TEM) images and selected area diffraction (SAED) patterns were collected using a JEOL JEM-2100 microscope working at 200 kV.

Synthesis of 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL)

2,6-Dicarboxylic-4-methyl phenol (0.98 g, 5 mmol) was dissolved in 25 cm³ dry dichloromethane in a three-necked round-bottom flask. Oxalyl chloride (1.1 cm³, 12.5 mmol) was added via syringe through a septum followed by the addition of 2 drops of dimethylformamide (DMF) under a flow of nitrogen. The resulting mixture was stirred at room temperature for 3 h and then concentrated under vacuum. The resulting crude, pale yellow acid chloride was redissolved in 25 cm³ dry dichloromethane for further reaction without any purification. In a separate three-necked round-bottom flask, 20 cm^3 dry dichloromethane, triethylamine (1.26 g, 12.5 mmol) and aniline (1.03 g, 11.0 mmol) were mixed under a flow of nitrogen. The crude acid chloride dissolved in dry dichloromethane was then added slowly to this mixture using a pressure-equalizing addition funnel. The resulting mixture was then stirred for 4 h during which time a white product separated out. The solid product was filtered and then purified by column chromatography using an 8:2 hexane-ethyl acetate mixture. Yield: 1.38 g (80%). Mp 222 °C. Found: C, 72.84; H, 5.26; N, 8.12%. C21H18N2O3 requires: C, 72.82; H, 5.24; N, 8.09%. IR (KBr, v, cm⁻¹) 3354 (w), 3281 (m), 1653 (s), 1597 (s), 1549 (s), 1491 (s), 1445 (s), 1326 (m), 1281 (m), 1254 (m), 1230 (w), 1173 (w), 1125 (w), 1080 (w), 948 (m), 793 (m), 759 (s), 725 (m), 685 (m), 570 (w), 507 (m). ¹H NMR (CDCl₃, $\delta_{\rm H}$, ppm) 14.02 (s, 1H, PhOH), 9.37 (s, 2H, NHC=O), 7.86 (s, 2H,

Ar), 7.67 (d, 4H, *J* = 4.8 Hz, Ar), 7.38 (t, 4H, *J* = 4.6 Hz, Ar), 7.18 (t, 2H, *J* = 4.3 Hz, Ar), 2.30 (s, 3H, CH₃).

Preparation of the metal complexes

Caution! The perchlorate salts used in this study are potentially explosive and therefore should be handled in small quantities with care.

[CuL₂(DMF)₂] (1). The ligand, HL, (0.35 g, 1.0 mmol) was dissolved in 25 cm³ methanol and a 10 cm³ solution of Cu(ClO₄)₂·6H₂O (0.19 g, 0.5 mmol) in methanol was added to it with stirring. Triethylamine (0.1 g, 1.0 mmol) in 5 cm³ methanol was then added drop wise. The resulting solution was refluxed for 1 h and after some time a greenish-brown crystalline compound started to appear. This was filtered and washed, first with chilled dry methanol, and then with dry diethyl ether. The compound obtained was dissolved in 25 cm³ dimethylformamide (DMF) and heated at 80 °C for 0.5 h. It was then left undisturbed overnight. Brown single crystals suitable for X-ray crystallography appeared. The crystals were filtered through a sintered glass crucible and washed with a 2:1 mixture of diethyl ether and DMF. Yield: 0.56 g (70%). Found: C, 63.92; H, 5.45; N, 9.40. C48H48CuN6O8 requires: C, 64.02; H, 5.37; N, 9.33%. FT-IR (KBr, v, cm⁻¹) 3253(w), 3039(w, br), 1662(s), 1639(s), 1595(s), 1523(s), 1496(m), 1446(s), 1323(m), 1295(s), 752(m), 692(m), 576(m). UV-Vis [in DMF, λ_{max} , nm (ε , dm³ mol⁻¹ cm⁻¹)]: 285 (37 000), 385 (25 000), 450 (550), 750 (80).

Synthesis of the 2-D hexagonal mesoporous silica matrix (HMS). The mesoporous material was prepared using a slightly modified procedure described previously.³⁸ The cationic surfactant cetyl trimethylammonium bromide (CTAB, 1.48 g) was added to an aqueous solution of sodium dodecyl sulfate (SDS, 0.24 g) with vigorous stirring at room temperature. Stirring was continued for another 30 min. Gel formation occurred immediately leading to a viscous suspension. Tetraethyl orthosilicate (1.75 g) was added to this suspension with continuous stirring over 30 min. After 2 h continuous stirring, tetraethylammonium hydroxide was added dropwise until the color of the solution turned white. The pH value of the final mixture was about 11. The resultant mixture was aged overnight while stirring at room temperature and then transferred into a polypropylene bottle and heated at 80 °C for 72 h without stirring. The solid produced was recovered by filtration, then washed several times with water, and dried at room temperature. The resulting powder was calcined at 700 K to remove the organic surfactants. The molar ratio of the various components was 1:0.5:0.1:90 (TEOS/CTAB/SDS/ H_2O).

Preparation of immobilized catalyst 1a. Immobilization of the complex $[CuL_2(DMF)_2]$ (1) was carried out by suspending 1.0 g of mesoporous silica in a 20 cm³ DMF solution containing 0.2 g of the complex, followed by vigorous stirring at room temperature for 4 h. The solid was then filtered, washed several times with DMF and dried under vacuum at ambient temperature. Found: C, 5.57; H, 0.39; N, 0.62%. 8.34 wt% immobilization of $C_{42}H_{34}CuN_4O_4$ requires: C, 5.58; H, 0.38; N, 0.62%.

Preparation of HMB–Si–HMS. The anchoring of (3-aminopropyl)triethoxysilane (3-APTES) into 2-D hexagonal mesoporous silica (HMS) was achieved by stirring 0.1 g HMS with 0.18 g (0.81 mmol) 3-APTES in dry chloroform at room temperature for 12 h under a N₂ atmosphere. The white, solid HMS– $[Si(CH_2)_3NH_2)_x$ produced was filtered and washed with chloroform and dichloromethane. This solid was then refluxed with 2.73 g 4-hydroxymethylbenzaldehyde (HMB) (20 mmol) in methanol (10 cm³) for 3 h at 60 °C. The resulting pale yellow solid HMB–Si–HMS was then collected by filtration and was dried in a desiccator (Scheme 1).

The catalytic oxidation of primary alcohols. The immobilized copper catalyst **1a** (0.02 gm) was dispersed in 5 cm³ toluene. A primary alcohol (1 mmol, 0.11 g) and TEMPO (1.6 mg, 0.01 mmol) were then added to this solution. The reaction mixture was allowed to stir under oxygen at a temperature of 80 °C. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation. The solution was then passed through a 60–120 mesh silica gel column and washed with 10 cm³ toluene. Chlorobenzene was added to the eluent as an internal standard and the products were quantified using GC.

X-ray crystallography

A single crystal of compound **1** was mounted on a glass fiber and coated with perfluoropolyether oil. Intensity data were collected at 150(2) K on a Bruker-AXS SMART APEX II diffractometer equipped with a CCD detector using graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data were processed with SAINT,³⁹ and absorption corrections were made with SADABS.³⁹ The structures were resolved using direct and Fourier methods and refined with a full-matrix least-squares method based on F² using SHELXTL⁴⁰ and SHELX-97 software packages.⁴¹ The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at geometrically calculated positions with fixed isotropic thermal parameters. The crystallographic data and selected details of the structural determination are given in Table 1.

Result and discussion

Synthesis and characterization of the metal complex [CuL₂(DMF)₂] (1)

The synthesis of 2,6-dicarboxylic-4-methyl phenol was achieved by following the method reported by Okawa *et al.*³⁶ The reaction of 2,6-dicarboxylic-4-methyl phenol with oxalyl chloride in the presence of catalytic amount of DMF affords the di-acid chloride, which reacts with aniline in presence of triethlylamine to give the ligand, HL. The synthesis of HL is outlined in Scheme 2. The mononuclear copper(II) complex is obtained from the reaction between one equiv. of both HL and $Cu(ClO_4)_2 \cdot 6H_2O$ in presence of one equiv. triethylamine with methanol as a solvent. At first we obtained a greenish-brown complex, which was then recrystallized from DMF to obtain $[CuL_2(DMF)_2]$ (1).

The ¹H NMR spectrum of the ligand, HL, was recorded in CDCl₃ and the chemical shift values and their related spectral



Scheme 1 Organic modification of a MCM-41 type 2-D HMS using 3-APTES in CHCl₃ and anchoring 4-hydroxymethylbenzaldehyde (HMB) onto 2-D HMS (in methanol).

assignments are given in the experimental section. Scheme S1 (ESI^{\dagger}) and Fig. S1 (ESI^{\dagger}) show the proton labelling and ¹H NMR spectrum of the HL ligand, respectively.

The FT-IR spectrum of the HL ligand exhibits two peaks at 3281 and 1599 cm⁻¹ due to the stretching and bending frequencies of NH, respectively (Fig. 1a). The stretching vibration relating to the amide carbonyl groups appears at 1650 cm⁻¹. The IR spectrum of complex **1** exhibits several diagnostic features. Two weak broad bands observed at about

Table 1 Crystallographic data of [CuL₂(DMF)₂] (1)

Empirical formula	$\mathrm{C}_{48}\mathrm{H}_{48}\mathrm{N}_{6}\mathrm{O}_{8}\mathrm{Cu}$	
Μ	900.46	
T/K	150(2)	
Crystal system	Monoclinic	
Space group	$P2_1$	
a/Å	9.950(4)	
b/Å	13.482(5)	
c/Å	17.253(6)	
$\beta/^{\circ}$	105.438(9)	
$U/Å^3$	2230.9(14)	
Ζ	2	
$D/\mathrm{g}~\mathrm{cm}^{-3}$	1.340	
μ/mm^{-1}	0.550	
F(000)	942	
Crystal size/mm	0.36 $ imes$ 0.28 $ imes$ 0.15	
No. of measured reflections	30 207	
No. of observed reflections	9046	
Parameters refined	574	
No. of reflections $[I > 2\sigma(I)]$	8450	
Goodness of fit, $S^{\tilde{a}}$	1.027	
Final R_1^{b} , $wR_2^{c} [I > 2\sigma(I)]$	0.0303, 0.0742	
R_1^{b} , wR_2^{c} (all data)	0.0344, 0.0770	

^{*a*} $S = [\sum w(F_o^2 - F_c^2)/(N - P)]^{\frac{1}{2}}$ where *N* is the number of data values and *P* the total number of parameters refined. ^{*b*} $R_1(F) = \Sigma ||F_o| - |F_c||\Sigma|F_o|$. ^{*c*} $wR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{\frac{1}{2}}$. 3255 and 3190 cm⁻¹ are due to the N-H stretching vibration, which is hydrogen-bonded to both coordinated phenolate oxygens and uncoordinated amide carbonyl oxygens. The C=O vibration in the ligand is observed at about 1640 cm⁻¹. On the other hand, the C=O vibration of the coordinated DMF appears at 1664 cm⁻¹.

The absorption spectroscopic behaviour of compound **1** was studied in dimethylformamide (DMF). The UV-Vis-NIR spectral data for this compound are given in the experimental section. Complex **1**, exhibits three very strong absorption bands at 286 nm ($\varepsilon = 73$ 600 dm³ mol⁻¹ cm⁻¹), 330 nm ($\varepsilon = 21$ 340 dm³ mol⁻¹ cm⁻¹), and 385 nm ($\varepsilon = 49$ 990 dm³ mol⁻¹ cm⁻¹) due to ligand centred π - π * transitions. The six-coordinated octahedral copper complex exhibits two bands in the visible range at 440 nm ($\varepsilon = 650$ dm³ mol⁻¹ cm⁻¹), which appears as a shoulder, and 750 nm ($\varepsilon = 78$ dm³ mol⁻¹ cm⁻¹). The shoulder at 440 nm is most likely due to a phenolate oxygen \rightarrow Cu^{II} ligand-to-metal charge transfer (LMCT) transition, while the other band observed is due to d-d transitions. Fig. 2 shows the Vis-NIR spectrum of compound **1**.

The thermal stability of $[CuL_2(DMF)_2]$ (1) has been studied over the temperature range 30–700 °C using thermogravimetric (TG) measurements. Fig. S2 (ESI†) shows the TG data of compound 1, which indicate that the solvated compound remains stable up to 140 °C and desolvation then occurs between 140 and 200 °C. The desolvated product is stable up to 315 °C. The observed weight loss (16.75%) is in agreement with the value (16.23%) expected for the loss of two DMF molecules. With a further increase in temperature from 315 to 700 °C, compound 1 eventually loses all of its organic backbone, producing CuO.

The electrochemical properties of complex **1** have been studied in dimethylformamide (DMF) solution. Complex **1** is found to undergo one quasi-reversible oxidation at about $E_{\frac{1}{2}}$ =



Scheme 2 The preparation of 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL).



Fig. 1 FT-IR spectra of complex 1, the mesoporous silica matrix and immobilized catalyst 1a (a) and the % transmittance of (-C=O)_{amide} vs. the weight of the immobilized catalyst obtained from FTIR (b).

+0.800 V ($\Delta E_{\rm p} = 0.085$ V at 0 to +1.0 V) and two successive irreversible reductions at about $E_{\frac{1}{2}} = -0.45$ and -0.73 V (Fig. S3a, ESI[†]). To assign these redox processes, we also carried out cyclic voltammetry experiments on the HL ligand in dimethyl-formamide (Fig. S3b, ESI[†]). The ligand demonstrates a quasi-reversible oxidation at about $E_{\frac{1}{2}} = +0.745$ V ($\Delta E_{\rm p} = 0.090$ V) and a quasi-reversible reduction at about $E_{\frac{1}{2}} = -0.715$ V ($\Delta E_{\rm p} = 0.20$ V). Therefore, the oxidation and the second reduction



Fig. 2 UV-Vis-NIR spectrum of complex 1 in dimethylformamide and the immobilized catalyst 1a (dispersed in dimethylformamide).

processes that occur in complex 1 are due to ligand-centered processes. The first reduction process observed can be assigned as the Cu^{II}/Cu^{I} reduction potential.

The X-band EPR spectrum of complex **1** has been captured in 4 : 1 ethanol/methanol solution at 77 K (Fig. S4, ESI†). The EPR spectrum shows an axially symmetric copper(II) center with $g_{\perp} = 2.05$ and $g_{||} = 2.26$. These values indicate that the ground state of Cu(II) is predominantly $d_x^{2} - y^{2}$.

The crystal structure of $[CuL_2(DMF)_2]$ (1)

An ORTEP representation of $[CuL_2(DMF)_2]$ (1) along with atom labels is shown in Fig. 3 and selected bond distances and angles are given in Table 2.

In the asymmetric unit, the copper(II) centre is coordinated with the two phenoxides and two carbonyl oxygens of the ligand, HL. The metal center is additionally coordinated with two carbonyl oxygens from DMF molecules. The coordination environment around the six-coordinated metal centre [CuO₆] may be considered to be a slightly distorted octahedron. It should be noted that, in terms of an octahedral description, the metal centre is located in the basal plane formed by the atoms O1, O2, O4, and O5. However, these atoms are displaced from the least-squares plane by \pm 0.015(3) Å and the metal ion is situated 0.0067(4) Å below this plane. Oxygen atoms O7 and O8 from the two coordinated DMF molecules are trans-axially disposed to the metal centre. The two Cu-O(phenolate) distances [1.9044(13) and 1.9061(13) Å] are identical, as are the two Cu-O(carbonyl) distances [2.0316(15) and 2.0387(15) Å]. On the other hand, the axial Cu–O(DMF) distances [2.3670(20) and 2.3400(20) Å] are significantly longer relative



Fig. 3 An ORTEP representation of the complex $[CuL_2(DMF)_2]$ (1) showing 50% probability displacement ellipsoids.

Bond distance	s (Å)	Bond angles (°)	
Cu(1)-(O1) Cu(1)-(O2) Cu(1)-(O4) Cu(1)-(O5) Cu(1)-(O7) Cu(1)-(O8)	$\begin{array}{c} 1.9044(13)\\ 2.0316(15)\\ 1.9061(13)\\ 2.0387(15)\\ 2.3670(20)\\ 2.3400(20)\end{array}$	$\begin{array}{c} O(1)Cu(1)O(2)\\ O(1)Cu(1)O(4)\\ O(1)Cu(1)O(5)\\ O(1)Cu(1)O(7)\\ O(1)Cu(1)O(8)\\ O(2)Cu(1)O(5)\\ O(2)Cu(1)O(4)\\ O(2)Cu(1)O(7)\\ O(2)Cu(1)O(8)\\ O(4)Cu(1)O(5)\\ \end{array}$	$\begin{array}{c} 92.12(6)\\ 179.03(8)\\ 88.54(6)\\ 89.53(8)\\ 91.35(8)\\ 178.74(10)\\ 87.01(6)\\ 85.50(8)\\ 96.09(8)\\ 92.34(6)\end{array}$
		O(4)Cu(1)O(7) O(4)Cu(1)O(8) O(5)Cu(1)O(7) O(5)Cu(1)O(8) O(7)Cu(1)O(8)	$90.82(8) \\ 88.33(8) \\ 93.44(7) \\ 84.96(8) \\ 178.15(9)$

to the Cu–O(axial) distances. The *trans*-axial O7–Cu–O8 angle is 178.15(9)°, while the *trans*-equatorial angles are 179.03(8)° for O1–Cu–O4 and 178.74(10)° for O2–Cu–O5 . The trigonal planes comprising O1, O2, and O7, and O4, O5, and O8 are inclined with respect to one another by 1.14°, which again indicates a slightly distorted octahedral geometry.

A noteworthy feature of the molecular structure of **1** is the occurrence of both intramolecular and intermolecular N–H···O bonds involving amide nitrogen and both coordinated phenolate oxygens and uncoordinated carbonyl oxygens, as listed in Table 3. The hydrogen atoms of amide nitrogens N2 and N4, are intramolecularly hydrogen-bonded to phenolate oxygens O1 and O4. On the other hand, N1 and N3 are involved in intermolecular hydrogen-bonding with uncoordinated amide carbonyl oxygens, O3 and O6. It should be noted that the amide nitrogen atoms act as donors while both types of oxygen act as acceptors. The donor–acceptor N···O distances lie between 2.601(3) and 2.793(3) Å and the N–H···O angles range from 139.00° to 153.00° (Table 3), indicating that the hydrogen bonds are very strong.

Table 3 Catalytic oxidation of benzyl alcohol alcohols under various conditions^a

Entry	Catalyst	Co-catalyst/base	Time (h)	Yield (%)
1	1a	Triethylamine	24	35
2	1a	Piperidine	24	50
3	1a	TEMPO	16	80
4^b	1	TEMPO	16	45
5 ^c		TEMPO	24	10

^a Reaction conditions: benzyl alcohol (1 mmol), base (1 mmol),

TEMPO (0.01 mmol), 20 mg catalyst (1a or 1) in toluene.

^b Homogeneous reaction in toluene. ^c Blank reaction in the presence of the mesoporous silica matrix and TEMPO only.

The packing diagram of compound 1 reveals several short interactions between aromatic hydrogen atoms and the centroid of the π cloud of another aromatic ring. Compound 1 exhibits one intermolecular C-H $\cdots\pi$ interaction in addition to two intramolecular interactions. Generally, the upper acceptable limit for the distance of a C-H hydrogen atom from the centroid of an aromatic ring in a C-H $\cdots\pi$ interaction is 3.5 Å. The metrical parameters for the C–H··· π interactions in compound 1 (Table S1, ESI^{\dagger}) indicate that the C-H··· π distances range from 2.80 to 3.02 Å, indicating that the C–H $\cdots\pi$ interactions are strong. Another interesting structural feature of this compound is the presence of an intermolecular π - π interaction between the aromatic ring composed of C2, C3, C4, C5, C6, and C7 and the aromatic ring composed of C23, C24, C25, C26, C27, and C28 (the distance between the two centroids is 3.53 Å). All these short interactions and the intermolecular hydrogen-bonding give rise to a two dimensional sheet structure in the compound, as shown in Fig. S5, ESI.[†]

Characterization of the immobilized catalyst

The FT-IR spectra of the mesoporous silica host and immobilized catalyst **1a** are shown in Fig. 1a. **1a** exhibits several bands in the 1700–1400 cm⁻¹ region, which can be attributed to the immobilization of compound **1** in the mesoporous silica host. These bands are not found in the spectrum of the mesoporous host. This result indicates that the immobilization of compound **1** in the mesoporous host was successful. In order to determine if the distribution of the copper complex in catalyst **1a** was homogenous, FTIR spectra were carried out in a quantitative fashion. The percentage transmittance (the –C=O group of the amide ligand was used as a probe) was plotted against the weight of sample used and a linear curve fit (Fig. 1b) was obtained, signifying a near homogeneous distribution of copper complex **1**.⁴²

The absorption spectroscopic behaviour of immobilized catalyst **1a** (dispersed in DMF) is shown in Fig. 2. Catalyst **1a** exhibits two bands in the visible range at 440 nm, which appears as a shoulder, and 730 nm due to phenolate oxygen \rightarrow Cu^{II} ligand-to-metal charge transfer (LMCT) and d–d transitions, respectively. This again demonstrates the immobilization of compound **1** in the mesoporous host. In addition, we have obtained UV-Vis-NIR spectra of complex **1** and immobilized catalyst **1a** in the solid state (Fig. S6, ESI[†]), which also



Fig. 4 Small angle X-ray diffraction patterns of the mesoporous silica host and immobilized complex catalyst 1a.

indicate the successful immobilization of complex **1** in the mesoporous silica matrix.

Small-angle X-ray diffraction patterns of the mesoporous host as well as immobilized catalyst 1a are shown in Fig. 4. In the low angle region $(2\theta \sim 1.5-5^{\circ})$, three characteristic Bragg reflections were observed. These diffraction lines can be indexed by assuming that the materials have hexagonal symmetry. The prominent d_{100} reflection at $2\theta \sim 2.35^{\circ}$ and the less intense d_{110} and d_{200} peaks at $2\theta \sim 3.85^{\circ}$ and $\sim 4.80^{\circ}$, respectively, correspond well to the 2D hexagonally arranged pore structure of the mesoporous silica framework. This confirms the long-range structural ordering of these materials. All of the peaks were well-resolved, which suggests the retention of the highly ordered structure even after the loading of the metal complex. The mesoporous host exhibits a relatively weak additional peak at $2\theta \sim 6.05^{\circ}$, which can be assigned to a d_{210} reflection. In the case of 1a, the weak reflection for d_{210} is suppressed and lost in the background noise.

N₂ sorption isotherms for the mesoporous matrix host and the immobilized catalyst, exhibit typical type IV isotherms with a steep increase that is due to capillary condensations, which are characteristic of mesoporous materials.43 N2 adsorptiondesorption isotherms for the mesoporous silica matrix and catalyst 1a are shown in Fig. 5. The BET surface area and average pore diameter of the 2D hexagonal mesoporous host were 1056 m² g⁻¹ and 2.9 nm, respectively. The Barrett-Joyner-Halenda (BJH) pore-size distribution for this 2Dhexagonal mesoporous material is centered at 2.9 nm, suggesting a very narrow range of pore sizes (Fig. S7, ESI[†]). Adsorption studies were also carried out on immobilized catalyst 1a. The surface area and pore diameter for immobilized catalyst **1a** were found to be 517 m² g⁻¹ and 2.35 nm, respectively. The surface area and pore diameter for catalyst 1a were smaller than those of the mesoporous silica host. The decrease in pore diameter may be attributed to the adherence of the metal centers to the inner walls of the pores. The pore



Fig. 5 N_2 adsorption–desorption isotherms for (a) mesoporous silica material and (b) immobilized complex **1a**.

walls are quite thin, which might help the catalytic sites to be located closer to the surface of the catalyst.

High resolution transmission electron microscopy (HRTEM) images of catalyst **1a** are shown in Fig. 6. Catalyst **1a** features hexagonal porous tubules in an open-ended lamellar type arrangement. When an electron beam falls on the 2-D hexagonal mesoporous silica perpendicular to the pore axis, the pores are seen to be arranged in patches composed of regular rows.^{44,45} A TEM micrograph of **1a** viewed along the pore axis reveals a hexagonal array with channel dimension of \sim 4 nm, which is consistent with the XRD results.

The C, H and N elemental analysis results indicate that complex **1** is immobilised in the mesoporous host as $[CuL_2]$ and that the overall loading of the complex is 8.34 wt%. It seems that the oxygen atoms present in the mesoporous silica matrix form a weak coordination to the copper atom and thus



Fig. 6 HRTEM image of the catalyst **1a**. Inset: Selected area electron diffraction pattern.

hold the copper(II) complex to the inner walls of the matrix. Moreover, complex **1** also contains four uncoordinated amide –NH groups, which can form strong hydrogen bonding interactions with oxygen atoms to prevent leaching of the immobilized complex from HMS. The FT-IR spectrum of immobilized catalyst **1a** exhibits strong broad features around $3500-3000 \text{ cm}^{-1}$, which can be attributed to strong hydrogen bonding interactions. The metal content of the catalyst **1a** was also investigated using EDS (SEM). EDS spectra obtained from different points on the material (Fig. S8, ESI†) confirm the presence of Cu in the mesoporous silica matrix.

Catalytic activity

The aerobic heterogeneous oxidation of alcohols was carried out using the immobilized copper(II) complex (1a) as a catalyst. In order to standardize the reaction conditions, we carried out the catalytic reaction with benzyl alcohol in the presence of various bases and using TEMPO as co-catalyst. Bases such as triethylamine and piperidine gave poor yields (Table 3, entries 1 and 2), whereas in the presence of TEMPO, the reaction gave an excellent yield (Table 3, entry 3). We also carried out the reaction homogeneously, which resulted in a relatively poor yield (Table 3, entry 4) under the same reaction conditions. A blank reaction was conducted without any catalyst under the same experimental conditions and this experiment demonstrated a remarkable decrease (Table 3, entry 5) in the conversion of the substrate. Therefore, we decided to carry out the catalytic reactions heterogeneously using TEMPO as a co-catalyst. In a typical general heterogeneous experiment, a mixture of the alcohol (1 mmol) and TEMPO (0.01 mmol) in 5 cm³ toluene was stirred at 80 °C. After completion of the reaction, the product in the reaction mixture was analyzed using gas chromatography. Products were identified by comparison with known standards. The effects of reaction time and the amount of catalyst used were thoroughly evaluated and benzyl alcohol was chosen as a standard substrate for this purpose. In order to further standardize the reaction conditions, a set of catalytic experiments were carried out using the immobilized catalyst (1a), benzyl alcohol (1 mmol) and TEMPO (1 mol%). The resulting solution was allowed to stir at 80 °C under aerobic conditions and the formation of benzaldehyde was monitored over time (Fig. 7). The conversion of the alcohol to the aldehyde increased with time, up to 16 h, after which no further oxidation was observed. It was also found that the oxidation reaction only provided benzaldehyde and no over-oxidation to benzoic acid was observed. To find out the effect that the amount of catalyst used had on the reaction, a separate set of catalytic reactions were carried out using different amounts of catalyst. The highest conversion of the alcohol was observed in the presence of 20 mg catalyst. Increasing the amount of catalyst further did not improve the yield of the reaction. Therefore, the optimum reaction conditions were 16 h reaction time and the use of 20 mg immobilized catalyst in toluene. A control experiment without either catalyst 1a or TEMPO showed no reaction.

In order to gain an insight into the effect of different starting materials on the yield of aldehyde obtained, various benzylic, allylic, and aliphatic alcohols were used as the starting materials. The results are listed in Table 4. Benzylic



Fig. 7 % Conversion of benzyl alcohol to benzaldehyde over time. (Catalyst used: 20 mg).

alcohols possessing both electron withdrawing and donating groups on the benzene ring, i.e., 4-nitro-, 4-bromo-, 4-methoxy-, and 4-methyl-benzyl alcohol (Table 4, entries 2-5), were oxidized, giving the corresponding aldehydes in high yields. The catalytic TONs obtained from the oxidation of the different benzylic alcohols were found to be moderate. On the other hand, the oxidation of allylic alcohols such as cinnamyl alcohol and 4-bromo cinnamyl alcohol (Table 4, entries 6 and 7) and aliphatic alcohols such as heptanol (Table 4, entry 8) and decanol (Table 4, entry 9) gave poor yields and required much longer reaction times. It can be seen from the proposed mechanism (Scheme S2, ESI[†]) that the alcohol coordinates to the copper(II) centre during the catalytic cycle. As the coordinating ability of aliphatic alcohols is greatly inferior to that of aromatic alcohols, the former show very poor yields even with longer reaction times. We have also carried out the reaction using secondary alcohols, such as 1-phenylethanol (Table 4, entry 10) and cyclohexanol (Table 4, entry 11), but they also exhibit very poor yields. Next, in order to study the selectivity of the reaction, the oxidation of a 1:1 mixture of benzyl alcohol and 1-phenylethanol was investigated. The reaction afforded benzaldehyde and acetophenone in 76% and 1% yields, respectively. It is worth mentioning that our catalyst exhibits very good TONs in contrast to most of the previously reported homogeneous and heterogeneous Cu(II) based catalysts used for the aerobic oxidation of benzylic alcohols, which is a very important factor for industrial viability.

Hot filtration test

In order to verify whether catalyst was leaching from the solid host during the reaction, the liquid phase of the reaction mixture was collected by centrifugation, at reaction temperature, after the oxidation reaction was 40% completed. The corresponding filtrate was then heated again and stirred under air. The reaction did not proceed any further after the filtering catalyst **1a** from the reaction vessel. This result suggests that

Table 4 The catalytic oxidation	n of different alcohols	using catalyst 1a ^a
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Entry	Alcohol	Product	Yield (%)	Time (h)	TON
1	ОН		80	16	432
2	O ₂ N-OH	O ₂ N-	75	20	406
3	Br	Br	79	18	428
4	МеО	MeO	81	16	438
5	Ме	Me	80	16	432
6	ОН	0	40	20	216
7	Вг	Br	35	20	189
8	ОН	~~~~ ⁰	20	24	108
9	ОН	~~~~~¢ ⁰	22	24	120
10	∕Он		5	24	28
11	—ОН	0	2	24	11

^{*a*} Reaction conditions: alcohol (1 mmol), TEMPO (0.01 mmol), catalyst (20 mg) in toleuene. ^{*b*} The number of moles of aldehyde formed per mole of catalyst.

the catalyst was not leaching from the catalyst during oxidation.

Three-phase test⁴⁶

To ascertain if the reactions are truly heterogeneous we performed a three-phase test on the oxidation of benzylic alcohols using a specially designed benzylic alcohol under the usual conditions. During this test, one of the reactants (a benzylic alcohol, namely, 4-hydroxymethylbenzaldehyde) is anchored to the modified surface of Si–HMS. The HMSanchored 4-hydroxymethylbenzaldehyde, HMB–Si–HMS, was prepared according to the method shown in Scheme 1. A solution of benzyl alcohol (1 mmol) and TEMPO (0.01 mmol) was stirred in the presence of immobilized copper catalyst **1a** (0.02 mg) and HMB–Si–HMS (1 g) at 80 °C under aerobic conditions for 16 h. The reaction mixture was collected by centrifugation. The solution was then passed through a 60–120 mesh silica gel column and washed with 10 cm³ toluene. Chlorobenzene was added to the eluent as an internal standard and the products were quantified using GC, which showed that over 75% of the benzyl alcohol had been converted to benzaldehyde, as expected.



Fig. 8 The catalytic activity of catalyst 1a for the oxidation of benzyl alcohol. The activity of the catalyst decreases slightly with the increasing number of catalytic cycles.

The residue obtained from the reaction mixture was then hydrolyzed with 2 N aqueous HCl solution for 3 h under refluxing conditions. The resulting solution was neutralized, extracted with ethyl acetate, concentrated, and the analyzed using GC. The only compound obtained from this process was 4-hydroxymethylbenzaldehyde. The expected oxidation product of 4-hydroxymethylbenzaldehyde, terephthalic aldehyde, was not detected in the extracted liquid. This clearly demonstrates that 4-hydroxymethylbenzaldehyde does not participate in a coupling reaction while anchored to HMS.

Recycling of the catalyst

A significant factor for the industrial viability of a heterogeneous catalytic method is in the ability to easily remove the catalyst from the reaction mixture and reuse it for subsequent reactions until the catalyst is sufficiently deactivated. The recyclability of the immobilized catalyst was examined using the reaction of benzyl alcohol at 80 °C under air, which was completed after 16 h. After the completion of reaction, the catalyst was recovered by centrifugation and then washed thoroughly with DMF followed by dichloromethane. The recovered catalyst was dried under vacuum at 90 °C overnight. The performance of the recycled catalyst in the alcohol oxidation reaction for to four successive cycles is shown in Fig. 8. It can be seen that the catalytic activity of recovered immobilized catalyst **1a** decreases marginally in each successive cycle.

Mechanistic study

In order to gain an insight into the mechanism of the catalytic oxidation of alcohols, the reaction with 1 mmol of benzyl alcohol and 1 mol% TEMPO was monitored spectrophotometerically under a nitrogen atmosphere at room temperature (Fig. 9). A strong MLCT band at 470 nm was generated in the visible region. This charge-transfer band is characteristic of copper(I) complexes. The orange color of the solution was



Fig. 9 Absorption spectra of immobilized catalyst **1a** with benzyl alcohol (---) and immobilized catalyst **1a**, benzyl alcohol and TEMPO (--).

stable under nitrogen, but diminished upon exposure to air. This clearly indicates that the reduction of copper(I) to copper(I) was taking place in the presence of the alcohol and TEMPO, under the inert atmosphere. We also carried out spectrophotometric measurements on a catalyst–benzyl alcohol mixture as well as a catalyst–TEMPO mixture. In both cases the formation of a MLCT band was not observed.

On the basis of the above observation, a mechanism for the catalytic oxidation can be proposed, as shown in Scheme S2 (ESI[†]), which was originally proposed by Sheldon *et al.*^{16a,b} In the proposed mechanistic cycle, the alcohol coordinates to the copper(II) centre. Meanwhile, TEMPO also coordinates to the copper(II) ion in a η^2 fashion. The coordination of TEMPO in its radical form to a Cu(II) center has previously been reported.⁴⁷ Abstraction of an α -hydrogen by the O' of TEMPO then takes place resulting in the formation of a Cu(I) species, TEMPOH and an aldehyde. The copper complex is then regenerated by the TEMPO-mediated oxidation of Cu(I) to Cu(II) after the aerobic oxidation of TEMPOH back to TEMPO.

Conclusion

We have synthesized a mononuclear copper(II) complex (1) using the diamide ligand 2,6-bis[(*N*-phenyl)amido]-4-methylphenol (HL). This complex was successfully immobilized in a mesoporous silica matrix. The immobilized copper complex (1a) was then exploited as a catalyst for the aerobic oxidation of alcohols to aldehydes using TEMPO as a co-catalyst. The conversion of various benzylic alcohols to the corresponding aldehydes occurred in high yields with moderate TONs. This method may also be used for the selective oxidation of primary alcohols in the presence of secondary alcohols. Moreover, the catalyst can be recovered and reused without significant loss of the catalytic activity.

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