

Oxidation of Ethylbenzene in the Presence of an MCM-41-Supported or Ionic Liquid-Standing Bischlorocopper(II) Complex

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Abstract A CuCl_2 complex with a pyridyl-ethanimine ligand has been prepared and examined as a catalyst for the oxidation of ethylbenzene with *tert*-butyl hydroperoxide at 30 °C, using acetonitrile or the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate as solvent. A heterogenised version of the complex based on a chemically modified ordered mesoporous silica is described.

Keywords Copper(II) · Ethylbenzene · Acetophenone · Catalytic oxidation · MCM-41 · Ionic liquids

1 Introduction

Acetophenone (PhCOMe) is commercially used in the production of perfumes, drugs, pharmaceuticals and resins, and may be obtained by the partial oxidation of ethylbenzene (PhEt) in the liquid phase, using an appropriate catalyst [1]. The primary industrial method involves the oxidation of PhEt using cobalt salts as homogeneous catalysts (e.g., cobalt acetate or cobalt cycloalkancarboxylate), manganese and/or bromide species as promoters,

acetic acid as solvent, and molecular oxygen or air as the oxidant [2]. This method suffers from several disadvantages, which include the corrosive nature of acetic acid, difficulty in solvent and catalyst recovery, and explosion hazards associated with the solvent and dioxygen. Considerable research has therefore focused on finding not only more efficient catalysts but also alternative solvents and oxidants. Interesting results have been reported for copper complexes combined with *tert*-butyl hydroperoxide (TBHP) as oxidant and acetonitrile as solvent [3–11], giving PhCOMe yields in the range of 40–60% (for reaction temperatures of 60–70 °C, except 25 °C in ref. [10], and reaction times of 6–24 h) and PhCOMe selectivity above 84%. The replacement of acetonitrile as a reaction solvent would be an important development, given its flammability and toxicity. Surprisingly, only a few papers have dealt with the use of ionic liquids (ILs) as solvents for the oxidation of PhEt [12, 13], despite the intensive research that has been carried out in the last decade in the area of catalysed oxidations in ILs [14]. ILs are potential “green” alternatives to volatile organic solvents, with the added advantage of facile catalyst and solvent recycling. Seddon and Stark [12] reported that the $\text{Co}(\text{acac})_2$ catalysed oxidation of PhEt in 1-hexyl-2,3-dimethylimidazolium tetrafluoroborate ($[\text{C}_6\text{dmim}]\text{BF}_4$) in the presence of perfluorohexane (added to concentrate the dissolved oxygen) gave PhCOMe as the only product with 25% yield within 24 h at 80 °C and 1 atm of O_2 . More recently Shaabani et al. [13] reported a PhCOMe yield of 77% within 7 h at 100 °C and 1 atm of O_2 using a cobalt(II) phthalocyanine complex as a catalyst in 1-butyl-3-methylimidazolium bromide ($[\text{C}_4\text{mim}]\text{Br}$) as the solvent.

A more common approach to improving the recyclability of homogeneous transition metal catalysts by immobilisation is the heterogenisation of molecular

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catalysts onto insoluble inorganic, organic or hybrid inorganic–organic supports [15, 16]. The challenge is to make a heterogeneous catalyst that is resistant to leaching of active species and exhibits the same properties and kinetics obtainable from the homogeneous system. With respect to the literature cited above for the copper-catalysed oxidation of PhEt, several of the papers deal with the immobilisation of the complexes onto a support, namely zeolite Y encapsulated Cu^{II} complexes of 9-, 12-, 14- and 16-membered tri- and tetraaza macrocyclic ligands [5–8], a Cu^{II} salen complex anchored on modified carbon nanotubes [9], a layered double hydroxide intercalated Cu^{II} complex of 2,2'-bipyridine-5,5'-dicarboxylate [10], and polymer anchored Cu^{II} complexes of 2-(α -hydroxymethyl)benzimidazole [11]. In several cases the catalytic performance of the supported materials (activity and selectivity to PhCOME) matched or even surpassed that of the unbound (“neat”) or model complexes, and the materials could be easily recovered and reused without loss of activity. For these catalysts, the reported PhCOME yields fall in the broad range of 7–56%, and PhCOME selectivities are higher (above 96%) than those reported for the homogeneous copper catalysts [5–11].

In the present work, a CuCl₂ complex with a pyridyl-ethanimine ligand has been prepared and examined as a catalyst for the oxidation of PhEt with TBHP at room temperature, using acetonitrile or the ionic liquid [C₄mim]PF₆ as solvent. The catalytic performance of a heterogenised version of this complex based on a chemically modified ordered mesoporous silica is also described.

2 Experimental

2.1 Materials and Methods

Microanalyses for CHN were performed at the University of Aveiro (M.M. Marques). The copper loadings were determined by ICP-OES at the Central Laboratory for Analysis, University of Aveiro (L. Carvalho). Room-temperature powder XRD data were collected on a Philips X'pert diffractometer with a curved graphite monochromator (Cu K α radiation) and a flat plate sample holder, in a Bragg–Brentano para-focusing optics configuration (40 kV, 50 mA). Samples were step-scanned in 0.02° 2 θ steps with a counting time of 2 s per step. Nitrogen adsorption isotherms at –196 °C were measured using a Gemini 2375 Micromeritics Instrument (Eng. M.C. Costa, University of Aveiro). The mesostructured materials were pre-treated at 120 °C prior to analysis. Transmission FT-IR spectra (KBr pellets) were measured on a Mattson 7000 FT-IR spectrometer with 2 cm^{–1} resolution. Attenuated total reflectance (ATR) FT-IR spectra were measured on

the same instrument equipped with a Specac Golden Gate Mk II ATR accessory having a diamond top-plate and KRS-5 focusing lenses with 4 cm^{–1} resolution. ¹H NMR spectra were measured in solution using a Bruker CXP 300 spectrometer. Solid-state NMR spectra were recorded at 79.49 MHz for ²⁹Si and 100.62/125.76 MHz for ¹³C on Bruker Avance 400/500 spectrometers. ²⁹Si magic angle spinning (MAS) NMR spectra were recorded with 40° pulses, a spinning rate of 5.0 kHz and 60 s recycle delays. ²⁹Si cross-polarisation (CP) MAS NMR spectra were recorded at 5 kHz with 4.25 μ s ¹H 90° pulses, 8 ms contact time, and 5 s recycle delays, and at 9 kHz with 3.4 μ s ¹H 90° pulses, 1.5 ms contact time, and 5 s recycle delays. ¹³C CP MAS NMR spectra were acquired with a 3.5 μ s 90° proton pulse and 2 ms contact time with spinning rates of 7–8.5 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane.

All air-sensitive operations were carried out using standard Schlenk techniques under nitrogen. Toluene (Scharlau, anhydrous 99.8%), dichloromethane (Sigma-Aldrich, dried, \geq 99.8%), ethanol (Panreac), 2-acetylpyridine (Aldrich, \geq 99%), propylamine (Aldrich, 98%) and 3-aminopropyltriethoxysilane (Aldrich, 97%) were purchased from commercial sources and used as received. CuCl₂·2H₂O was purchased from Riedel-de Haën and dehydrated under vacuum for several hours prior to use. Purely siliceous MCM-41 was synthesised hydrothermally at 80 °C for 5 days in a 1 L PTFE bottle under basic conditions [17]. [(C₁₄H₂₉)NMe₃]Br was used as the templating agent and sodium silicate solution as the silica source [18]. The calcined product (540 °C/6 h) was dehydrated prior to use by heating at 180 °C for 2 h under vacuum. Powder XRD (hkl in parentheses): 2 θ (°) = 2.43 (100), 4.23 (110), 4.89 (200), 6.44 (210); $a = 2d_{100}/\sqrt{3} = 41.94$ Å.

2.2 Synthesis

2.2.1 *N*-(*n*-Propyl)-1-(2-pyridyl)ethanimine (L)

The following procedure was adapted from the one described by Haddleton et al. [19, 20]. Propylamine (1.83 g, 0.03 mol) was added to a solution of 2-acetylpyridine (2.5 g, 0.02 mol) in toluene (50 mL), and the mixture was refluxed for 48 h. After this time, the solvent and excess amine were removed by evaporation under reduced pressure. The FT-IR spectrum of the resultant residue showed that there was still some unreacted 2-acetylpyridine. More propylamine was added (1.44 g, 0.024 mol) and the solution was stirred under reflux for a further 48 h. After removing the solvent and excess amine, FT-IR analysis of the product confirmed that all of the 2-acetylpyridine had reacted. ATR FT-IR (cm^{–1}):

$\nu = 3054\text{w}, 2959\text{m}, 2930\text{m}, 2898\text{sh}, 2871\text{m}, 1638\text{s} (\text{C}=\text{N}), 1585\text{s}, 1564\text{s}, 1465\text{s}, 1433\text{s}, 1375\text{sh}, 1356\text{w}, 1340\text{sh}, 1299\text{m}, 1285\text{w}, 1242\text{m}, 1146\text{w}, 1097\text{w}, 1086\text{sh}, 1043\text{m}, 992\text{m}, 963\text{w}, 922\text{w}, 897\text{m}, 781\text{vs}, 743\text{s}, 637\text{w}, 618\text{s}, 575\text{s}, 514\text{w}, 404\text{s}, 367\text{w}, 354\text{w}, 321\text{w}$. ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 8.58\text{--}8.57$ (m, 1H), 8.09–8.06 (m, 1H), 7.70 (dt, $J = 1.6, 7.7$ Hz, 1H), 7.27 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H), 3.49 (t, $J = 7.1$ Hz, 2H), 2.36 (s, 3H), 1.85–1.73 (m, 2H), 1.03 (t, $J = 7.4$ Hz, 3H).

2.2.2 [N-(n-Propyl)-1-(2-pyridyl)ethanimine]copper(II) chloride ($\text{Cu}(\text{L})\text{Cl}_2$) (**1**)

Complex **1** was prepared by following the procedure described previously for $[\text{Cu}(2,2'\text{-bipyridine})\text{Cl}_2]$ [21], except that ethanol was used as the solvent instead of a mixture of ethanol and methanol, and a 10% excess of CuCl_2 was used. Yield: 3.17 g, 52%. Anal. calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Cl}_2\text{Cu}$ (296.68): C, 40.5; H, 4.75; N, 9.45. Found: C, 40.25; H, 4.75; N, 9.4. FT-IR (KBr, cm^{-1}): $\nu = 3435\text{br}, 3098\text{w}, 3069\text{w}, 3029\text{w}, 2958\text{m}, 2944\text{w}, 2875\text{w}, 1630\text{s} (\text{C}=\text{N}), 1597\text{vs}, 1571\text{m}, 1475\text{w}, 1463\text{w}, 1441\text{m}, 1426\text{w}, 1375\text{s}, 1326\text{s}, 1305\text{m}, 1263\text{m}, 1247\text{w}, 1203\text{sh}, 1164\text{s}, 1138\text{w}, 1105\text{m}, 1048\text{m}, 1021\text{vs}, 976\text{w}, 945\text{w}, 914\text{w}, 882\text{w}, 783\text{vs}, 753\text{m}, 674\text{w}, 645\text{m}, 591\text{s}, 539\text{w}, 473\text{w}, 458\text{w}, 415\text{m}, 351\text{w}, 324\text{m}$.

2.2.3 MCM-41 Grafted with Aminopropylsilyl Groups (MCM-41-APS)

A mixture of MCM-41 (6.0 g), 3-aminopropyltriethoxysilane (6.36 mL, 0.027 mol) and toluene (50 mL) was stirred for 24 h under reflux. After filtering off the solution the colourless solid was washed several times with toluene and vacuum-dried at 100 °C for several hours. Elemental analysis found: C, 8.1; H, 2.70; N, 2.0%. FT-IR (KBr, cm^{-1}): 3419br, 3325sh, 2948sh, 1639m, 1544m, 1470w, 1449w, 1412sh, 1161s, 1077s, 957w, 796s, 687w, 555sh, 462s. ^{13}C CP MAS NMR: $\delta = 56.9$ (CH_3CH_2), 42.2 (CH_2NH_2), 21.8 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 15.8 (CH_3CH_2), 9.4 (CH_2Si). ^{29}Si MAS NMR: $\delta = -110.2$ (Q^4) ($\text{Q}^n = \text{Si}(\text{O}-\text{Si})_n(\text{OH})_{4-n}$). ^{29}Si CP MAS NMR: $\delta = -59.5$ (T^2), -66.5 (T^3), -110.0 (Q^4) ($\text{T}^m = \text{RSi}(\text{OSi})_m(\text{OEt})_{3-m}$).

2.2.4 MCM-41 Functionalised with a Pyridyl-imine Ligand (MCM-41-L)

Following the procedure described by Shamim et al. [22], 2-acetylpyridine (1.27 mL, 0.011 mol) was added dropwise to a suspension of MCM-41-APS (4.06 g) in toluene (50 mL), and the mixture was stirred under reflux for 1 week. The resultant light brown powder was filtered,

washed several times with toluene and CH_2Cl_2 , and vacuum-dried at room temperature. FT-IR (KBr, cm^{-1}): 3434br, 1637m, 1598sh, 1569w, 1473w, 1437w, 1411sh, 1234s, 1153sh, 1083vs, 962w, 793m, 752w, 696w, 565w, 460s. ^{13}C CP MAS NMR: $\delta = 164.8$ ($\text{C}=\text{N}$), 155.0 (py-C), 148.3 (py-C), 136.9 (py-C), 122.0 (py-C), 58.7 (CH_3CH_2), 49.3 ($\text{CH}_2\text{N}=\text{C}$), 41.6 (CH_2NH_2), 28.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{N}=\text{C}$), 21.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 16.8 (CH_3), 8.9 (CH_2Si). ^{29}Si MAS NMR: $\delta = -109.2$ (Q^4). ^{29}Si CP MAS NMR: $\delta = -60.0$ (T^2), -66.3 (T^3), -101.1 (Q^3), -108.9 (Q^4).

2.2.5 Immobilisation of CuCl_2 (MCM-41-L/ CuCl_2)

CuCl_2 (0.62 g, 4.6 mmol) was added to a suspension of MCM-41-L (1.5 g) in ethanol (40 mL) under nitrogen, and the mixture was stirred for 12 h at room temperature. The brown solid was filtered off, washed several times with ethanol and vacuum-dried. FT-IR (KBr, cm^{-1}): 3396br, 1631s, 1609sh, 1572w, 1535w, 1478w, 1433w, 1235s, 1156sh, 1085vs, 958w, 793m, 695w, 557sh, 459s.

2.3 Catalytic Studies

The liquid-phase catalytic oxidation of ethylbenzene was carried out at 30 °C, using 70% aqueous TBHP (Sigma-Aldrich, denoted TBHPaq), 5–6 M TBHP in decane (Sigma-Aldrich, denoted TBHPdec) or 30% aqueous H_2O_2 (Panreac, denoted $\text{H}_2\text{O}_2\text{aq}$), in batch mode. TBHPdec and acetonitrile were pre-dried using activated molecular sieves (4 Å), while the ionic liquid $[\text{C}_4\text{mim}]\text{PF}_6$ was pre-dried under vacuum for 2 h at 100 °C. All of the reactions were carried out under air (autogenous pressure) and stirred magnetically in a closed borosilicate 5 mL reaction vessel immersed in a thermostated water bath. Typically, the micro reactor was loaded with 17 μmol of copper, 1.9 mmol of substrate, 3.8 mmol of oxidant and solvent. The solvent was a $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (4.2 v/v) mixture when TBHPaq or $\text{H}_2\text{O}_2\text{aq}$ were used (to ensure that only one liquid phase was formed), or only CH_3CN for TBHPdec, with a total reaction volume fixed at 2.5 mL for all experiments. For complex **1** additional catalytic tests were performed under biphasic liquid–liquid conditions using $[\text{C}_4\text{mim}]\text{PF}_6$ (150 μL). The course of the reactions was monitored using a Varian 3800 GC equipped with a DB-5 (J&W scientific) capillary column (30 m \times 0.25 mm; 0.25 μm) and a flame ionisation detector, using H_2 as the carrier gas. The reaction products were identified by GC–MS (Trace GC 2000 Series (Thermo Quest CE Instruments)—DSQ II (Thermo Scientific), equipped with a fused silica capillary DB-5 type column (30 m \times 0.25 mm; 0.25 μm film thickness)), using He as the carrier gas.

3 Results and Discussion

3.1 Catalyst Preparation and Characterisation

The ligand *N*-(*n*-propyl)-1-(2-pyridyl)ethanimine (L) was prepared from the condensation of 2-acetylpyridine with propylamine. The ^1H NMR and FT-IR spectra of L were in agreement with published data [19, 20]. A similar method was used to functionalise the ordered mesoporous silica MCM-41 with pyridyl-ethanimine groups (Scheme 1). Thus, treatment of calcined and dehydrated MCM-41 with a refluxing solution of 3-aminopropyltriethoxysilane in toluene gave surface-bound aminopropylsilyl (APS) groups at a loading of 1.42 mmol g^{-1} (based on the nitrogen content of 2.0%). The C/N molar ratio of 4.7 for MCM-41-APS suggests that, on average, the APS groups were anchored through two Si–O–Si bonds, leaving one residual SiOEt group (theoretical C/N = 5). Treatment of MCM-41-APS with a refluxing solution of 2-acetylpyridine in toluene gave the ligand-silica MCM-41-L. Elemental analysis revealed a carbon content of 15.1% and a C/N molar ratio of 5.6 (Table 1), which are lower than the theoretical values of 17.5% and 5.8 (calculated on the basis of the initial C and N contents in MCM-41-APS, and assuming complete conversion of the surface-bound APS groups to the desired pyridyl-ethanimine). For 75% conversion of APS groups the theoretical C and N contents are 15.4 and 3.15% (Table 1), respectively (C/N = 5.7), which are in agreement with the observed values of 15.1 and 3.15%.

The ligand-silica MCM-41-L was further characterised by nitrogen adsorption at $-196\text{ }^\circ\text{C}$, IR spectroscopy, and ^{13}C and ^{29}Si MAS NMR spectroscopy. The purely siliceous

MCM-41 starting material exhibited a type IV nitrogen adsorption isotherm (characteristic of mesoporous solids) and possessed fairly high S_{BET} and V_p values of $884\text{ m}^2\text{ g}^{-1}$ and $0.78\text{ cm}^3\text{ g}^{-1}$, and a narrow pore size distribution curve with a maximum (d_p) at 3.3 nm width (Table 1). After grafting of APS groups and treatment with 2-acetylpyridine to give MCM-41-L, the S_{BET} , V_p and d_p values decreased to $428\text{ m}^2\text{ g}^{-1}$, $0.31\text{ cm}^3\text{ g}^{-1}$ and 2.4 nm. The FT-IR spectrum of MCM-41-L exhibited weak bands at 1,569 and $1,598\text{ cm}^{-1}$, assigned to pyridine ring stretching vibrations. A band with medium intensity at $1,637\text{ cm}^{-1}$ is attributed to overlapping C=N stretching (from the imine group) and water (adsorbed from the atmosphere) bending modes (Table 1). The presence of pyridyl-ethanimine groups in MCM-41-L was confirmed by ^{13}C CP MAS NMR spectroscopy. MCM-41-APS exhibits five peaks between 0 and 60 ppm that are readily assigned to the carbon atoms of the propyl and residual ethoxy groups (Fig. 1A). The same five resonances are observed for MCM-41-L, which seems to confirm the elemental analysis results indicating that not all of the aminopropyl groups were converted to the pyridyl-ethanimine ligand. New peaks at 28.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{N}=\text{C}$), 49.3 ($\text{CH}_2\text{N}=\text{C}$), 120–155 (pyridyl ring carbons) and 164.8 ppm (C=N) are assigned to anchored *N*-(*n*-propyl)-1-(2-pyridyl)ethanimine groups. The derivatisation of the MCM-41 surface was also followed by ^{29}Si MAS NMR spectroscopy (Fig. 1B). Unmodified MCM-41 displays two broad overlapping resonances in the ^{29}Si CP MAS NMR spectrum at -100.8 and -111.1 ppm, which are due to $\text{Si}(\text{OSi})_3(\text{OH})$ (Q^3) and $\text{Si}(\text{OSi})_4$ (Q^4) species of the silica walls. A weak shoulder is observed at -91.9 ppm for geminal silandiol species, $\text{Si}(\text{OSi})_2(\text{OH})_2$ (Q^2). For the modified material MCM-41-APS, two additional signals

Scheme 1 Preparation of complex **1** and MCM-41-L/ CuCl_2

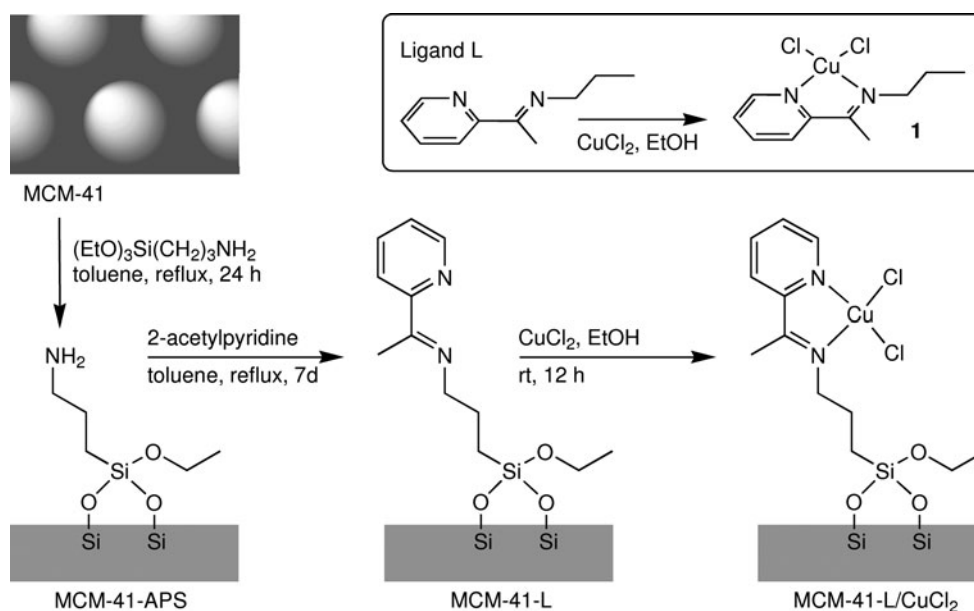


Table 1 Physicochemical properties of the prepared materials

Sample	EA calcd ^a /found (%)	S _{BET} ^b (m ² g ⁻¹)	V _p ^c (cm ³ g ⁻¹)	d _p ^d (nm)	FT-IR main features (cm ⁻¹)
MCM-41	–	884	0.78	3.3	–
MCM-41-L	C, 15.4/15.1 N, 3.15/3.15	428	0.31	2.4	1637 ^e , 1598 ^f , 1569 ^f
MCM-41-L/CuCl ₂	C, 11.8/11.7 N, 2.57/2.45 Cu, 3.9/4.1	195	0.18	2.4	1631 ^e , 1609 ^f , 1572 ^f

^a The calculated values correspond to the following scenarios: for MCM-41-L, 75% conversion of the surface-bound APS groups in MCM-41-APS to the desired pyridyl-ethanimine; for MCM-41-L/CuCl₂, one-third of the pyridyl-ethanimine groups in MCM-41-L revert back to APS groups during immobilisation of CuCl₂, with all remaining pyridyl-ethanimine groups complexing with CuCl₂, ^b BET specific surface area, ^c total pore volume, ^d maximum of the pore size distribution curve, ^e assigned to C=N stretching vibration, ^f assigned to pyridine ring stretching vibrations

appear at -59.5 ppm ($T^2 = RSi(OSi)_2(OEt)$) and -66.5 ppm ($T^3 = RSi(OSi)_3$) for the organosilica species, with the former bipodally anchored species being dominant (consistent with the elemental analysis data). The derivatisation of surface silanol groups is confirmed by the reduction of the Q^3 and Q^2 resonances relative to the Q^4 resonance. The spectra for MCM-41-APS and MCM-41-L are quite similar except that the latter shows a slight increase in the relative intensity of the T^3 resonance, which indicates that the relative proportion of tripodally anchored species may have increased during exposure of MCM-41-APS to the refluxing solution of 2-acetylpyridine in toluene.

The ligand *N*-(*n*-propyl)-1-(2-pyridyl)ethanimine (L) and the ligand-silica MCM-41-L were subsequently treated with CuCl₂ in ethanol to give the copper-containing catalysts Cu(L)Cl₂ (**1**) and MCM-41-L/CuCl₂. CHN microanalyses for **1** were consistent with the expected formula. Complexation of the ligand L with CuCl₂ resulted in a shift of the infrared C=N stretching vibration from 1,638 to 1,630 cm⁻¹, while the pyridine ring stretching vibrations shifted from 1,564 and 1,585 cm⁻¹ to 1,571 and 1,597 cm⁻¹. The elemental analysis data for MCM-41-L/CuCl₂ indicate that during the immobilisation of CuCl₂ approximately one-third of the pyridyl-ethanimine groups fragmented (possibly by reaction with residual water) to give surface-bound APS groups and free 2-acetylpyridine (removed during the washing procedure), such that the molar ratio between surface-bound pyridyl-ethanimine groups and APS groups changed from about 3:1 to 1:1. Assuming that all remaining pyridyl-ethanimine groups complexed with CuCl₂, the calculated analyses for MCM-41-L/CuCl₂ are 11.8% C, 2.57% N and 3.9% Cu, which are close to the found values of 11.7% C, 2.45% N and 4.1% Cu (Table 1). Despite the significant loss of organic ligand, the inclusion of CuCl₂ led to considerably lower S_{BET} (195 m² g⁻¹) and V_p (0.18 cm³ g⁻¹) values, although d_p (2.4 nm) remained unchanged. The changes in the textural properties (Table 1) may be due to partial pore blockage

caused by complexation reactions taking place at the pore entrances. Concerning the FT-IR spectra, as found for complex **1** the immobilisation of CuCl₂ in MCM-41-L resulted in a shift of the C=N stretching vibration to lower frequency, while the pyridine ring stretching vibrations shifted to higher frequency (Table 1).

3.2 Catalysis Studies

The catalytic performance of MCM-41-L/CuCl₂ was investigated in the oxidation of PhEt at 30 °C with TBHP (in decane, TBHPdec) as oxidant and acetonitrile as solvent. The reaction of PhEt did not take place throughout 48 h when carried out (i) in the presence of MCM-41-L (without copper) and with TBHP, or (ii) in the presence of MCM-41-L/CuCl₂ and without TBHP. Hence, both the copper catalyst and TBHP are required for the catalytic oxidation of PhEt. The reaction of PhEt with TBHPdec in the presence of MCM-41-L/CuCl₂ gave PhCOME as the major product in 28%/44% yield at 6 h/24 h (29%/45% conversion) (Table 2). *tert*-Butyl 1-phenylethyl peroxide (PhCH(OO*t*Bu)Me) was a minor product formed in less than 1% yield. These catalytic results for the first run compare favourably with those obtained for previously investigated copper complexes supported on zeolite Y [6], carbon nanotubes [9] and layered double hydroxides [10]. However, more promising results have been reported for some supported transition metal complexes, using TBHP, O₂ or H₂O₂ as oxidants: PhCOME yields greater than 85% using TBHP or O₂ [23, 24], and PhCOME yields of up to ca. 40% using H₂O₂ [11, 25], under different reaction conditions.

The related model complex Cu(L)Cl₂ (**1**), used under similar reaction conditions (same initial molar ratios of PhEt:TBHP:Cu), exhibited inferior catalytic performance to the MCM-41-supported complex, giving PhCOME in 21%/22% yield at 6 h/48 h and PhCH(OO*t*Bu)Me as a by-product (Table 2); the turnover number (TON)

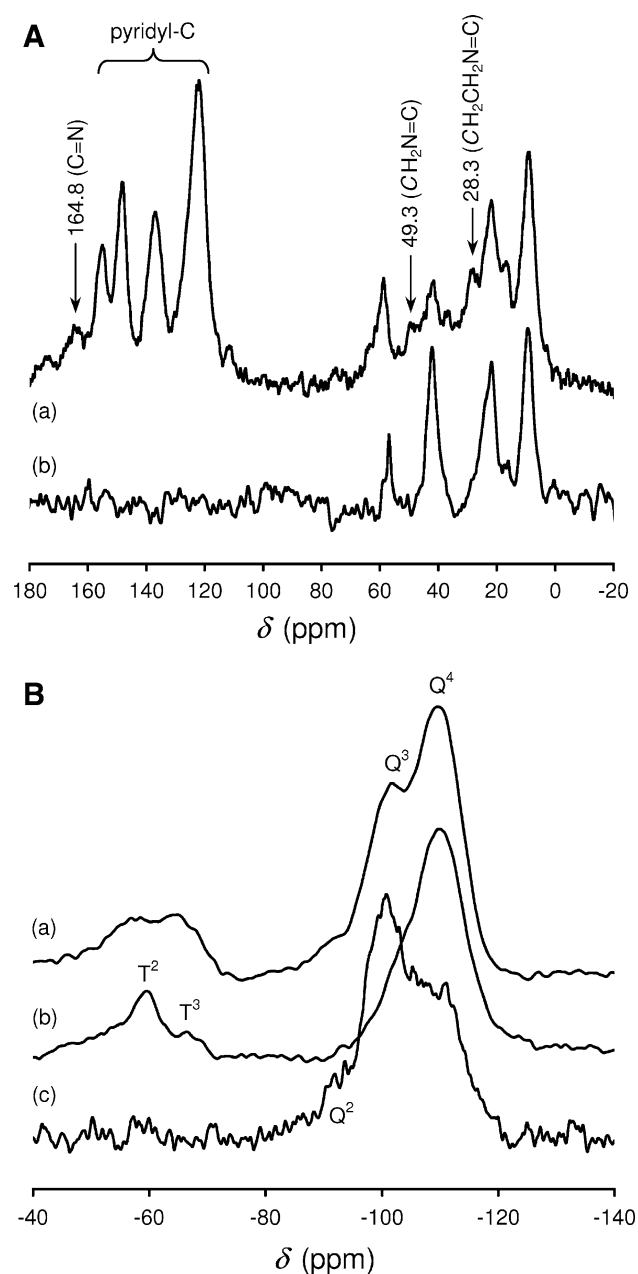
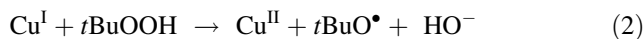
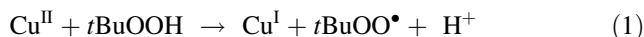


Fig. 1 ^{13}C (A) and ^{29}Si (B) CP MAS NMR spectra of (a) MCM-41-L, (b) MCM-41-APS and (c) MCM-41. Selected ^{13}C resonances due to the supported pyridyl-imine ligand (a) are identified in A

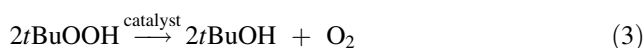
calculated at 24 h reaction is lower for **1** compared to MCM-41-L/CuCl₂ (27 and 50 mol mol_{Cu}⁻¹, respectively). The formation of PhCH(OO*t*Bu)Me as a by-product of the reaction of PhEt has been reported for copper(I) complexes used as catalysts, under N₂ atmosphere, at 25 °C; performing the reaction of PhEt under an oxygen atmosphere significantly enhanced PhCOMe yield and selectivity [26].

For the bulk and supported catalysts, the catalytic results were not affected by the presence of visible light, indicating that photo-induced reaction pathways may be

neglected. The addition of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol to the reaction system completely inhibited the reaction of PhEt, indicating that a free radical chain mechanism is involved. Hence, copper species are responsible for the initiation steps, which are probably one-electron redox processes according to Eqs. 1 and 2 [27].



The kinetic profiles for Cu(L)Cl₂ (**1**) and MCM-41-L/CuCl₂ reach plateaus within 4 and 6–24 h reaction, respectively (Figs. 2, 3). A possible reason for the slowing down of the reaction of PhEt is the copper-catalysed “non-productive” decomposition of TBHPdec into molecular oxygen and *tert*-butanol according to the overall Eq. 3:



This possibility was checked by (i) performing iodometric titration for the reaction of the catalyst with TBHPdec, and (ii) re-charging the micro-reactor with TBHPdec (in half the amount added initially) at 4 h and further monitoring the reaction of PhEt. The first test for **1** gave 96% TBHPdec decomposition within 6 h reaction, whereas for MCM-41-L/CuCl₂ TBHPdec decomposition at 6 h/24 h reaction was 74%/92%; no TBHPdec decomposition was observed for MCM-41-L. The higher catalytic activity of **1** for the “non-productive” decomposition TBHPdec in comparison to that of MCM-41-L/CuCl₂ correlates with the more drastic slowing down of the reaction of PhEt in the former case. Similar results were reported previously for the complex Cu(2,2'-bipyridine)Cl₂ and a heterogenised version of this complex in a layered double hydroxide (i.e., the oxidant decomposition was less extensive for the supported catalyst) [10]. For the bulk and supported catalysts, test (ii) showed that the reaction continued after addition of more TBHPdec, achieving 50 and 70% conversion at 48 h for **1** and MCM-41-L/CuCl₂, respectively (Figs. 2, 3), with PhCOMe being the main product (48 and 69% yield, respectively). Hence, it seems that the reaction of PhEt eventually slows down because TBHPdec is decomposed faster than PhEt is oxidised, becoming a limiting reagent. Since the reaction of PhEt without TBHP, under air atmosphere, in the presence of the copper catalysts did not take place throughout 48 h (as discussed above), one may expect that the contribution of molecular oxygen (formed in situ via the decomposition of TBHP) to the catalytic reaction is negligible.

The use of TBHPaq as oxidant instead of TBHPdec (for both reaction systems only one liquid phase was formed) led to a slower reaction of PhEt in the presence of MCM-41-L/CuCl₂: 5%/23% conversion at 6 h/24 h for TBHPaq compared with 29%/45% for TBHPdec. With TBHPaq as

Table 2 Catalytic oxidation of ethylbenzene with TBHPdec, at 30 °C

Sample	Reaction conditions ^a	TON ^b (mol mol _{Cu} ⁻¹)	Conv. ^c (%)	Yield ^d (%)	Select. ^e (%)
1	1Cu:112PhEt:224TBHP 92 L CH ₃ CN	27	24/24	24/22	98/93
1	1Cu:112PhEt:224TBHP 18 L IL	22	20/27	18/25	92/94
1	1Cu:56PhEt:112TBHP 18 L IL	35 (31) ^f	62/69 (56/65) ^f	62/68 (53/62) ^f	99/99 (95/96) ^f
MCM-41-L/CuCl ₂	1Cu:112PhEt:224TBHP 92 L CH ₃ CN	50 (23) ^f	45/47 (20/25) ^f	44/46 (10/9) ^f	98/97 (49/36) ^f

^a Copper:PhEt:TBHP molar ratios and volume of solvent (IL = [C₄mim]PF₆), ^b turnover number calculated at 24 h, ^c PhEt conversion at 24 h/48 h, ^d PhCOME yield at 24 h/48 h, ^e PhCOME selectivity at 24 h/48 h, ^f the data in *parentheses* are for run 2

oxidant, PhCOME yield at 24 h was 21% and PhCH(OO*t*Bu)Me was formed in less than 2% yield. Hence, water has a negative effect on the catalytic performance of MCM-41-L/CuCl₂, possibly because the imine group hydrolyses back to the ketone and the amine, resulting in the release of copper ions into the liquid phase. When H₂O₂aq was used instead of TBHP(aq or dec), no reaction took place, probably because the copper-catalysed decomposition of H₂O₂ into molecular oxygen plus water was in strong competition with the oxidation of PhEt. Iodometric titration revealed complete decomposition of H₂O₂ for MCM-41-L/CuCl₂, and negligible H₂O₂ decomposition for MCM-41-L; observed initial “bubbling” of the reaction mixture may be due to the release of gaseous O₂. While the inefficiency of this catalyst when the oxidant is molecular oxygen is comparable to that reported for other supported copper complexes (ca. 4% PhCOME yield at 135 °C [28]), better results have been reported using H₂O₂ as oxidant (up to ca. 40% PhCOME yield at 25–80 °C [10, 11, 29]).

The catalyst stability of MCM-41-L/CuCl₂ was investigated in the reaction of PhEt with TBHPdec by (i) performing a second 24 h batch run (after separating the catalyst by centrifugation, washing with *n*-hexane and drying at room temperature overnight), (ii) performing a leaching test by filtering the solid catalyst through a 0.2 μm PVDF w/GMF Whatman membrane at 30 °C after 2 h reaction and leaving the reaction solution to stir for a further 22 h, and (iii) measuring the amount of copper in solution after one batch run by ICP-OES. The catalyst recycling test (i) revealed a severe decrease in reaction rate from the first to the second run (45% conversion and TON = 50 mol mol_{Cu}⁻¹ for run 1; 20% conversion and TON = 23 mol mol_{Cu}⁻¹ for run 2; Table 2), probably due to leaching of active metal species into the liquid bulk during catalysis (Fig. 3). This hypothesis was confirmed by the ICP-OES analyses, which revealed that ca. 11 mol% of the initial amount of copper was leached into the liquid bulk (which turned yellow in color). The leaching test (ii)

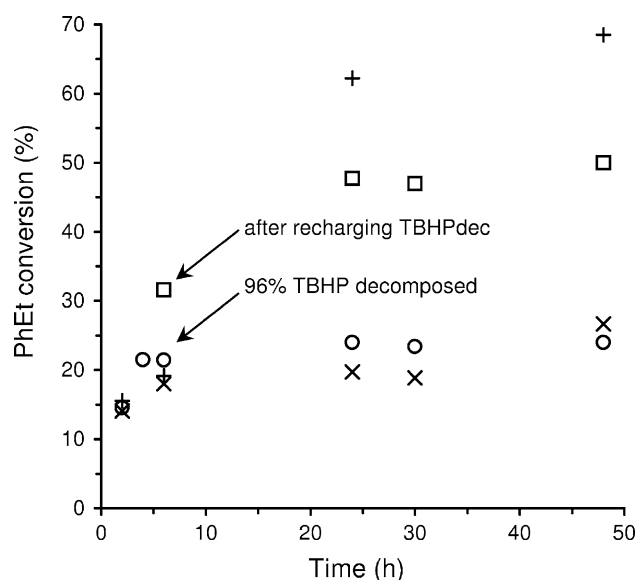


Fig. 2 Kinetic profiles of PhEt oxidation with TBHPdec in the presence of complex **1**, at 30 °C, using acetonitrile as solvent ((*open circles*) run 1, (*open squares*) run 1 with a re-charge of TBHPdec at 4 h reaction) or [C₄mim]PF₆ (molar ratio Cu:PhEt:TBHP = 1:112:224 (*times*) or 1:56:112 (*plus*))

showed an increment in conversion of 22% in the time interval of 2–24 h, compared with 32% in the presence of catalyst and without catalyst filtration. Performing the leaching test with the addition of a radical scavenger at 2 h reaction (after catalyst filtration) showed no significant increase in conversion until 24 h (Fig. 3), indicating that the leached active species gave rise to a free radical mechanism, in agreement with that discussed above for the model complex. Following the characterization studies, it is possible that the complexation reactions took place at the pore entrances. The leached copper species may correspond to those situated closer to the external surface of the catalyst, where they may be more susceptible to desorption.

Further catalytic tests were performed for complex **1** dissolved in the IL [C₄mim]PF₆. This IL was chosen since

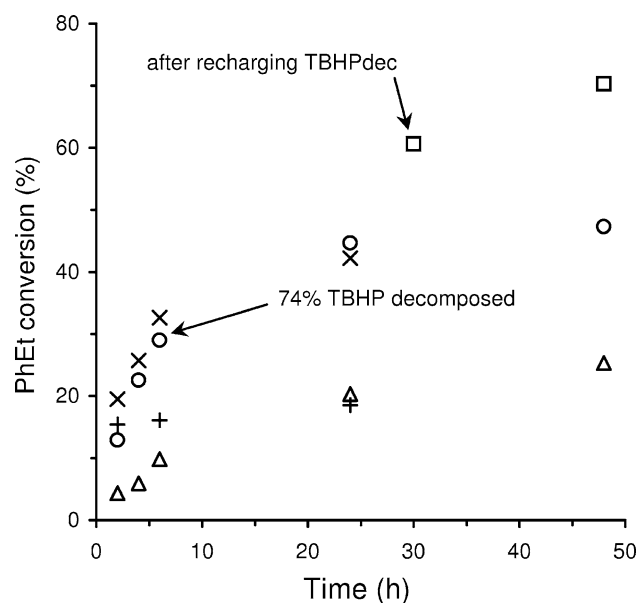


Fig. 3 Kinetic profiles of PhEt oxidation with TBHPdec in the presence of MCM-41-L/CuCl₂, at 30 °C: (open circles) run 1, (open triangles) run 2, (open squares) run 1 with a re-charge of TBHPdec at 24 h, (times) leaching test with catalyst filtration at 2 h reaction, (plus) leaching test with catalyst filtration plus addition of a radical scavenger at 2 h reaction

it is readily accessible, relatively cheap, somewhat hydrophobic (water has a negative effect on the catalytic performance, as discussed above), completely dissolves the catalyst, and the products may be efficiently extracted from the catalyst/IL mixture using *n*-hexane as solvent. In previous work, [C₄mim]PF₆ was found to be quite effective for the catalytic oxidation of PhEt at high temperatures (125 °C) [30]. The stoichiometric oxidation of PhEt in the IL may be neglected, since for the IL [C₆dmim]BF₄ no reaction of PhEt took place at 80 °C [12]. The reaction of PhEt with TBHPdec in the presence of **1**/[C₄mim]PF₆, at 30 °C, gave 18%/25% PhCOME yield at 24 h/48 h (20%/27% conversion) and a TON at 24 h of 22 mol mol⁻¹_{Cu} (Table 2). These results are comparable with those observed for the **1**/TBHPdec/acetonitrile homogeneous reaction system, suggesting that the nature of the active species is similar. The PhCOME yields for the catalysts/IL system are improved by increasing the amount of catalyst: a two-fold increase in the amount of **1** led to 62%/68% PhCOME yield at 24 h/48 h (62%/69% conversion). Under the latter conditions, the catalyst/IL system was recycled after extracting the products from the IL phase with *n*-hexane, and adding TBHPdec and PhEt to the IL (free of reagents/products, as confirmed by GC analysis) in the same amounts as those used for run 1. The *n*-hexane solution after extraction of the products was colorless. A comparison of the kinetic profiles of runs 1 and 2 shows only a slight decrease in conversions and PhCOME yields,

which may be due to the solvent extraction of some active species (Table 2).

4 Conclusion

Condensation 2-acetylpyridine with amines is a convenient and simple route to bidentate pyridyl-imine ligands. We have shown that a pyridyl-ethanimine–CuCl₂ complex is an active homogeneous catalyst for the oxidation of ethylbenzene using *tert*-butyl hydroperoxide as oxidant. Under mild reaction conditions (30 °C) the catalyst is selective for the oxidation of ethylbenzene to acetophenone. When the ionic liquid [C₄mim]PF₆ is used as solvent instead of acetonitrile, acetophenone yields in the range of 60–70% are possible for reaction times of 24–48 h, and the catalyst/IL system can be readily recycled and reused with only a minor drop in catalytic performance. A heterogenised version of the Cu^{II} complex was successfully prepared by immobilising CuCl₂ in an ordered mesoporous silica functionalised with a pyridyl-ethanimine ligand. This catalyst is more active than the homogeneous counterpart partly due to the more efficient use of the oxidant for converting the substrate. More work needs to be done to improve the stability of the supported catalyst since the material is prone to leaching of active copper species into the liquid phase under the reaction conditions used for ethylbenzene oxidation.

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