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Ethoxysilane appended M(II) complexes and their SiO₂/MCM-41 supported forms

as catalysts for efficient oxidation of secondary alcohols

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ABSTRACT

Divalent transition metal complexes ML₂ (M = Mn 1; Co 2; Cu 3; Zn 4), possessing an ethoxysilane group as a part of the bidentate Schiff base ((*E*)-1-((3-(triethoxysilyl)propylimino)methyl)naphthalen-2ol (L)), have been synthesized. While the copper complex **3** has been isolated in an analytically pure form and characterized by spectroscopic and single crystal XRD studies, the formation of complexes **1**, **2**, and **4** in solution has been verified by ESI mass spectroscopy and subsequently used for further catalyst preparation without their isolation. Treatment of the in situ formed **1-4** with pre-activated silica in boiling toluene produces the catalysts **5-8**, respectively. The copper complex **3** was also treated with MCM-41 in boiling toluene to obtain CuL₂@MCM-41 (**9**). Elemental analysis (CHN), ESI MS, IR, UV-vis., ¹³C & ²⁹Si NMR, EPR, P-XRD, TGA, BET, SEM and TEM have been used to characterize the compounds. Compounds **3** (homogeneous) and **5-9** (heterogeneous) have been utilized as catalysts in the oxidation of secondary alcohols to corresponding carbonyls in the presence of H₂O₂, *t*-BuOOH, and C₆H₅C(CH₃)₂OOH. **3** and **9** have shown better catalytic activity than the rest of the catalysts investigated. Combination of **9** with H₂O₂ is the best catalytic system due to its efficiency and reusability besides being environment friendly.

KEYWORDS: Schiff base, coordination, spectroscopy, heterogeneous catalysis, oxidation, green chemistry

1. Introduction

Owing to the applications of carbonyl compounds as building blocks for drugs, dyes, plastic additives and fine chemicals,¹ their preparation is pivotal in synthetic chemistry. The oxidation of alcohols to carbonyl compounds has been carried out initially by the use of stoichiometric amount of inorganic oxidants such as HNO₃, producing redundant wastes.² Replacement of these oxidants by metal free peroxo oxidants, including hydrogen peroxide (HP), *tert*-butyl hydrogen peroxide (TBHP) and cumene hydroperoxide (CHP) has been well acknowledged in the recent literature.² These attractive oxidants are however ineffective in the absence of catalysts. A variety of catalysts have been reported for alcohol oxidation such as metal oxides,³ layered double hydroxides,⁴ polyoxometalates,^{2g} photocatalyst,⁵ metal complexes of carbenes⁶ and Schiff base complexes.⁷ Schiff base complexes of first row late transition metals are attractive due to their concerted advantages of catalytic activity, low cost and reusability, and well cooperation with the metal free peroxo oxidants.^{2e,7-8}

In the perspective of green chemistry, heterogeneous catalysts are preferred over the corresponding homogenous analogues. Schiff base complexes can be heterogenized by anchoring them on solid supports such as alumina,⁹ graphene,¹⁰ carbon nanotubes,¹¹ synthetic and bio-polymers,¹² zeolite,^{7,13} and montmorillonite clay¹⁴. Among these, great emphasis has been placed on the use of SiO₂ due to its remarkable physical (high surface area, easy availability and, good mechanical and thermal stability) and chemical properties (flexible surface silanol groups) and tunable porosity.¹⁵ Moreover, SiO₂ supported complexes combine the advantages of homogeneous and heterogeneous catalysts as organic-inorganic hybrids.^{15a,16}

Schiff base complexes can be chemically installed on SiO₂ through a suitably designed organic linker. Ethoxysilane compounds ($-Si(OR)_3$), due to their ability to condense effectively with surface -OH groups of SiO₂, are being often employed as linkers.¹⁷ 3- (Aminopropyl)triethoxysilane (APTES) is of particular interest due to its versatile $-NH_2$ group which could form attractive imine bond (showing excellent electron affinity to transition metals) with aldehydes. This imine bond can fix the metal ions firmly onto SiO₂ through coordination (M-N).¹⁸ As it is a chemical adsorption, it could effectively minimize the leaching of metal ions from silica surface and extend the catalyst's reusability further.

Though many imine functionalized SiO₂ supported catalysts have been synthesized using APTES in the literature, ^{15a,16a,18b,19} no model Schiff base complex compound possessing APTES tail has been isolated in analytically pure form, except the Pd(II) complex reported by Bedford et al.^{17a} If such APTES attached Schiff base complexes are isolated and characterized by single crystal XRD, they can be considered as the molecular models for their corresponding SiO₂ supported heterogeneous catalysts. On the other hand, isolating APTES appended Schiff base

complexes is indeed difficult due to hydrolysable ethoxysilane groups,²⁰ as evidenced by the presence of only two reports on isolation of such Schiff base compounds.^{17a}, ^{20b}

Keeping these facts in mind, we have attempted and successfully isolated a new Cu(II) Schiff base complex 3 containing APTES in the present study. Analogous SiO_2 supported complexes (Mn(II) 5, Co(II) 6, Cu(II) 7 and Zn(II) 8) and also MCM-41 anchored Cu(II) complex 9 have been synthesized from the same APTES ligand system. Using these synthesized complexes, we have developed a sufficiently environmental benign catalytic system for the oxidation of secondary alcohols with different metal free peroxo oxidants (HP, TBHP and CHP) in acetonitrile. The details are described in this contribution.

2. Experimental Section

2.1. Materials and methods

APTES, cetyltrimethylammonium bromide (CTAB) and tetraethylorthosilicate (TEOS) were purchased from Sigma Aldrich. 2-Hydroxy-1-napthaldehyde (Fluka) and diphenylmethanol (Loba Chemie) were used as procured. Metal acetates ($Mn(OAc)_2.4H_2O$, $Co(OAc)_2.4H_2O$, $Cu(OAc)_2.H_2O$ and $Zn(OAc)_2.4H_2O$) were purchased from Merck. Mesoporous SiO₂ (MCM-41) was synthesized by following an earlier reported procedure.²¹

Melting point of compound **3** was determined in capillary tube and reported uncorrected. CHN data for **3** was obtained on a Thermo Finnigan (FLASH EA 1112) microanalyzer. IR spectral studies of the KBr diluted compounds were performed on a Perkin Elmer Spectrum One Infrared Spectrometer. Varian Cary Bio 100 and Shimadzu 3600 UV-vis spectrophotometers were used to record solution and solid-state electronic spectra of the compounds, respectively. Bruker 400 and 500 MHz NMR spectrometers were used to obtain ¹H and CP MAS (¹³C and ²⁹Si) NMR spectra, respectively. Mass spectral data of L and **3** were collected using water Q-TOF micro mass spectrometer. Thermal studies of the prepared compounds were carried out in the range of 30-800 °C using Perkin Elmer Pyris Diamond TGA instrument under dynamic N₂ atmosphere. P-XRD analysis was performed on a Philips X'pert Pro (PANAnalytical) diffractometer using Cu-Kα radiation (λ = 1.54190 Å). X-band EPR spectra were analyzed using JEOL FA 200 EPR spectrometer at 100 K. N₂ adsorption-desorption studies of the mesoporous materials were carried out on a Quantachrome Autosorb-1C analyzer.

2.2. Synthesis of L

Ethanolic solution of 2-hydroxy-1-naphthaldehyde was added to APTES (1:1 ratio) and stirred at room temperature (RT) for 8 h. In this reaction, activated type 4A molecular sieve was used to scavenge the water from the reaction because this molecular sieve is sodium

aluminosilicate possessing no surface hydroxyl groups, which can interact with APTES.²² After removing the molecular sieves by filtration, the solvent was removed to obtain a brown viscous / sticky liquid, which was characterized by both NMR and mass spectroscopy. ¹H NMR (400 MHz, CDCl₃): 0.7 (m, 2H, CH₂CH₂CH₂Si); 1.2 (m, 9H, OCH₂CH₃); 1.9 (m, 2H, CH₂CH₂CH₂Si); 3.6 (m, 2H, CH₂CH₂CH₂Si); 3.9 (m, 6H, OCH₂CH₃); 6.9-7.9 (m, 6H, ArH); 8.7 (s, 1H, CH=N); 14.3 (s, 1H, OH). ESI-MS: 375.19 (calculated); 376.19 (M+H]⁺ and 398.19 [M+Na]⁺(found).

2.3. Synthesis of 3

Equimolar (1 mmol) mixture of 2-hydroxy-1-naphthaldehyde and APTES was taken in ethanol in the presence of activated molecular sieves and allowed to stir under RT for 8 h. To the resultant brown solution, 0.5 mmol of Cu(OAc)₂.H₂O was added and stirring was continued for 8 h. After filtration, the obtained mixture was stored at 5 °C for about a week to obtain brown crystals. Yield: 0.698 g (86%). M.p: \approx 230 °C. Anal. Calcd. for C₄₀H₅₆CuN₂O₈Si₂: C, 58.71; H, 7.29; N, 3.67. Found: C, 59.12; H, 6.95; N, 3.45. FT-IR (KBr disc, cm⁻¹): 2962 (s), 2873 (s), 1617 (s), 1463 (s), 1381 (s), 975 (s), 953 (s), 798 (s). ESI-MS: 811.29 (calculated); 812.34 [M+H]⁺ (found).

2.4. Synthesis of 5-9

Equimolar mixture of 2-hydroxy-1-naphthaldehyde and APTES (1 mmol) was taken in ethanol in presence of activated molecular sieves and allowed to stir at RT for 8 h. To the brown solution obtained, 0.5 mmol of $M(OAc)_2.xH_2O$ was added and stirred for 8 h. After removing ethanol under vacuum, toluene was added to the in situ formed complexes 1-4 (M: Mn(II) 1; M: Co(II) 2; M: Cu(II) 3 and M: Zn(II) 4). These toluene solutions were treated under reflux with 1.5 g of pre-activated silica for 48 h. The obtained solid was filtered, washed repeatedly with ethanol and dried at 100 °C to yield 5-8, respectively.

For the synthesis of MCM-41 based catalyst **9**, in situ formed compound **3** was treated with 1.5 g MCM-41. The anchoring and reaction work was carried out as described above for the preparation of **5**-**8**.

2.5. Synthesis of ditolylmethanol

Ditolylmethanol was prepared by following a modified version of the previously reported procedure.²³ Magnesium turnings (1.87 g, 77 mmol) and a pinch of iodine were mixed in THF under N_2 atmosphere followed by the addition of 4-bromotoluene (10.48 g, 59 mmol) at RT and heated (40 °C) for 1 h. After cooling this mixture to RT, ethyl formate (1.95 g, 26.5 mmol) and

THF were added. The obtained solution was kept under heating (40 °C) for 30 mins and overnight stirring at RT. To this, saturated NH₄Cl solution was added and the organic part was extracted with CH₂Cl₂ to get an oily product. Upon trituration with petroleum ether, white crystals of ditolylmethanol was collected. M.p \approx 81 °C. IR (KBr disc, cm⁻¹): 3313 (br); 3100 (w); 3020 (w); 2910 (w); 1495 (s). ¹H NMR (400 MHz, CDCl₃): 7.3 (d, 4H, ArH), 5.8 (d, 1H, JHH=32 Hz, CH(OH)) 7.1 (d, 4H, ArH) 2.3 (s, 6H).

2.6. Procedure for oxidation reactions

A two-necked RB flask equipped with a magnetic bar was charged with 10 ml acetonitrile. To this, alcohol (1 mmol), oxidant (15 mmol) and catalyst (16 mg for **3** and 50 mg for **5**-**9**) were added sequentially. This catalytic mixture was kept under reflux at 60 $^{\circ}$ C until the completion of reaction. The progress of reaction has been monitored by analysing the aliquots of reaction at regular intervals using GC-MS analysis. A Perkin-Elmer gas chromatograph annexed with mass spectrometer (GC-MS CLAURUS 500) was used to analyse the reaction aliquots under the flow of helium carrier gas. The retention time was assigned to the products by comparing with standard values. They were further supported by mass spectrometry. *n*-Decane was used as an internal standard.

2.7. SEM and TEM analyses

Changes in morphology of SiO₂ after chemical modification were studied using a LEO1530 Gemini Scanning Electron Microscope. FEG-SEM images of platinum coated MCM-41 and **9** were obtained on a JEOL JSM-7600 microscope. TEM images of MCM-41 and **9** were taken using Philips CM 200 microscope at 100 kV. Prior to TEM imaging, samples were dispersed in toluene and placed on holey carbon grids.

2.8. Single crystal X-ray diffraction studies

Single crystal X-ray diffraction data of compound **3** were collected on a Rigaku Saturn 724+ CCD diffractometer with a Mo-K α radiation source ($\lambda = 0.71075$ Å) at 120 K under continuous flow of cooled N₂ gas. Rigaku CrystalClear software was used in data integration and indexing. Multi-scan method was employed to correct absorption. WinGX module²⁴ was used for performing all the calculations. The structure was solved by direct methods using SIR-92.²⁵ The final refinement of the structure was carried out using full least-square methods on F² using SHELXL-2014.²⁶ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically as rigid atoms in their idealized locations.

3. Results and Discussion

3.1. Synthesis of compounds L and 1-9



Scheme 1 Synthesis of complexes 1-4

Schiff base ligand (L) was prepared by the condensation of APTES with 2-hydroxy-1naphthaldehyde in ethanol and isolated as a viscous brown liquid. To prepare 1-4, $M(OAc)_{2.x}H_2O$ was directly added to the reaction mixture of APTES and 2-hydroxy-1naphthaldehyde in the presence of activated molecular sieves at RT (Scheme 1). After filtration, solvent was slowly evaporated. In the case of Cu(II) complex 3, the complex could be isolated as brown single crystals. The as synthesized complexes 1-4 were dried under vacuum for extended periods to remove any occluded ethanol. In order to prepare the heterogeneous catalysts 5-9 (Scheme 2 and 3), the dried samples of 1-4 were treated with required amount of SiO₂ (for 5-8) or MCM-41 (for 9) in toluene and subsequently refluxed for 48 h to ensure the maximum condensation of the silica surface hydroxyl groups with the Si-OEt groups of the complexes.



Scheme 2 Anchoring of complexes 1-4 on SiO₂ to produce supported catalysts 5-8.



Scheme 3 Anchoring of copper complex 3 inside MCM-41 to produce catalyst 9

3.2. Single crystal X-ray crystallography

Although several APTES based materials have been reported, the examples of discrete compounds of APTES isolated in pure form are very few due to the easily hydrolysable ethoxy silane groups.^{16b,17a,17b,27} In the present work, we were able to obtain single crystals of **3** through slow evaporation of an ethanol solution of the compound at 5 °C. The ORTEP diagram of the centrosymmetric molecule of **3** is shown in Fig. 1. The asymmetric part of the unit cell contains one independent Cu(II) ion with 50% occupancy (present at the inversion center) and one chelating ligand L⁻. Selected crystallographic data for **3** are summarised in Table 1. The four-coordinate Cu(II) ion adopts square-planar coordination geometry, and is surrounded by *trans* distribution of phenolate oxygen and aldimine nitrogen from two *N*,*O*-chelates of deprotonated ligand L⁻. The average Cu-O and Cu-N distances and O-Cu-N bond angles are similar to those found in analogous systems.²⁸ Further, the naphthalene rings are in the same plane (dihedral angle between both the naphthaldiminato planes is < 1⁰).



Fig. 1 ORTEP diagram of **3** (ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for clarity)

3.3. IR Spectroscopy

IR spectrum of **3** shows the metal-coordinated azomethine (M-N=CH-) stretching at 1617 cm⁻¹ and vibrations of Si-OC₂H₅ at 969, 1072 and 1101 cm⁻¹, respectively. Aromatic and aliphatic –CH vibrations are found in the region of 2900-3050 cm⁻¹ while the aromatic C-C vibrations appear at 1470 and 1545 cm⁻¹. Similarly, the IR spectra of **1**, **2** and **4** have also been recorded prior to their treatment with SiO₂. The spectral characteristics of these complexes are similar to those of **3** (see ESI). SiO₂ and MCM-41 exhibit their characteristic peaks at ≈1090 and 800 cm⁻¹ (anti-symmetric and symmetric stretches of Si–O–Si bond, respectively), 460 cm⁻¹ (bending vibrations of O–Si–O units), 980 cm⁻¹ (Si–OH stretching) and 3450 cm⁻¹ (SiO-H stretch). SiO₂ and MCM-41 supported complexes **5-9** also reveal these peaks along with the characteristic peaks of –CH=N, -CH and -C=C at the respective wavenumbers. This confirms the presence of aromatic functionalities on silica surface as a result of chemical modification.

3.4. UV-visible spectroscopy

Fig. 2 illustrates UV-visible spectrum of **3** in ethanol, showing four different electronic transitions. The π - π^* transition of aromatic ring and the -CH=N unit appears at 230 nm while the n- π^* transition of non-bonded electrons is observed at 305 nm. Ligand to metal charge transfer (LMCT) transition (L-Cu) is found at 380 nm.²⁹ The characteristic d-d transition appears at \approx 650 nm, indicating possible square planar geometry around copper in **3** (d⁹ Cu(II) system), with an unpaired electron of d_x²-_y² ground state.³⁰ These electronic transitions such as π - π^* , n- π^* and charge transfer are invariably present in SiO₂ and MCM-41 supported complexes **5-9**, albeit with

lower intensities (see ESI). The d-d transitions are found at ≈ 510 nm for 5^{31} and at around 650 nm for 6, 7 and 9.^{18d,32}



Fig. 2 UV-visible spectrum of 10^{-5} M solution of **3** in ethanol (inset: d-d transition of **3** at 10^{-3} M concentration)



Fig. 3 a) Solid state CP MAS ¹³C NMR of 8 and b) Solid state CP MAS ²⁹Si NMR of 8

3.5. NMR spectroscopy

For the NMR spectral studies, the diamagnetic Zn(II) complexes **4** and **8** have been examined as model compounds. Unlike in the case of **L**, no –OH resonance has been found in the ¹H NMR spectrum of **4** (see ESI). Besides, noticeable shift is observed for the –CH=N resonance due to complexation. Solid state CP MAS ¹³C and ²⁹Si NMR spectra of **8** are shown in Fig. 3. In the ¹³C NMR spectrum, distinctive resonances for the three carbons of the propyl chain are observed at 43.01 (C₁), 23.67 (C_m) and 10.35 ppm (C_n), respectively. The resonances appearing in the region 105-163 ppm are due to the aromatic carbons (C_{b-j}). The phenolic (C_a) and imine carbons (C_k) resonate at 177.13 and 170.03 ppm, respectively. Additional peaks at 60 ppm are due to residual ethoxy groups.³³ The ²⁹Si NMR spectrum of **8** shows a major peak at -112.61 ppm (a distinctive peak of Q⁴ sites (SiO₄Si)). Appearance of low intensity peaks corresponding to Q³ (-101.71 ppm) (SiO₃Si(OR)) and Q² (-97.20 ppm) (SiO₂Si(OR)₂) sites

indicates a high degree of condensation between ethoxy groups of **4** and surface silanol groups of SiO₂ during the preparation of **8**. Presence of T^2 (-58.82 ppm) (CSi(OSi)₃) and T^3 (-67.01 ppm) (CSi(OSi)₂(OR)) resonances also lend evidence for the high degree of condensation.



Fig. 4 TGA profiles of SiO₂, 5-7, MCM-41 and 9 (inset: TGA profile of 3)

3.6. Thermal Analysis

Thermal analysis of complex 3 and the supported catalysts 5-9 were carried out in the range 30-800 °C at a heating rate of 10 °C/min (Fig. 4). Complex 3 is thermally stable up to 270 °C and then it undergoes decomposition in three different steps: 0-100 °C (3%), 270-290°C (36%) and 290-600°C (39%). First step corresponds to the removal of physically adsorbed water molecules (3%) while second step is assigned to the decomposition of ethoxy silane groups. The final weight loss occurs due to the removal of aromatic moieties. The remaining 22% matches with the expected amount of CuO and SiO₂ residue. To support the identity of the residual compounds, 3 has been bulk pyrolyzed at 800 °C under N2 and subsequently subjected to P-XRD analysis (see ESI).³⁴ The SiO₂ supported complexes 5-7 do not exhibit any sharp decomposition steps as compared to 3. However the weight-loss during thermal analysis of 5-7 may include the elimination of physically adsorbed water molecules and, organic moieties and dehydroxylation of surface silanols. The remnant weight % could be due to the metal oxides and dehyroxylated SiO₂. MCM-41 and catalyst 9 show different TG patterns as compared to those of SiO_2 and 5-7. The percentage of physisorbed water is higher in case of MCM-41 than SiO_2 as this is also evident from the IR studies. The difference between residual amounts (%) of modified and bare forms of SiO₂/MCM-41 supports firm anchoring of 3 on SiO₂/MCM-41. The lowest residue (%) that obtained in case of 9 suggests the effective loading of 3 in MCM-41 than SiO₂.

3.7. EPR Study

To understand the electronic and geometrical properties of the compounds in detail, their X-band (9.427 Hz) EPR spectra were recorded at 100 K under a flow of liquid N₂. EPR spectrum of **3** (Fig. 5a) shows the typical hyperfine structure corresponding to four coordinated (N₂O₂) Cu(II) mononuclear complexes. The anisotropic pattern of **3** reveals four well resolved peaks in the low field region and one intense peak in the high field region (characteristic of Cu(II) system with one unpaired electron). The order of *g* tensor values ($g_{ll}>g_{2}>2.0023$) indicates the presence of unpaired electron in $d_x^2-y^2$ orbital with ²B_{1g} ground state and suggests the square planar geometry. The calculated g_{ll}/A_{II} value (130 cm) further supports this without any appreciable tetrahedral distortion.³⁵ Kivelson and Neiman have reported that g_{ll} value is less than 2.3 for Cu(II) complexes with covalent type of Cu-ligand interactions and accordingly Cu-L interaction is found to be covalent in **3**.³⁶ The exchange coupling factor (G) is calculated from the equation, G=(g_{ll} -2)/(g_{2} -2) to be 3.63. This proves that complex **3** is axial with minimal exchange interaction.^{35b,37}



Fig. 5. EPR spectrum of a) 3 in toluene; Solid state EPR spectra of b) 7 and c) 9 at 100 K.

The solid state EPR spectra of Cu(II) complexes supported SiO₂ and MCM-41 samples 7 and 9 are shown in Fig. 5b and 5c, respectively, while those for 5 and 6 are given in supplementary data (see ESI). EPR spectrum of compound 5 shows a 11 lines pattern at 100 K due to the hyperfine interaction, matching with the spectra of other monomeric Mn(II) complexes (I=5/2).³⁸ EPR spectrum of 5 at RT exhibits a sextet line pattern with $g\approx 2$ and a hyperfine coupling constant of 93.7 G. These parameters further support +2 oxidation state of Mn and presence of Mn(II) species in SiO₂'s surface. The broadness of these signals is due to the distribution of Mn(II) species on SiO₂'s surface which further evidences the heterogeneity around the grafted species as found in the similar hybrid materials.³⁹ The EPR spectrum obtained for 6 is very broad due to the differences in relaxation parameters and spin-spin interaction between Co(II) ions.⁴⁰

As in the case of EPR spectrum of **3**, EPR spectrum (Fig. 5b) of SiO₂ supported Cu(II) catalyst **7** shows axial nature and indicates $d_x^2 - y^2$ ground state ($g_{ll} > g_{\perp} > 2.0023$ and G=4.65). The larger G value is due to the absence of exchange coupling as a result of well dispersion of Cu(II)

centres from each other with appreciable distance. The structural index g_{II}/A_{II} of **7** is 107.4 cm, distinctive of a square-derived geometry. MCM-41 supported Cu(II) catalyst **9** also exhibits EPR pattern (Fig. 5c) similar to **7** with the parameters ($g_{II}>g_{\perp}>$ 2.0023, G=4.46 and $g_{II}/A_{II}=104.22$ cm), suggesting square-derived geometry with $d_x^2 - d_y^2$ ground state. The larger G value supports well dispersion of Cu(II) centers on MCM-41. The larger value of A_{II} for both **7** and **9** may be due to the electrostatic interaction of silica skeleton.⁷ These observations suggest that the geometry of Cu(II) is same in free state (**3**) as well as supported forms (**7** and **9**).

3.8. Surface area measurements

MCM-41 exhibits Type IV isotherm, high BET surface area and large pore diameter analogous to other mesoporous materials.⁴¹ Anchoring of **3** on MCM-41 greatly alters the isotherm pattern of MCM-41 (Fig. 6). BET surface area and pore volume of MCM-41 are found to change after anchoring (Table 2; see ESI). While pure MCM-41 displays pore diameters in the range 1.2-34 nm, **9** exhibits maximum number of pores typically of 1.6 nm diameter. This decrease in pore size could be due to the filling of Cu(II) complex inside the pores of MCM-41. Decrease in surface area of MCM-41 is the evidence for the successful installation of **3** on MCM-41. Partial amorphization of layered phase of MCM-41 during the course of anchoring **3** may also contribute to such decrease.⁴² N₂ sorption studies of SiO₂ and **7** were also carried out (see ESI).



Fig. 6. N₂ adsorption-desorption isotherms of MCM-41 and 9 at 77 K

3.9. Powder XRD (P-XRD) studies

Wide angle P-XRD patterns of SiO_2 , MCM-41 and **5-9** are given in supplementary data (see ESI). They look very similar except for minor variations in the intensity of the peaks.

Compounds **5-8** show peaks with less intensity compared to parent SiO₂ (particularly at $2\theta \approx 20^{\circ}$, characteristic peak of the topological structure of SiO₂), due to the filling of pores or a reduction in X-ray scattering contrast between the channel walls of silicate framework and the organic part. Low angle P-XRD pattern of MCM-41 (Fig. 7) shows the characteristic peaks of its hexagonal ordered mesoporous lattice at $2\theta=2.1^{\circ}$ (100), 3.9° (110) and 4.4° (200).^{18c,43} As compared to MCM-41, the intensity and the positions of these characteristic peaks are significantly changed in case of **9**. This could once again be due to the lowering of local order like variations in wall thickness or reduction of scattering contrast between the channel wall of silicate framework and Schiff base ligand in **9**.^{18b,44}



Fig. 7 Low angle P-XRD patterns of MCM-41 and 9

3.10. SEM and TEM analysis

The changes in surface properties of SiO₂ and MCM-41 after the anchoring of complexes have been investigated by SEM and TEM analyses (Fig. 8 and 9, respectively). Parent SiO₂ surface is found to exhibit relatively smooth surface as compared to 5-7. The elemental mapping images of the catalysts confirm the incorporation of 3 (see ESI). FEG-SEM and TEM images reveal spherical shaped MCM-41 particles (average size 250 nm) with properly arranged mesoporous channels. These mesoporous channels cannot be seen in case of 9 (Fig. 9d) as a result of metal complex anchoring and these anchored particles are visible in the surface of MCM-41.



Fig. 8 SEM images of a) SiO₂, b) 5, c) 6 and d) 7



Fig. 9 a) SEM images of a) MCM-41 (inset: FEG-SEM) and b) 5 (inset: FEG-SEM); TEM images of c) MCM-41 and d) 9

3.11. Catalytic studies

Owing to the industrial and commercial applications of carbonyl compounds, the prepared catalysts **3**, **5**-7 and **9** were utilized in the conversion of secondary alcohols (diphenylmethanol, ditolylmethanol and isopropanol) to corresponding carbonyl compounds in the presence of three different oxidants (H_2O_2 , *t*-BuOOH and $C_6H_5C(CH_3)_2COOH$). According to Corma *et al.*, solvent plays crucial role in catalysis⁴⁵ and we have used acetonitrile as it functioned well both in homogeneous and heterogeneous catalysis.^{15a,19a,46} The reaction temperature was optimized to 60 °C. Both TLC and GC methods were utilized to monitor the progress of the reaction. The results obtained for the catalytic oxidation are summarized in Scheme 4 and Table 3.

 $R \xrightarrow{OH} R \xrightarrow{Catalyst, ROOH} R \xrightarrow{O} R \xrightarrow{O} R$

Scheme 4. Catalytic oxidation of secondary alcohols with peroxides in CH₃CN at 60 °C.

To compare the catalytic activity of homogeneous and similar heterogeneous catalysts, catalytic runs were carried out with **3**, **7** and **9**. Although **3** and **9** exhibit similar catalytic behaviour, the marginally better catalytic activity of **3** is consistent with its complete homogeneity with the substrates in the catalytic mixture. Among the heterogeneous catalysts, **9** has shown better catalytic activity than **7** due to the mesoporosity and high surface area of MCM-41. Catalyst **6** exhibited better catalytic activity than other SiO₂ supported catalysts (**5** and **7**). Irrespective of the catalysts and oxidants, maximum conversion (99%) is quickly reached for isopropanol oxidation, while selectivity has however been found to be similar for all the three substrates. The catalytic activity of present catalysts is comparable to (often better than) the previously reported catalytic systems (see ESI).^{2d,2e,3,5,7,47}

3.11.1. Plausible mechanism



Scheme 5. Schematic showing the formation of pentacoordinated Cu(II)-peroxo complex.

In general, oxidation of organic compounds like alkanes and alcohols with peroxides catalyzed by transition metal complexes follows peroxidative mechanism.⁴⁸ Occurrence of this mechanism can be easily verified by the formation of corresponding peroxo complex. By following the procedure reported earlier,^{48b} one equivalent of **3** was mixed with ten equivalents of H_2O_2 in presence of two equivalent triethylamine using CH₃OH:CH₃CN (1:1) solvent mixture. The formed pentacoordinated peroxo complex (Scheme 5) was characterized by analysing its geometry using UV-vis. spectroscopy (Fig. 10). Below 450 nm, the spectrum looks similar to the parent complex **3** while above 450 nm it looks quite different. The expected LMCT band of HOO-Cu (\approx 370 nm) may be superimposed with that of L-Cu. Instead of showing only one broad d-d transition band at 650 nm, [CuH(L)₂OOH] displays two d-d transition bands at 621 and 740. Bands at 621 and 740 nm are collectively assigned to square pyramidal geometry and an additional shoulder at 700 nm proposes that the metal geometry has undergone distortion.⁴⁹

This implies that the peroxidative mechanism of oxidation of alcohols is operative in the present case. In the first step hydrogen peroxide gets coordinated to the complex, followed by

the abstraction of 'OH radical from the coordinated hydrogen peroxide. This would lead to the formation of the unstable hypervalent $[(L)_2HCu(III)O]$ metal centre. With the addition of another hydrogen peroxide to this Cu(III) centre, peroxo radical ('OOH) is forced to leave the coordination sphere which leads to abstraction of hydrogen radical from alcohol. This leads to regeneration of peroxide and catalyst, and also the formation of ketones (Scheme S1, see ESI).



Fig. 10 UV-vis spectrum showing d-d transitions of [Cu(L)₂OOH] in CH₃OH:CH₃CN (1:1)

3.11.2. Reusability of 7 and 9

The reusability of **7** and **9** was examined over five consecutive catalytic runs under identical reaction conditions. Prior to the next catalytic run, the used catalyst was filtered from the reaction mixture, washed twice with diethyl ether and dried at 100 °C. The immediate loss of conversion percentage (8 and 3% for **7** and **9**, respectively) was observed during the second run due to the leaching of physically adsorbed catalytic sites from SiO₂ and MCM-41. However after second run, no such loss was noted until at least the fifth catalytic run. In fifth run, catalyst **7** and **9** showed 82% and 93% conversion, respectively (Fig. 11). Moreover, it is found that the structural integrity of catalyst has not been changed even after its reuse as evidenced by the IR spectral study (see ESI).



Fig. 11. Reusability of 7 and 9 in diphenylmethanol with H_2O_2 in acetonitrile at 60 °C for 7 and 2 h, respectively

4. Conclusions

We have successfully isolated an ethoxysilane appended Cu(II) complex **3** and anchored it on both SiO₂ and MCM-41. Analogous SiO₂ supported Mn(II), Co(II) and Zn(II) systems were also synthesized. All the new heterogeneous systems have been characterized quite exhaustively using multiple techniques and further employed as catalysts for the oxidation of isopropanol, diphenylmethanol and ditolylmethanol. MCM-41 supported catalyst **9** has shown better catalytic activity than the other catalytic systems investigated. Based on the UV-vis spectroscopic control, a peroxidative mechanism has been proposed. From the catalytic reusability observed, it can be concluded that the catalysts reported here can be effectively used in the repeated catalytic cycles using H_2O_2 as the oxidant.

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Table 1 Crystal data for 3

Table 1	
Crystal data for 3	
Compound	$[Cu(L)_2]$ (3)
Formula	$C_{40}H_{56}CuN_2O_8Si_2$
Formula weight	812.58
Temperature/K	120(2)
Wavelength/Å	0.71075
Crystal system	Monoclinic
Space group	P21/c
a/Å	18.252(4)
b/Å	7.3054(15)
c/Å	17.044(4)
α/ ^o	90
β/ ^o	117.001(4)
$\gamma/^{o}$	90
Volume/Å ³	2024.9(8)
Ζ	2
Density (calculated)/Mgm ⁻³	1.333
Absorption coefficient/mm ⁻¹	0.651
<i>F</i> (000)	962
Reflections collected	14114
R _{int}	0.0375
Data/restraints/parameters	3546/0/242
Goodness-of-fit on F^2	1.070
$R_1, wR_2 [I > 2\sigma(I)]$	0.0371, 0.0989
R_1 , wR_2 [all data]	0.0375, 0.0992

Table 2

Results of N₂ sorption studies of SiO2, 7, MCM-41 and 9

Sample	BET Surface area	Pore volume	Pore size
	(m^2/g)	(cc/g)	(nm)
SiO ₂	155	0.52	1.4
7	86	0.33	1.5
MCM-41	1087	0.6	1.2-3.4
9	81	0.09	1.6

Table 3

Results of alcohol oxidation catalyzed by current catalysts with three different oxidants in acetonitrile at 60 °C

Cat Substrate		Time [h]		Conversion ^d		Yield &				
Cut.	Cat. Substrate	а	b	с	а	b	с	selec	livity	(%)
3		1	1	1	>99	>99	>99	100	100	100
5		6	6	3	>99	>99	>99	100	100	100
6		5	4.5	2.5	>99	>99	>99	100	100	100
7		7	7	4	>99	>99	>99	100	100	100
9		2	1.5	1.5	>99	>99	>99	100	100	100
3		4	2.5	2	>99	>99	>99	100	100	100
5	ᆺᅅᅻᆺ	8	7	5.5	>99	>99	>99	100	100	100
6	ΩÜ	6.5	5.5	5	>99	>99	>99	100	100	100
7		10	8.5	7	>99	>99	>99	100	100	100
9		5	3.5	3	>99	>99	>99	100	100	100
3		0.5	0.5	0.5	>99	>99	>99	100	100	100
5	<u></u> он	3.5	3	2	>99	>99	>99	100	100	100
6		3	1.5	1	>99	>99	>99	100	100	100
7		4	3	2.5	>99	>99	>99	100	100	100
9		1	0.5	0.5	>99	>99	>99	100	100	100

Reaction conditions: catalyst (¹16 mg and ²⁻⁶50 mg), substrate (1mmol) oxidant (15 mmol), solvent (CH₃CN, 10 ml) ^aH₂O₂; ^b*t*-BuOOH; ^cC₆H₅C(CH₃)₂OOH; ^d Analysed by GC Note: No notable conversion was obtained either in the absence of catalyst and oxidant

R^MR RMANUS 20

Graphical Abstract

Highlights

- A new Cu(II) square planar complex possessing ethoxysilane tail has been isolated.
- SiO₂ supported Mn(II), Cu(II), Co(II) and Zn(II) catalysts have been synthesized and characterized.

Acceleration

• The synthesized catalysts are found to be useful in catalyzing secondary alcohol oxidation.