Liquid-phase oxidation catalysed by copper(II) immobilised in a pillared layered double hydroxide

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ABSTRACT

A novel type of supported copper(II) catalyst was prepared by the treatment of a Zn–Al layered double hydroxide containing 2,2′-bipyridine-5,5′-dicarboxylate (BDC) anions with a solution of $CuCl_2$ in ethanol. The Cu loading in the recovered material, designated as LDH-BDC/Cu, was ca. 4%, with an approximate BDC:Cu:Cl molar ratio of 2:1:1. The catalytic performance of LDH-BDC/Cu was examined in the liquid-phase oxidation of styrene, ethylbenzene, cyclohexane and cyclooctane at room temperature, using acetonitrile/water as solvent, and hydrogen peroxide (30%) or *tert*-butyl hydroperoxide (70%) as terminal oxidant. The main products were benzaldehyde from styrene (up to 14% yield at 24 h), acetophenone from ethylbenzene (up to 8% yield at 24 h), and a mixture of cyclohexanol and cyclohexanone from cyclohexane (up to 5% yield at 24 h). For styrene oxidation using H_2O_2, benzaldehyde was the only observed reaction product (6–11% yield at 24 h), whereas the same reaction carried out in homogeneous phase using the complex [Cu(bipy)Cl$_2$] (bipy = 2,2′-bipyridine) gave the byproducts 2-hydroxy-acetophenone (HAP) and benzoic acid (BAc) in addition to the main product benzaldehyde (60–90% selectivity, 9–11% yield at 24 h). When *t*-BuOOH was used as the oxidant for styrene oxidation in the presence of LDH-BDC/Cu, the byproducts HAP, BAc and acetophenone (each with yields of 1–9% at 24 h) were formed in addition to benzaldehyde (5–14% yield at 24 h). Recycling tests for the latter system showed that the solid LDH-BDC/Cu could be recovered at the end of a catalytic run and used in a second run. For the oxidation of styrene and ethylbenzene using H_2O_2 or *t*-BuOOH as oxidants, titration experiments showed that LDH-BDC/Cu was significantly more efficient than [Cu(bipy)Cl$_2$] in terms of the "productive" consumption of the oxidant.

1. Introduction

In recent years, considerable progress has been made in the use of copper catalysts for the oxidation of alkanes, alkenes, alcohols, arenes, benzylic substrates, ketones and sulfides, with molecular oxygen, hydrogen peroxide, *tert*-butyl hydroperoxide (*t*-BuOOH) or peroxyesters being the preferred terminal oxidants [1]. Copper(II) complexes bearing 2,2′-bipyridine (bipy) and its substituted derivatives have been extensively studied and used as catalysts for the oxidation of cyclohexane [2], the oxidative coupling of 2,6-dimethylphenol [3], the oxidation of veratryl alcohol with molecular oxygen [4], the oxidation of secondary 1-heteroaryl alcohols to the corresponding heteroaromatic ketones with aqueous *t*-BuOOH [5], and asymmetric allylic oxidation and cyclopropanation [6]. In addition to these homoge-

neous systems, some authors have studied the heterogenisation of copper-2,2′-bipyridines using an organic or inorganic support. For example, [Cu(bipy)$_2$]$^{2+}$–bentonite was shown to catalyse the oxidation of benzyl alcohol, hexanol and cyclohexanol to the corresponding aldehyde or ketone in 42–98% yields, with *t*-BuOOH as the oxidant [7,8]. Sato et al. reported an effective poly(2,2′-bipyridine-5,5′-diyl)-CuCl$_2$ catalyst for the synthesis of dimethyl carbonate by oxidative carbonylation of methanol [9,10]. The catalyst could be easily recycled by filtration, and the initial catalytic activity was maintained for three reaction runs.

Some of us recently described the application of a layered double hydroxide (LDH) pillared by 2,2′-bipyridine-5,5′-dicarboxylate (BDC) anions as a "solid ligand" for photofunctional species and/or metal catalysts [11,12]. Specifically, the Zn–Al LDH was examined as a nanoporous matrix to complex [MoO$_2$Cl$_2$(THF)$_2$] [11] and LnCl$_3$ (Ln = Eu, Gd) [12] from solution. The Mo-containing material was an active and recyclable catalyst for the selective epoxidation of olefins in liquid-phase. In the present work, we have used the

organic-anion-pillared LDH as a support for $CuCl_2$, and examined the performance of the resultant material as a catalyst for the oxidation of cyclohexane, cyclooctane, ethylbenzene and styrene, using t-BuOOH and H_2O_2 as oxidants.

2. Experimental

2.1. Characterisation methods

Microanalyses for CHN were carried out at the Department of Chemistry, University of Aveiro (M.M. Marques). Zn, Al and Cu were determined by ICP-AES at the Central Laboratory for Analysis, University of Aveiro (L. Carvalho). SEM with coupled EDS was carried out on a Hitachi SU-70 (S-4100) instrument using a 15 kV accelerating voltage. Conventional X-ray powder diffraction (XRPD) data were collected for all samples at room temperature on an X'Pert MPD Philips diffractometer, equipped with an X'Celerator detector, a graphite monochromator (Cu K_α X-radiation, λ = 1.54060 Å) 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° 2θ steps with a counting time of 10 s per step. The XRPD measurements as a function of temperature were carried out in situ using the same diffractometer equipped with an Anton-Parr GmbH HTK16 high temperature chamber containing a Pt heating filament and a Pt–Pt/Rh (10%) thermocouple. The powdered sample was deposited on the filament that also acts as sample holder. Heating rates of 10 °C min^{-1} were used. At a given temperature, samples were step-scanned in 0.04° 2θ steps with a counting time of 1 s per step. Thermogravimetric analysis (TGA) was performed under air with a Shimadzu TGA-50 system at a heating rate of 5 °C min^{-1}. IR spectra were obtained from KBr pellets using a FTIR Mattson-7000 spectrophotometer. Diffuse reflectance UV–vis spectra were measured on a JASCO V-560 instrument using MgO as a reference.

2.2. Synthesis

All solvents and starting materials were purchased from commercial sources and used as received. The complex [Cu(bipy)Cl$_2$] was prepared using the procedure described by Canhota et al. [2], and gave satisfactory elemental analysis and IR data.

2.2.1. LDH-NO$_3$

A solution of Zn(NO$_3$)$_2$·6H$_2$O (19.63 g, 66 mmol) and Al(NO$_3$)$_3$·9H$_2$O (12.38 g, 33 mmol) in decarbonated, deionised (DD) water (100 mL) was added at a rate of 1 mL min^{-1} to DD water (150 mL) using a Metrohm 776 Dosimat. The addition was carried out under N$_2$ and the pH of the mixture was maintained at 8–9 with a 2 M NaOH solution dosed using a Metrohm Model 718 Stat Titrino operating in the STAT mode. The resultant gel-like slurry was aged at 50 °C for 5 h, filtered and washed several times with DD water, and stored as an aqueous slurry in a closed container (total volume ca. 100 mL). For analysis, 20 mL of this slurry was filtered and the solid dried at room temperature under reduced pressure in a vacuum desiccator. Anal. Calcd for Zn$_{0.68}$Al$_{0.32}$(OH)$_2$(NO$_3$)$_{0.29}$(CO$_3$)$_{0.015}$·0.8H$_2$O: Zn, 36.93; Al, 7.17; C, 0.15; H, 3.01; N, 3.37. Found: Zn, 37.10; Al, 7.05; C, 0.20; H, 2.80; N, 3.35%. IR (cm^{-1}): 3451br, 1613br, 1383vs, 825m, 707br, 605s, 555sh, 425s, and 313m.

2.2.2. LDH-BDC

Two equivalents of KOH in DD water (20 mL) were added to a solution/suspension of 2,2′-bipyridine-5,5′-dicarboxylic acid (0.80 g, 3.3 mmol) (ca. 65% in excess over that theoretically required for complete exchange of nitrate anions in LDH-NO$_3$) in DMF (25 mL) at 70 °C. An aqueous suspension of LDH-NO$_3$ (26 mL,

1.5 g LDH) was then added and the mixture stirred for 48 h at 50 °C. The solid product was isolated by filtration, washed several times with DD water and dried at room temperature under reduced pressure in a vacuum desiccator. Anal. Calcd for Zn$_{0.68}$Al$_{0.32}$(OH)$_2$(C$_{12}$H$_{6.6}$N$_2$O$_4$)$_{0.21}$(CO$_3$)$_{0.015}$·0.9H$_2$O: Zn, 28.65; Al, 5.56; C, 19.62; N, 3.79; H, 3.37. Found: Zn, 28.90; Al, 5.53; C, 19.9; N, 3.70; H, 3.43. TGA up to 150 °C revealed a sample weight loss of 13.0% (calcd for the loss of 0.9H$_2$O: 10.4%; for loss of 1.1H$_2$O: 12.5%). IR (cm^{-1}): 1612vs, 1594sh, 1558w, 1473w, 1380vs, 1247w, 1160w, 1133w, 1037m, 840m, 775m, 619m, 561w, 426vs, and 325w.

2.2.3. LDH-BDC/Cu

LDH-BDC (0.7 g) was dried under reduced pressure at 150 °C for 2 h. CuCl$_2$·2H$_2$O (0.17 g, 1.0 mmol) and ethanol (40 mL) were added and the suspension stirred at room temperature for 19 h. After filtering off the solution, the pale bluish green solid was washed several times with ethanol and dried under reduced pressure. Anal. Calcd for Zn$_{0.68}$Al$_{0.32}$(OH)$_2$(C$_{12}$H$_{6.1}$N$_2$O$_4$)$_{0.21}$(CuCl)$_{0.1}$(CO$_3$)$_{0.015}$·0.1 (C$_2$H$_6$O)·0.2H$_2$O: Zn, 28.32; Al, 5.50; Cu, 4.05; C, 20.92; N, 3.75; H, 2.75. Found: Zn, 28.2; Al, 5.45; Cu, 4.0; C, 20.8; N, 3.69; H, 3.10. IR (cm^{-1}): 1614vs, 1559w, 1472w, 1380vs, 1303w, 1260w, 1162w, 1133w, 1038m, 842m, 776m, 709w, 669w, 620w, 561w, 425s, 323w, and 302w.

2.3. Catalysis studies

The liquid-phase catalytic oxidations of cyclohexane, cyclooctane, ethylbenzene and styrene were carried out at 25 °C, using aqueous t-BuOOH (70%) or aqueous H_2O_2 (30%) as oxidant. All reactions were carried out under air (autogeneous pressure) and stirred magnetically in a closed borosilicate 10 mL reaction vessel immersed in a thermostated oil bath. Typically, three sets of reaction conditions (RCi, i = 1, 2, 3) were used and the total reaction volume was fixed at 2.5 mL for all experiments: RC1—LDH-BDC/Cu or [Cu(bipy)Cl$_2$] in an amount equivalent to 1.7 µmol of copper, 1.9 mmol of substrate, 1.9 mmol of oxidant, and MeCN:H$_2$O (v/v) ratio of 2.4; RC2—LDH-BDC/Cu or [Cu(bipy)Cl$_2$] in an amount equivalent to 1.7 µmol of copper, 1.9 mmol of substrate, 3.8 mmol of oxidant, and MeCN:H$_2$O (v/v) ratio of 4.2; RC3—LDH-BDC/Cu or [Cu(bipy)Cl$_2$] in an amount equivalent to 17 µmol of copper, 1.9 mmol of substrate, 3.8 mmol of oxidant, and MeCN:H$_2$O (v/v) ratio of 4.2. Experiments were performed using 1,2-dichloroethane, ethanol or methanol as alternative solvents to acetonitrile. The reaction mixtures were homogeneous with ethylbenzene and styrene. With cyclohexane and cyclooctane, a separate (upper) organic phase formed (supernatant "oily" droplets), and acetone (2 mL) was added after 24 h to homogenise the mixture and avoid sampling irreproducibility. Undecane was used as an internal standard added after the reaction. Samples were withdrawn at 24 h of reaction and analysed immediately (in the case of LDH-BDC/Cu after separation of the solid catalyst by centrifugation) using a Varian 3800 GC instrument equipped with a FID detector and a CP WAX 52CB (30 m × 0.53 mm) column for cyclohexane and cyclooctane, or a SPB-5 capillary column (20 m × 0.25 mm) for ethylbenzene and styrene, with hydrogen as the carrier gas. The method of standard addition (accounting for matrix effects) was used for product quantification. The reaction products were identified by GC–MS (HP 5890 Series II GC; HP 5970 Series Mass Selective Detector) using He as carrier gas. The % conversion and % yield at a given time (t) were calculated using the formulae: % conversion = 100 × [(initial moles of substrate) − (moles of substrate at t)]/(initial moles of substrate); % yield of product = 100 × (moles of product at t)/(initial moles of substrate).

3. Results and discussion

3.1. Synthesis and characterisation

A Zn–Al layered double hydroxide (LDH) pillared by 2,2′-bipyridine-5,5′-dicarboxylate (BDC) anions was prepared as described previously by ion exchange of the nitrate ions in an LDH precursor [11,12]. In agreement with Ref. [11], the complete exchange of nitrate anions was evidenced by elemental analysis, vibrational spectroscopy and powder XRD. In our previous report [11], the final material had a Zn/Al molar ratio of 1.45 and CHN microanalysis was consistent with the full dissociation of all the carboxylic acids groups of all the BDC guest species. In the present work, the exchanged solid, designated as LDH-BDC, has a higher Zn/Al molar ratio of 2.15 and an unexpectedly high carbon content. It is assumed that the excess organic moiety is due to some protonated BDC anions also being present in the material produced. Accordingly, the elemental analysis data indicates the formula $Zn_{0.68}Al_{0.32}(OH)_2(C_{12}H_{6.6}N_2O_4)_{0.21}(CO_3)_{0.015} \cdot 0.9H_2O$, where about 30% of the carboxylic acid groups are protonated. The intercalation of such free acid groups is not uncommon in LDH chemistry, especially when excess carboxylate anions are used in the exchange (as in this work) [13–15]. Interestingly, the ratio of BDC molecules to total LDH cations $(Zn^{2+} + Al^{3+})$ is 0.21 [i.e., 0.21/(0.68 + 0.32)] for LDH-BDC, which is very close to the ratio of 0.204 found for the material with Zn/Al = 1.45. This strongly suggests that the packing arrangement of BDC molecules in the interlayer region is very similar for the two materials, despite the different layer charge densities. The existence of a unique and stable aggregate is presumably driven by $\pi-\pi$ interactions between the aromatic rings and the need to effectively fill the available space. In LDH-BDC, the intercalation of fully deprotonated carboxylate anions must be unfavourable since this would lead to a less stable aggregate with more separated guest species. Based on these considerations, the two materials should have very similar interlayer separations and this is indeed the case: d_{003} = 18 Å for both materials (Fig. 1(a)) [11]. The IR spectra are also very similar, showing intense bands at 1612 and 1380 cm^{-1} for the asymmetric and symmetric vibrational modes of carboxylate groups. No band for ν(CO) of RCOOH groups (expected around 1690 cm^{-1} by reference to the spectrum of 2,2′-bipyridine-5,5′-dicarboxylic acid) could be observed for LDH-BDC, possibly due to the reduced intensity and overlap with the strong ν_{as}(OCO) band. Other factors that may be responsible for the failure to observe the ν(CO) band are: (i) confinement effects and/or hydrogen-bonding with the OH groups of the Zn–Al double hydroxide layer, which may promote a broadening of the band and a shift to lower frequency, and (ii) partial ionisation of H$^+$ in the layers after intercalation in the RCOOH form [13].

The thermal stability of LDH-BDC was studied by thermogravimetric analysis and by measuring powder XRD patterns at increasing temperatures in the range 25–550 °C. TGA shows that the removal of physisorbed and interlayer water occurs as a weight loss of 13% between room temperature and 150 °C (Fig. 2). This is followed by an abrupt loss of 6.4% between 190 and 230 °C, which is attributed to the partial elimination of structural hydroxyl groups in the basic layers. No further significant weight loss takes place until 350 °C, at which point the total dehydroxylation of the host layers and the decomposition of the organic guests are initiated. The residual mass of 46.8% at 600 °C is in very good agreement with the theoretical value of 46.4% calculated on the basis of the formula given above and the assumption that the residue will have the overall composition $Zn_{0.68}Al_{0.32}O_{1.16}$ (likely to be a mixture of zinc oxide (zincite) and $ZnAl_2O_4$ (gahnite, spinel) phases). Upon heating LDH-BDC to 65 °C, the equally spaced 00*l* reflections observed in the 2θ range of 3–30° broaden significantly and are shifted slightly to higher angles (Fig. 1). The shift corresponds to a decrease in the
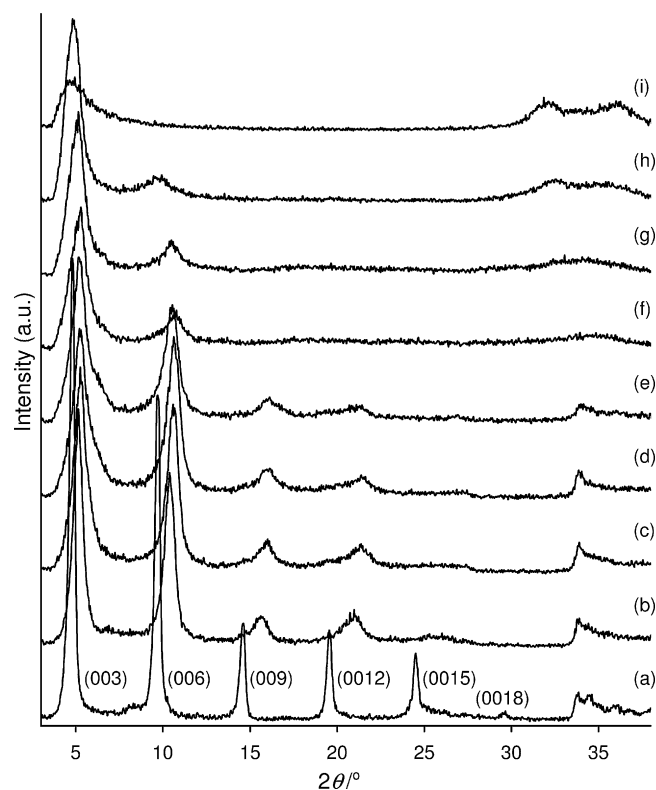

Fig. 1. Powder XRD patterns of LDH-BDC recorded at: (a) room temperature, (b) 65 °C, (c) 100 °C, (d) 150 °C, (e) 200 °C, (f) 260 °C, (g) 350 °C, (h) 450 °C and (i) 550 °C.

basal spacing (d_{003}) of about 1 Å. No further significant change takes place up to 200 °C. Between this temperature and 350 °C, the 0 0 3 and 0 0 6 reflections are retained, while the remaining higher order basal reflections disappear. Changes in the region 30–40° 2θ are due to the partial dehydroxylation that occurs around 220 °C. The retention of the first two basal reflections during this process is the additional evidence for the presence of a very stable close packed arrangement of BDC molecules between the inorganic lay-
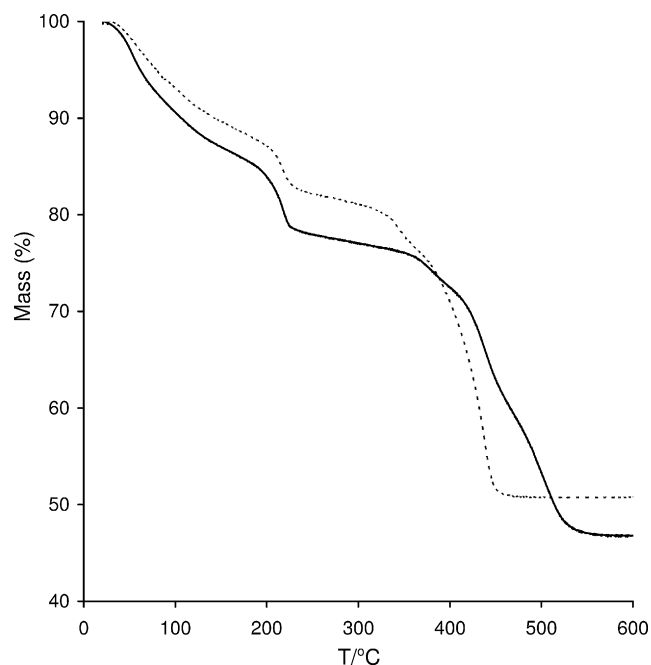

Fig. 2. TGA curves of LDH-BDC (—) and LDH-BDC/Cu (·····).

ers. In the temperature range 350–550 °C, decomposition of the guest molecules leads to the collapse of the ordered layered structure, and the formation of zinc oxide is indicated by the appearance of broad reflections around 32°, 36° and 57° 2θ.

The thermal analysis studies established that LDH-BDC could be heated to 150 °C without having a detrimental effect on the structural integrity of the basic layers or the arrangement of guest molecules. Therefore, prior to the final immobilisation step, physisorbed and interlayer water were removed from LDH-BDC by heating at 150 °C for 2 h under reduced pressure. The solid was then treated with a solution of $CuCl_2$ (ca. 1 equiv. with respect to BDC) in ethanol at room temperature for 19 h, giving a pale bluish green solid (LDH-BDC/Cu) that was filtered, washed with ethanol, and dried under reduced pressure [16]. ICP-AES, CHN microanalyses and SEM-EDS indicated the following chemical composition: $Zn_{0.68}Al_{0.32}(OH)_2(C_{12}H_{6.1}N_2O_4)_{0.21}(CuCl)_{0.1}(CO_3)_{0.015} \cdot 0.1 (C_2H_6O) \cdot 0.2H_2O$, where the BDC/Cu and Cu/Cl molar ratios are ca. 2 and 1, respectively. The TGA curve of LDH-BDC/Cu is quite similar to that of LDH-BDC, except that the onset of full decomposition is shifted by about 25 °C to lower temperature (Fig. 2). The residual mass of 50.7% at 600 °C is in fair agreement with the theoretical value of 49.7% calculated on the basis of the above formula and the assumption that the residue will have the overall composition $Zn_{0.68}Al_{0.32}Cu_{0.1}O_{1.26}$. Powder XRD of LDH-BDC/Cu (not shown) confirmed that the basal spacing was unchanged compared with that for LDH-BDC. No shifts occurred in the infrared stretching frequencies of the carboxylate groups, which suggests that these groups do not interact with the copper ions. A weak band at 302 cm^{-1} is attributed to a terminal copper–chlorine stretching mode [17–19]. Other bands (expected below 300 cm^{-1}) characteristic of either bridging copper–chlorine or copper–organic ligand stretching modes could not be reliably discerned. The bluish green color of LDH-BDC/Cu is typical of copper(II)-2,2′-bipyridines with metal:ligand ratios of either 1:1 or 1:2 [2,20–23]. Accordingly, the diffuse reflectance UV–vis spectrum (not shown) exhibits a very broad d–d band between 600 and 900 nm, with a maximum at 750 nm (13.3×10^3 cm^{-1}). For comparison, $[Cu(bipy)Cl_2]$ and $[Cu(bipy)_2Cl]Cl$ display broad bands centred at about 14.1×10^3 cm^{-1} and 12.4×10^3 cm^{-1}, respectively [21,22]. When recrystallised from water/ethanol, the complex $[Cu(bipy)Cl_2]$ has a distorted square pyramidal geometry, in which one of the chlorine atoms is terminal and the other interacts with the copper centre of an adjacent molecule [20]. The 1:2 complex $[Cu(bipy)_2Cl]Cl$ has trigonal bipyramidal geometry in the solid state, with only terminal copper–chlorine bonds [24]. Taking into account the final Cu:BDC and Cu:Cl molar ratios in LDH-BDC/Cu, as well as the position of the electronic absorption maximum, the possibility that a large fraction of the immobilised copper ions are actually coordinated to two bipyridine ligands must be considered (Fig. 3). Characterisation by element-specific techniques such as Cu K-edge EXAFS would help to clarify these matters.

3.2. Catalysis studies

The catalytic performances of $[Cu(bipy)Cl_2]$ and LDH-BDC/Cu were investigated in the oxidation of styrene, ethylbenzene, cyclohexane and cyclooctane at 25 °C as a function of the type of oxidant (aqueous t-BuOOH or H_2O_2), the catalyst:substrate:oxidant mole ratio, and the solvent. $[Cu(bipy)Cl_2]$ was chosen as the reference complex because: (i) it was reported to be more active than $[Cu(bipy)_2Cl]Cl$ and $[Cu(bipy)_3]Cl_2$ in the oxidation of cyclohexane with H_2O_2 [2], and (ii) the immobilisation of copper(II) in LDH-BDC was carried out using a Cu:BDC mole ratio of 1. To the best of our knowledge, $[Cu(bipy)Cl_2]$ has only previously been studied as a catalyst for the oxidation of cyclohexane [2], benzene [25] and tetralin [26].
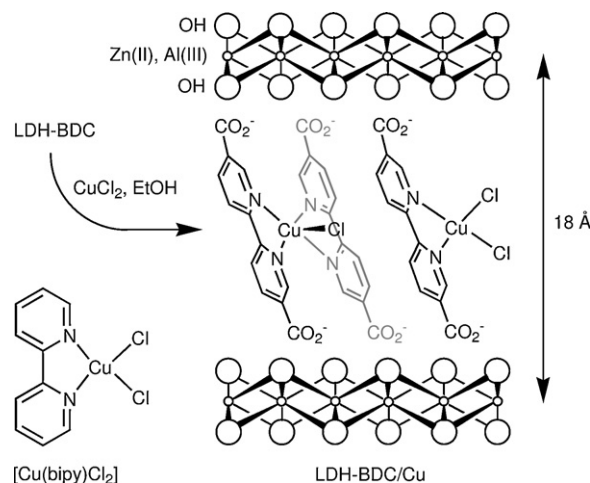

Fig. 3. Schematic representation of the copper(II) catalysts used in the present work, showing for LDH-BDC/Cu the two types of species that are most likely to exist in the interlayer regions.

3.2.1. Oxidation of styrene and ethylbenzene

3.2.1.1. Performance with aqueous H_2O_2 as oxidant. A solvent mixture of acetonitrile/water was used under the different reaction conditions referred to as RC1, RC2 and RC3 (see Section 2.3). Water is needed to completely solubilise $[Cu(bipy)Cl_2]$ [2], and studies of the $[Cu(bipy)Br_2]$-TEMPO system (TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy) for the oxidation of primary alcohols to aldehydes have indicated that the Cu(I) species formed during the catalytic cycle may be stabilised by the coordination of acetonitrile molecules [27]. Control experiments performed over LDH-BDC under identical conditions showed only negligible conversion indicating that the pillared LDH host is inactive for oxidation. In contrast, LDH-BDC/Cu gave turnover numbers (TONs) in the range of 7–115 $mol_{substrate}$ mol_{Cu}^{-1} (calculated for 24 h reaction, under different applied reaction conditions), indicating that

Table 1
Catalytic oxidation of styrene in the presence of $[Cu(bipy)Cl_2]$ or LDH-BDC/Cu at 25 °C, using $MeCN/H_2O$ as solvents.

Catalyst	Oxidant/RC[a]	Conv.[b] (%)	Y[c] (%)	TON[d] ($mol\,mol_{Cu}^{-1}$)
$[Cu(bipy)Cl_2]$	H_2O_2/RC1	9.9	8.8	107
	H_2O_2/RC2	13.6	10.5	148
	H_2O_2/RC3	16.3	10.5	18
	t-BuOOH/RC1	14.2	4.0[e]	154
	t-BuOOH/RC2	25.2	2.9[f]	274
	t-BuOOH/RC3	58.6 (23.7)	2.4[g]	64 (26)
LDH-BDC/Cu	H_2O_2/RC1	7.1	7.1	77
	H_2O_2/RC2	10.6	10.6	115
	H_2O_2/RC3	6.1	6.1	7
	t-BuOOH/RC1	11.2	7.7[h]	122
	t-BuOOH/RC2	8.2	4.6[i]	89
	t-BuOOH/RC3	29.7 (18.2)	13.7[j]	32 (20)

[a] Oxidant and reaction conditions as described in Section 2.

[b] Substrate conversion at 24 h. Values in brackets are for the second 24 h run using the recycled catalysts.

[c] Benzaldehyde yield at 24 h. Other products were mainly benzoic acid (BAc) and 2-hydroxy-acetophenone (HAP).

[d] Turnover number for 24 h reaction. Values in brackets are for the second 24 h run using the recycled catalysts.

[e] BAc and HAP were formed in 4.9 and 5.4% yields, respectively.

[f] BAc and HAP were formed in 8.5 and 12.0% yields, respectively.

[g] BAc and HAP were formed in 17.3 and 37.3% yields, respectively.

[h] BAc and HAP were formed in 1.4 and 2.1% yields, respectively.

[i] BAc and HAP were formed in 0.8 and 2.8% yields, respectively.

[j] BAc, HAP and acetophenone were formed in 1.5, 9.2 and 5.2% yields, respectively.

Table 2
Catalytic oxidation of ethylbenzene in the presence of [Cu(bipy)Cl$_2$] or LDH-BDC/Cu at 25 °C.

Catalyst	Solvent[a]	Oxidant/RC[b]	Conv.[c] (%)	Y[d] (%)	TON[e] (mol mol$_{Cu}^{-1}$)
[Cu(bipy)Cl$_2$]	MeCN + H$_2$O	H$_2$O$_2$/RC1	5.5	2.6	60
		H$_2$O$_2$/RC2	8.1	4.1	88
		H$_2$O$_2$/RC3	12.2	8.6	13
		t-BuOOH/RC1	16.3	4.2	177
		t-BuOOH/RC2	23.1	12.0	251
		t-BuOOH/RC3	48.9	43.0	53
	DCM + H$_2$O	*t*-BuOOH/RC3	21.4	11.1	23
	DCE + H$_2$O	*t*-BuOOH/RC3	17.7	12.8	19
	MeOH + H$_2$O	*t*-BuOOH/RC3	0.8	0.8	1
	EtOH + H$_2$O	*t*-BuOOH/RC3	1.4	1.1	2
LDH-BDC/Cu	MeCN + H$_2$O	H$_2$O$_2$/RC1	8.0	8.0	87
		H$_2$O$_2$/RC2	5.8	4.0	63
		H$_2$O$_2$/RC3	8.0	5.0	9
		t-BuOOH/RC1	2.1	2.0	23
		t-BuOOH/RC2	5.0	4.1	54
		t-BuOOH/RC3	7.0	7.0	8
	DCM + H$_2$O	*t*-BuOOH/RC3	7.1	6.3	8
	DCE + H$_2$O	*t*-BuOOH/RC3	4.8	4.5	5
	MeOH + H$_2$O	*t*-BuOOH/RC3	0	0	0
	EtOH + H$_2$O	*t*-BuOOH/RC3	1.3	1.3	1

[a] DCM = dichloromethane and DCE = dichloroethane.

[b] Oxidant and reaction conditions as described in Section 2.

[c] Substrate conversion at 24 h.

[d] Acetophenone yield at 24 h. When H$_2$O$_2$ was used as the oxidant the byproducts were mainly phenols and quinones, and for *t*-BuOOH the main byproduct was *tert*-butyl 1-phenylethyl peroxide.

[e] Turnover number for 24 h reaction.

the active sites contain copper. Reactions carried out without liquid oxidant gave no substrate conversion, which shows that the autocatalytic oxidation of the substrate with molecular oxygen can be neglected under the reaction conditions used. With one exception (the oxidation of ethylbenzene with H$_2$O$_2$/RC1), the reactions with [Cu(bipy)Cl$_2$] were overall somewhat faster (observed TON = 13–148 mol$_{substrate}$ mol$_{Cu}^{-1}$) than those with LDH-BDC/Cu (Tables 1 and 2). Possible explanations are: (1) a fraction of active sites in LDH-BDC/Cu are inaccessible to the reagent molecules, (2) internal diffusion limitations, and (3) differences in the nature of the solvated and supported copper species (the presence of intercalated species with a metal:organic-ligand ratio of 1:2 instead of, or in addition to 1:1). Still, the catalytic performance of LDH-BDC/Cu for the oxidation of ethylbenzene with aqueous H$_2$O$_2$ is quite reasonable compared with other host–guest systems reported in the literature. For example, NaY-encapsulated copper(II) complexes of macrocyclic ligands were found to be inactive for this reaction [28]. In the case of [Cu(bipy)Cl$_2$], the RC1/2 conditions (0.09 mol% Cu, oxidant/substrate = 1 and 2, respectively) always gave higher TONs than RC3 conditions (0.9 mol% Cu, oxidant/substrate = 2), possibly due to catalyst solubility limitations. Nevertheless, the higher catalyst amount used for RC3 led to conversions at 24 h of 16.3% for styrene and 12.2% for ethylbenzene, both of which are higher than those reached using RC1/2. For LDH-BDC/Cu, the RC1/2 conditions also gave the highest TONs, but not always the highest conversions.

In the presence of LDH-BDC/Cu, the reaction of styrene gave benzaldehyde as the only product in 6–11% yield at 24 h (Table 1). The reaction in the presence of [Cu(bipy)Cl$_2$] was less selective, giving 2-hydroxy-acetophenone (HAP) and minor amounts of benzoic acid (BAc) in addition to the main product benzaldehyde (Fig. 4), which was obtained in 9–11% yield at 24 h. For both catalysts the main product in the reaction of ethylbenzene was acetophenone, and the byproducts (formed via oxidation of the aromatic ring) were 2-ethyl-*p*-benzoquinone and ethyl-phenol isomers (Fig. 4 and Table 2). The simultaneous oxidation of the aromatic ring to give these byproducts is not unexpected given that [Cu(bipy)Cl$_2$] was recently reported to give 4% conversion (after 24 h) in the oxidation of benzene with hydrogen peroxide at 25 °C [25]. There is considerable interest in finding reusable solid catalysts for the selective

oxidation of ethylbenzene to acetophenone, especially since the latter product is an important intermediate for perfumes, drugs and pharmaceuticals [28]. Even though the product spectrum was similar for both Cu-containing catalysts, the selectivity to acetophenone was different depending on the reaction conditions, and under the RC1 conditions with LDH-BDC/Cu acetophenone was the only product formed in 8% yield at 24 h.

3.2.1.2. Comparison of H$_2$O$_2$ and t-BuOOH as oxidants. It is known that the type of oxidant can strongly affect the catalytic activity of copper complexes [28]. With the exception of the oxidation of styrene under RC3 conditions (Fig. 5), the use of *t*-BuOOH as oxi-
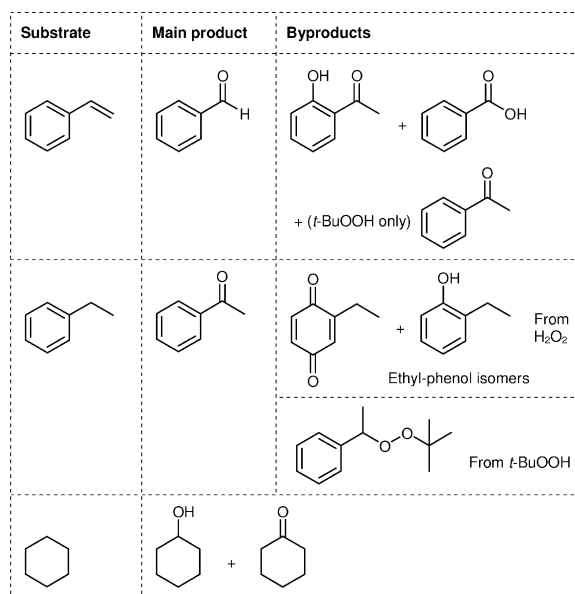

Fig. 4. Representation of the products detected in the liquid-phase oxidation of styrene, ethylbenzene and cyclohexane at room temperature, using aqueous hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant, and [Cu(bipy)Cl$_2$] or LDH-BDC/Cu as catalyst.
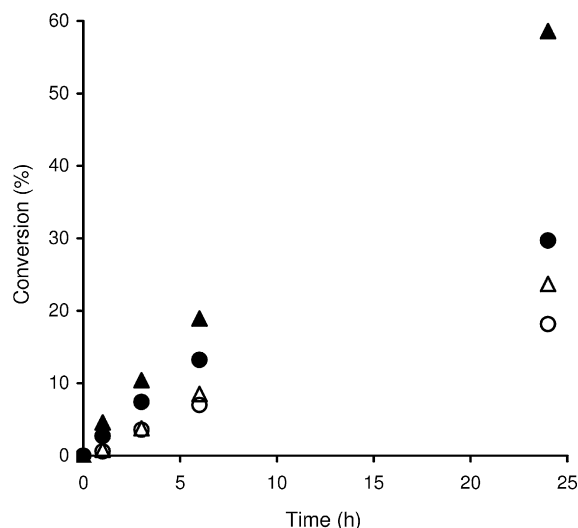
Fig. 5. Kinetic profiles for the first (solid symbols) and second (open symbols) runs of styrene conversion in the presence of [Cu(bipy)Cl$_2$] (triangles) and LDH-BDC/Cu (circles), using *t*-BuOOH as oxidant under RC3 conditions.

dant instead of H$_2$O$_2$ in the presence of LDH-BDC/Cu did not lead to major differences in conversion at 24 h, although the type of oxidant did have an influence on the product spectrum (Tables 1 and 2). The main product in the ethylbenzene reaction continued to be acetophenone, but whereas the byproducts with H$_2$O$_2$ were mainly phenols and quinones, *t*-BuOOH gave *tert*-butyl 1-phenylethyl peroxide (Fig. 4). The catalytic activity with *t*-BuOOH as the oxidant is comparable with that reported for a NaY-encapsulated copper(II) complex of a macrocyclic ligand [28]. For styrene/LDH-BDC/Cu, a wider product spectrum was obtained for *t*-BuOOH than for H$_2$O$_2$ (which gave only benzaldehyde). Under the RC3 conditions, conversion and TON were nearly five times higher for *t*-BuOOH (29.7%, TON = 32) than for H$_2$O$_2$ (6.1%, TON = 7), and the products were mainly benzaldehyde, acetophenone, HAP and BAc. It seems that the reaction mechanism is different for each oxidant.

In general, the products obtained with [Cu(bipy)Cl$_2$] and LDH-BDC/Cu were similar, using the same oxidant. The use of *t*-BuOOH instead of H$_2$O$_2$ in the presence of [Cu(bipy)Cl$_2$] had a clear promotional effect on the reaction rate, especially for RC3 conditions: 58.6% (Fig. 5) and 16.3% styrene conversion at 24 h for *t*-BuOOH and H$_2$O$_2$, respectively (Table 1), and 48.9 and 12.2% ethylbenzene conversion for *t*-BuOOH and H$_2$O$_2$, respectively (Table 2). As seen for [Cu(bipy)Cl$_2$]/H$_2$O$_2$, conversion at 24 h for [Cu(bipy)Cl$_2$]/*t*-BuOOH increased in the order: RC1 < RC2 < RC3, while RC3 gave the lowest TON.

For all reactions with styrene as the substrate no styrene oxide was detected with these catalysts, which contrasts with that found previously for other copper complexes using *t*-BuOOH as oxidant and acetonitrile as solvent. For example, Cu(NTB)Cl$_2$·4H$_2$O [NTB = tris(2-benzimidazolylmethyl)amine] gave mainly the epoxide in ca. 12% yield after 12 h at 60 °C, with benzaldehyde as the main byproduct [29], and [Cu(L)(H$_2$O)](ClO$_4$) [HL = 1-(N-*ortho*-hydroxy-acetophenimine)-2-methyl-pyridine] gave 42% epoxide yield after 24 h at 70 °C [30].

The "productive" consumption of the oxidant (PCox) was investigated in the reaction of styrene or ethylbenzene in MeCN/H$_2$O under RC1 conditions. The PCox was estimated using the formula %PCox = [100 × (moles of substrate consumed)/(moles of oxidant consumed, measured by iodometric titration)]. A reaction stoichiometry of substrate:oxidant = 1:1 is assumed and oxidant consumption in consecutive reactions is neglected for the sake of simplicity. Blank titrations performed for LDH-BDC (without copper) plus oxidant, in the absence of substrate, revealed no mea-

surable decomposition of the oxidant. Taken together with the observation that, as mentioned in Section 3.2.1.1, control experiments performed over LDH-BDC showed only negligible substrate conversions, these results indicate that no reaction occurs between the substrate and the oxidant. For the reactions of styrene and ethylbenzene with H$_2$O$_2$ or *t*-BuOOH, the PCox at 24 h was 65–91% for LDH-BDC/Cu and 9–28% for [Cu(bipy)Cl$_2$], suggesting that the undesired decomposition of the hydroperoxide oxidants is more significant in the latter case. Copper species formed from the decomposition of [Cu(bipy)Cl$_2$] (e.g., via ligand displacement) may be responsible for the relatively low PCox.

The influence of the oxidant:substrate mole ratio and of the amount of copper-containing catalyst on competitive substrate oxidation and oxidant decomposition was further investigated for the oxidation of ethylbenzene with *t*-BuOOH. Increasing the oxidant:substrate mole ratio from 1 (RC1 conditions) to 3 did not have a significant effect on the reaction in the presence of LDH-BDC/Cu (2–5% conversion and 82–95% acetophenone selectivity), and led to a significant decrease in PCox from 70 to 3%, at 24 h (somewhat consistent with the fact that increasing oxidant concentration did not improve TON). Competitive adsorption effects of the reagents/solvents on the hybrid support may affect the PCox and chemical transformations of the metal species may occur in a concentrated oxidant medium. A 10-fold increase in the amount of LDH-BDC/Cu (for *t*-BuOOH/ethylbenzene mole ratio of 3) increased ethylbenzene conversion from 2.9 to 9.8% and PCox from 3 to 72%, which may be related to the presence of a greater number of active sites (e.g., closer to pore entrances) accessible to the substrate molecules to be oxidised. In the case of [Cu(bipy)Cl$_2$], a 10-fold increase in the amount of complex (for an oxidant:substrate mole ratio = 3) led to an increase in conversion from 28.8 to 46.9%, and in acetophenone yield from 16.6 to 36.9%, but PCox decreased by a factor of ca. 0.5, in contrast to that observed for LDH-BDC/Cu, which, according to the above discussion, may be related to a higher concentration of metal species formed from reaction of [Cu(bipy)Cl$_2$] in the oxidizing medium.

3.2.1.3. Solvent effects. The influence of the solvent was investigated for the reaction of ethylbenzene with *t*-BuOOH under RC3 conditions in the presence of LDH-BDC/Cu or [Cu(bipy)Cl$_2$]. Dichloromethane, dichloroethane and MeCN gave similar results with LDH-BDC/Cu as the catalyst (Table 2), but in the case of [Cu(bipy)Cl$_2$] the TON at 24 h with MeCN as the co-solvent was more than double that with the chlorinated solvents, possibly due to stabilisation of intermediate metal species by MeCN [27]. MeCN and the chlorinated solvents led to much higher conversions and acetophenone yields than ethanol and methanol, which resulted in TONs of 2 mol mol$_{Cu}$$^{-1}$ or less. It is possible that the oxidation of the solvent molecules took place, competing with that of the substrate, although it was not possible to confirm this by GC–MS. On the other hand, the alcohols are somewhat nucleophilic and may coordinate to the copper centre originating poorly active/inactive species. For example, in the [copper(II)/TEMPO]-catalysed oxidation of benzyl alcohol to benzaldehyde, the lack of reactivity found when pyrazole–naphthol compounds were used as ligands was attributed to the presence of the naphtholic donor group [31].

3.2.1.4. Catalyst stability. The stability of [Cu(bipy)Cl$_2$] and LDH-BDC/Cu was investigated by carrying out a second run for the reaction of styrene with *t*-BuOOH under the RC3 conditions (Fig. 5). In the case of [Cu(bipy)Cl$_2$], substrate and oxidant were added to the micro reactor at 24 h and the mixture was stirred for a further 24 h. For LDH-BDC/Cu, the solid was separated from the liquid-phase after 24 h by centrifugation, thoroughly washed with acetonitrile and dried at room temperature overnight prior to reuse. For both catalysts, conversion increased with time in each run; in the case of

[Cu(bipy)Cl$_2$], conversions at 6/24 h were 18.9/58.6% and 8.5/23.7% for runs 1 and 2, and those for LDH-BDC/Cu were 13.2/29.7% and 7.0/18.2% for runs 1 and 2. The decrease in the reaction rate from the first to the second 24 h run culminated in a decrease in the TON by a factor of 0.6 for [Cu(bipy)Cl$_2$] and 0.4 for LDH-BDC/Cu (Table 1). In the reactions with [Cu(bipy)Cl$_2$] (but not LDH-BDC/Cu) trace amounts of free bipy ligand were sometimes detected, suggesting that the chemistry of peroxides towards the free copper complex may involve ligand displacement. In the case of LDH-BDC/Cu, ICP-AES of the solid recovered after catalysis indicated no measurable copper leaching. To further assess this point, the filtrate obtained after the first 24 h run was recharged with styrene and *t*-BuOOH, and left to react for a further 24 h. During this period no substrate conversion took place, as observed for a separate blank experiment (first 24 h run) carried out in the absence of LDH-BDC/Cu. The deactivation of LDH-BDC/Cu between the first and second runs may be due to changes in the nature of the active species in the oxidising medium. Additionally, the byproduct of the decomposition of *t*-BuOOH, *t*-butanol, may have a negative influence on the catalytic activity (as suggested above for the solvents MeOH and EtOH).

3.2.2. Oxidation of cyclohexane and cyclooctane

The catalytic performances of [Cu(bipy)Cl$_2$] and LDH-BDC/Cu were further investigated in the oxidation of cycloalkanes using H$_2$O$_2$ as oxidant under RC1 conditions at 25 °C, which are equivalent to those used by Antunes and co-workers for the oxidation of cyclohexane in the presence of [Cu(bipy)Cl$_2$] [2]. Control experiments indicated that no reaction took place in the presence of the copper-free material LDH-BDC. The cyclohexane conversions at 24 h were 5% for LDH-BDC/Cu and 4% for [Cu(bipy)Cl$_2$], originating cyclohexanol and cyclohexanone as the only products (acid products were not detected by titration of the reaction mixture with NaOH). These two products are important raw materials for the production of adipic acid and caprolactam, both of which are intermediates used in the production of nylon [32,33]. When the substrate was cyclohexanol the only reaction product was cyclohexanone, obtained in 5% yield for [Cu(bipy)Cl$_2$] and 3% yield for LDH-BDC/Cu (after 24 h reaction), which indicates that the ketone is produced from the consecutive oxidation of the alcohol. Similar results were obtained for the reaction of cyclooctane, originating cyclooctanone and cyclooctanol as the only products, with RC1/H$_2$O$_2$ conditions giving the highest conversion at 24 h of 4%. The partial oxidation of cycloalkanes with these catalysts is therefore slow compared with that observed for the aromatic substrates. Under RC1 conditions, a 4% conversion corresponds to a TON of 45 mol mol$_{Cu}$$^{-1}$. For comparison, TONs of ca. 5 mol mol$_M$$^{-1}$ (12 h reaction; M = Fe, Cu) were reported for the same reaction carried out at 25 °C in the presence of mesoporous MCM-41 catalysts containing immobilised iron and copper [34].

The 4% cyclohexane conversion found with [Cu(bipy)Cl$_2$] as catalyst (confirmed by performing four replicate experiments) is much lower than the value of 43% reported by Antunes and co-workers [2]. Furthermore, unlike these authors, we detected no cyclohexyl hydroperoxide by GC–MS. Overall, our results using H$_2$O$_2$ as the oxidant more closely resemble those obtained by Antunes and co-workers using *t*-BuOOH instead of H$_2$O$_2$. The differences in catalytic performance of [Cu(bipy)Cl$_2$] encountered between the two works may be partly due to the different methods (sample preparation and calibration) applied for product quantification.

The following changes to the reaction conditions for the oxidation of cyclohexane all failed to enhance the rate of the reaction (conversions at 24 h were always less than 4%): (i) doubling the oxidant:substrate mole ratio (i.e., applying RC2/H$_2$O$_2$); (ii) adding ca. 0.1 M NaHCO$_3$ [35] or HNO$_3$ [36] to the cyclohexane/[Cu(bipy)Cl$_2$]/H$_2$O$_2$ reaction system; (iii) using dichloroethane, ethanol, methanol or the ionic liquid 1-butyl-

3-methylimidazolium tetrafluoroborate as co-solvents instead of MeCN (conversions were always less than 2%); (iv) increasing the MeCN/H$_2$O (v/v) ratio or using only MeCN as co-solvent (such that the only water in the reaction medium came from the oxidant solution added); (v) increasing the reaction temperature to 50 °C. The ineffectiveness of the latter change may be because partial catalyst deactivation and/or competitive decomposition of the oxidant are enhanced at higher temperature.

Slightly better results were obtained for cyclohexane oxidation into cyclohexanol and cyclohexanone in the presence of [Cu(bipy)Cl$_2$] under the RC3 conditions (higher catalyst loadings): 8.8% and 8.2% conversion at 24 h using *t*-BuOOH and H$_2$O$_2$ as oxidants, respectively. This constitutes quite good catalytic performance when compared with some other reports of copper(II) catalysed cyclohexane oxidation. For example, with [Cu(ethylenediamine)$_2$](NO$_3$)$_2$ as the catalyst in the oxidation of cyclohexane with *t*-BuOOH, 5% conversion and 90% cyclohexanol/cyclohexanone selectivity were registered after 24 h reaction under reflux [37]. Similarly, mononuclear copper(II) complexes containing picolinate [38] and N,N-bis(2-pyridylmethyl)-β-alanineamide [39] ligands were found to be poor oxygenation catalysts. On the other hand, copper(II) complexes containing triethanolamine [36] and bis-(2-pyridylmethyl)amine [40] ligands were reported to be highly active and selective catalysts or catalyst precursors for the oxidation of cyclohexane, in acetonitrile, by aqueous H$_2$O$_2$ at room temperature, giving cyclohexanol/cyclohexanone yields up to ca. 67 and 39%, respectively, after 24 h.

4. Concluding remarks

The supported material LDH-BDC/Cu exhibits similar catalytic performance to the complex [Cu(bipy)Cl$_2$] when used as a catalyst for the oxidation of cyclohexane with H$_2$O$_2$ in acetonitrile/water at room temperature. When an oxidant:substrate:catalyst mole ratio of 100:100:0.1 is used, 4–5% cyclohexane is converted to a mixture of cyclohexanol and cyclohexanone after 24 h. In the case of [Cu(bipy)Cl$_2$], a conversion of ca. 8% is possible by using twice the amount of oxidant and ten times the amount of catalyst. For the substrates styrene and ethylbenzene, oxidised using either H$_2$O$_2$ or *t*-BuOOH, the reactions using [Cu(bipy)Cl$_2$] are generally faster than those performed in the presence of LDH-BDC/Cu. Reasons for this difference may include differences in the "productive" consumption of the oxidant, and the presence of intercalated species with a metal:organic-ligand ratio of 1:2 instead of, or in addition to, 1:1. Titration experiments show that the LDH-BDC/Cu system is significantly more efficient than the homogeneous system containing [Cu(bipy)Cl$_2$] in terms of the "productive" consumption of the oxidant, under RC1 conditions and for high catalyst loadings. The type of oxidant influences the product spectrum of the 24-h reaction of ethylbenzene: [Cu(bipy)Cl$_2$] and LDH-BDC/Cu originate mainly acetophenone, and the byproducts are mainly phenols and quinones for H$_2$O$_2$ and *tert*-butyl 1-phenylethyl peroxide for *t*-BuOOH. For styrene/LDH-BDC/Cu, a wider product spectrum (benzaldehyde, benzoic acid, 2-hydroxy-acetophenone, acetophenone) is obtained for *t*-BuOOH than for H$_2$O$_2$ (only benzaldehyde). The ICP-AES analysis of the solid recovered from the second reaction run of styrene oxidation using *t*-BuOOH indicated no copper leaching, although partial catalyst deactivation was observed. The exact factors which influence catalyst deactivation have not been identified. Nevertheless, the supported catalyst possesses the following advantages over the unsupported (homogeneous) molecular catalyst: (i) a lower decrease in substrate conversion from the first to the second runs, (ii) catalytic activity for oxidizing hydrocarbons under very mild reaction conditions with relatively high PCox, and (iii) easier separation (by simple filtration) from the reaction products, which facilitates recycling. The use of other supports for CuCl$_2$ such as meso-

porous silicas functionalised with bipyridine and related ligands may give promising results with respect to activity and stability.

Acknowledgements

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[16] Generally, LDHs containing metal complexes of chelating ligands can be prepared in two different ways: (i) directly by intercalation of the metal complex, or (ii) indirectly by forming the metal complex between the host layers following intercalation of the ligand. We have used method (ii) in the present work because it allows interference from water to be minimised, i.e., physisorbed and interlayer water can be removed from LDH-BDC prior to treatment with a solution of $CuCl_2$ in ethanol. Method (i) would entail the preparation of the complex $[Cu(BDC)Cl_2]$ and its subsequent intercalation by ion exchange with LDH-NO_3. For solubility reasons, the intercalation would have to be performed using water as (co)solvent, which is also the best solvent for ion exchange reactions with LDHs. However, under these conditions the water molecules would replace Cl in the complex, and the intercalation would be compromised by the competing exchange of chloride anions for nitrate anions.
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