Journal of Molecular Catalysis A: Chemical 357 (2012) 125–132

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Single site anchored novel Cu(II) catalysts for selective liquid–gas phase O_2 oxidation of *n*-alkanes

Gopal S. Mishra[a,*], Anil Kumar[b], Pedro B. Tavares[a]

[a] *Centor de Qimica (CQ-VR), Universidade de Trás-os Montes e Alto Douro (UTAD), Vila Real 5001801, Portugal*
[b] *Department of Chemical Engineering, Indian Institute of Technology Kanpur (IITK), Kanpur 208016, India*

ARTICLE INFO

Article history:
Received 29 September 2011
Received in revised form 27 January 2012
Accepted 30 January 2012
Available online 7 February 2012

Keywords:
Cu catalyst
Oxidation
n-alkanes
Batch reactor
Turnover number

ABSTRACT

The pentacoordinate schiff-base trialkoxysilane Cu(II) complexes, *i.e.* Cu[Sal(PMeOSi)DPTA], (**III-a**) and Cu[Cl-Sal(PMeOSi)DPTA], (**III-b**) were synthesized and covalently anchored on SiO_2 and Al_2O_3 matrixes as supported hybrid catalysts (*i.e.* **III-a**/SiO_2 as **Catal.-1**, **III-b**/SiO_2 as **Catal.-2**, **III-a**/Al_2O_3 as **Catal.-3** and **III-b**/Al_2O_3 as **Catal.-4**). The characterization of supported Cu(II) complexes were performed with SEM-EDX, TGA, ICP, FT-IR and EPR analysis. Catalytic tests were conducted in the oxidation (O_2) of *n*-alkanes under relatively mild conditions, in a batch rocking type reactor. Remarkable high catalytic TONs, from 1468 up to 2422, were observed. **Catal.-2** provided the best overall yield, 25.2% with 92% selectivity for *n*-hexane and 20.1% with 75% selectivity for *n*-heptane. A 20% improvement in the yields was obtained with PCA as co-catalyst. The impact of both *C*- and *O*- centred radical traps were also assessed in order to establish a radical mechanism.

1. Introduction

The transformation of hydrocarbons into valuable oxygenated products, *e.g.* alcohols, ketones and carboxylic acids, catalyzed by supported metal catalysts, has attracted great attention. Supported metal catalysts have several typical advantages over the homogenous ones such as easy of removal, selectivity, low toxic and reusable [1–6]. Nevertheless, hydrocarbons (alkanes) are rather inert and usually show typically low convertibility and selectivities with various oxidants [7,8]. Oxidation using molecular O_2 is much attractive route because of its low cost, ready availability in air and environmentally benign nature compared to the other oxidants [9]. Generally, oxidation of alkanes requires a suitable catalyst along with high temperatures and pressures. These alkanes usually undergo competitive reactions, such as cracking [10a], isomerization [10b], dehydrogenation [10c], cyclization [10d], alkylation [10e], metathesis [10f], oligomerization [10g] and polymerization [10a,g].

In fact, several supports such as silica, alumina, MCM-41, SBA-15 and clays, have been used for the immobilization of metal complexes as supported catalysts [11,12]. The anchoring of the metal complexes have been achieved mainly through the interaction between the silanol groups of the supporting matrices and the terminal groups of the metal complexes (*e.g.* –Cl, $–NH_2$, –CN and $–OCH_3$) [15]. In particular, pentacoordinate schiff-base ligands are known for reversible, $–N_3$ and $–O_2$ metal coordination [13,14]. The application of these anchored ligands with Cu, as supported catalyst, is still an open field of research. Only recently their catalytic properties were tested with Vanadium catalyst [15].

Illustrative cases of *n*-hexane oxidation (and cyclohexane) with air and dioxygen mixtures in the presence of metal oxides (Ni_2O_3, MoO_3, $CuCl_2$, and Fe_2O_3) over ZSM-5 were used in a bubble plasma reactor, leading to a diversity of hydroxylated and carbonyl compounds [16]. Another example of partial *n*-hexane oxidation with O_2 was reported with Pt-Rh catalyst in single gauze auto-thermal reactor at 200 °C [17], producing various oxygenated products (70% overall selectivity, including 35% 2,5-dimethyltetrahydrofuran). The Mn-exchanged zeolites were used for *n*-hexane with oxygen at 130 °C and it produced a diverse range of oxidation products [18]. The Zr complexes over SiO_2 were also produced a broad product distribution (cyclohexanone, methyl-2-pentane, methyl-cyclopentane, 4-methyl-1-pentane and toluene). However, the cyclohexanone was the only oxygenated product obtained at 160–200 °C [19]. In the partial O_2 oxidation of *n*-heptane with immobilized V-complexes several oxidised products were created (heptane-2-one, heptan-4-one, heptan-2-ol, heptan-ol, trans-3-hepten-2-one, octan-2-ol, octanoic acid, heptaldehyde and heptanoic acid) [20]. Some molecular sieves were used for *n*-heptane oxidation at 300–400 °C leading to the formation of mixtures of heterocyclic compounds [21]. We have also reported 58% selectivity of hexan-2-one as main product for *n*-hexane oxidation with molecular O_2

---

* Corresponding author. Fax: +351 259350480.
E-mail addresses: mishrags@utad.pt, mishrags@gmail.com (G.S. Mishra).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2012.01.030

(at 160 °C), which was catalysed by modified SiO_2/V catalysts [22].

The current article deals with the synthesis of schiff-base trialkoxysilane pentacooardinate Cu(II) complexes, Cu[Sal(PMeOSi)DPTA], **(III-a)** and Cu[Cl-Sal(PMeOSi)DPTA], **(III-b)** and they were covalently anchored as supported hybrid catalysts (**Catal.-1** to **Catal.-4**). These catalysts were tested in the O_2 oxidation of *n*-hexane and *n*-heptane in order to obtain high turnover numbers (TONs) and high selectivity of corresponding functionalized alcohol and ketone under relatively mild conditions.

2. Experimental

2.1. General materials and methods

The reagents *i.e.* bis(aminopropyl)amine (DETA), potassium carbonate, 2-pyrazinecarboxylic acid (PCA), 3-amino-2-pyrazinecarboxylic acid (APCA), 2,6-pyrizinedicarboxylic acid (DPCA), silica gel (SiO_2), (all form Acros), salicylaldehyde (Sal), 3-idopropyl trimethoxysilane, picolinic acid (PA), 5-hydroxy-2-pyrazinecarboxylic acid (HPCA), alumina (Al_2O_3), acetonitrile (all from Sigma), 5-chlorosalicylaldehyde, Cu(II) acetylacetonate $[Cu(acac)_2]$, tetrahydrofuran, (all from Merck) were used as received. The solvents *i.e.* ethanol, *n*-hexane, *n*-heptane, *n*-pentane, toluene (all from Janssen) were purified and dried by standard methods.

FT-IR spectra (4000–400 cm^{-1}) were recorded on a *Unicam Research Series* spectrophotometer in transmission mode, using KBr pellets; wave numbers in cm^{-1} (*vs* = very strong, s = strong, m = medium, w = weak, br = broad). Elemental analyses were carried out on a *Fisons EA-1108* analyzer. TGA was performed on a *TA Instruments Q50* thermogravimetric analyzer. FAB mass spectra were obtained on a *Trio-2000 Fisons spectrophotometer*. Mass calibration for data system acquisition was achieved using CsI. ICP was used for metal content detection in *Perkin Elmer Plasma-400* (sample was digested in HF + HNO_3). GC analysis was carried in the *FISONS GC-8000 series* equipped with FID detector (DB-WAX column 60 m; internal diameter: 0.32 mm). GC-MS were performed in the *Carlo-Erba Auto/HRGC/MS* spectrophotometer. Morphology of catalysts was performed in Scanning Electron Microscopy (SEM) *in the FEI Quanta 400,* equipped with an EDS detector (*EDAX*). EPR spectra were recorded in the *X band Bruker ESP 300E* spectrophotometer, at room temperature and calibrated with diphenylpicrylhydrazyl (dpph).

2.2. Synthesis of Cu(II) complexes and characterization

2.2.1. Synthesis of Cu[Sal(PMeOSi)DPTA], (III-a)

The trialkoxysilane pentacoordinate schiff-base ligand and Cu(II) complex **III-a** were prepared according to published method [23] (Scheme 1: *Step. A*). It is soluble in most of the polar solvents and quite insoluble in non-polar solvents. Characterization: FT-IR: 3100 cm^{-1} (s, C–H, ring); 2938 cm^{-1} and 2943 (w, C–H); 1622 cm^{-1} (s, C=N); 1567 cm^{-1} (s, C=C); 1165 cm^{-1} (s, Si–O); 1092 cm^{-1} (s, C–N). Elemental analysis (calcd. for $C_{26}H_{37}N_3O_5SiCu$): C, 55.45%; H, 6.62%; N, 7.46%, Found: C, 55.32%; H, 6.51%; N, 7.60%. FAB^+-Mass: $m/z = 565$ $[(M+H)^+, 100]$, 438 $[(M+(Si(-OCH_3)_3))^+, 17]$, 397 $[(M-\{(CH_2)_3Si(-OCH_3)_3\}^+, 13]$, 119 $[(Si(-OCH_3)_3)^+, 42]$. EPR analysis: $g_{||} = 2.1481$, $g_{\perp} = 2.0522$.

2.2.2. Synthesis of Cu[Cl-Sal(PMeOSi)DPTA], (III-b)

The newly synthesized complex **III-b** was initially obtained by the ligand **II-b** [15]. The $Cu[(acac)_2]$ (100 mg, 3.8×10^{-3} mol) was added in the THF 50 mL solution of ligand **II-b**, (215.2 mg, 3.8×10^{-3} mol) and refluxed for 4 h. The mixture was concentrated and diethyl ether was added until no more green solid gets precipitated. Solid **III-b** (Yield: 91%) was isolated by filtration and washed with *n*-pentane. It is soluble in most of the polar solvents and quite insoluble in non-polar solvents (Scheme 1: *Step. A-III*). Characterization: *FT-IR:* 3095 cm^{-1} (s, C–H, ring); 2926 cm^{-1} and 2944 (w, C–H); 1590 cm^{-1} (s, C=N); 1605 cm^{-1} (s, C=C); 1159 cm^{-1} (s, Si–O); 1110 cm^{-1} (s, C–N). Elemental analysis (calcd. for $C_{26}H_{37}N_3O_5SiCu = 563.2$ mol. wt.): C, 55.39%; H, 6.59%; N, 7.45%, Found: C, 55.12%; H, 6.11%; N, 7.52%. FAB^+-Mass: $m/z = 564$ $[(M+H)^+, 100]$, 442 $[(M+(Si(-OCH_3)_3))^+, 18]$, 399 $[(M-\{(CH_2)_3Si(-OCH_3)_3\}^+, 14]$, 120 $[(Si(-OCH_3)_3)^+, 44]$. EPR analysis: $g_{||} = 2.0921$, $g_{\perp} = 1.9834$.

2.3. Synthesis of supported catalysts

The wet-impregnation method [24] was used for the immobilization of complexes **III-a** and **III-b** with silanol groups of Al_2O_3 or SiO_2 [25]. Each of the Cu complexes, **III-a** and **III-b** (50 mg) was dissolved in dry toluene (50 mL), in presence of K_2CO_3. Then Al_2O_3 and SiO_2 (1.0 g) were separately added and the resulting mixture heated under reflux overnight with the elimination of MeOH. After that, the solid supported catalysts were washed several times with toluene and dried at 40 °C for 12 h. Finally, the complex **III-a,** 44 mg on SiO_2 (**Catal.-1**), **III-b,** 43 mg on SiO_2 (**Catal.-2**), **III-a**, 41 mg on Al_2O_3 (**Catal.-3**) and **III-b**, 43 mg on Al_2O_3 (**Catal.-4**) were anchored (Scheme 1: *Step. B*).

The identity of the supported Cu complexes was confirmed by analytical methods *i.e.* SEM-EDX, TGA, FT-IR and ICP analysis.

2.4. Oxidation procedure and product analysis

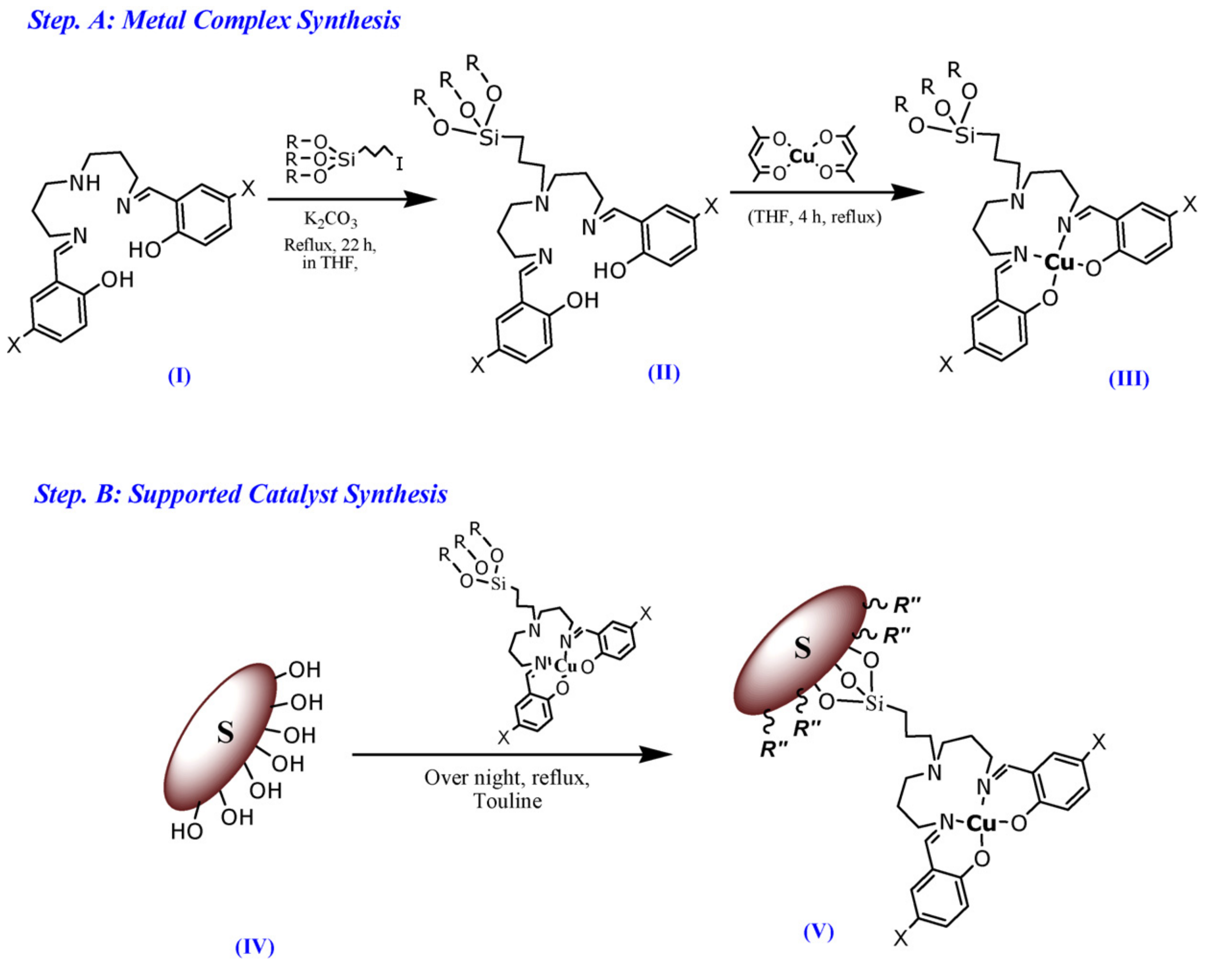
Teflon layered rocking type SS batch reactor (52 cm^3) was used for conducting the oxidation reaction. The inner temperature of the reactor was monitored by a thermocouple. For each experiment, the reactor was charged with the *n*-alkane and the catalyst, closed, the air was removed and O_2 was introduced. At the end of the reaction, the solid catalyst was separated from the liquid product by filtration, washed several times with acetonitrile and oven dried at 60 °C for over night, for further recycling studies.

The products were quantitatively analyzed by GC (30 μL of pentanone added as internal standard to 1.0 mL of the reaction solution) and further identified by GC–MS. He gas was used as the carrier gas. The yield was calculated as the mole of product formed per mole of reactant feed and the product selectivity was calculated as mole of single product per mole of total formed products. TONs were calculated as mole of products (alcohols + ketones) per mole of anchored Cu complex on support. For alkyl-hydroperoxide tests, the excess of triphenylphosphine was added in the product mixture (20 min. before GC analysis) and for radical traps tests, $CBrCl_3$ and Ph_2NH (8 mg) were used for added separately each reaction.

3. Results and discussion

3.1. Synthesis of complexes and immobilisation

The trimethoxysilyl pentacoordinate schiff-base ligands (**II-a** and **II-b**) have five-coordination sites [15,22]. These ligands with donor sets of two phenolate oxygen, two schiff base nitrogens and another tertiary amine nitrogen have been reacted with the terminal iodo- group of 3-iodopropyl-trimethoxysilane. Two different aldehydes such as salicylaldehyde (Sal) and 5-chlorosalicylaldehyde (Cl-Sal) were used for complex synthesis. The $Cu(C_5H_7O_2)_2$ was added in the next reaction step to obtain Cu(II) complexes, *i.e.* **III-a** and new **III-b** (Scheme 1). The proposed structures of Cu(II) complexes were supported by FAB-mass, FT-IR, EPR and elemental analysis.



Where, $\mathbf{R} = OCH_3$, $\mathbf{X} = H$ *for* ***a*** *and* Cl *for* ***b***, $\mathbf{R''}$ *= other anchored unit,* $\mathbf{S} = SiO_2$ *or* Al_2O_3,
V = Catal.-1, Catal.-2, Catal.-3 and Catal.-4

Scheme 1. Synthesis of pentacoordinate schiff-base trialkoxysilane Cu(II) complexes and covalently anchored supported hybrid Cu catalysts.

In the FT-IR spectra of all the ligands show a broad shoulder *ca.* $3400\ \text{cm}^{-1}$ which was due to the –OH; the latter is no longer visible after the coordination with Cu species. Emergence of a band in the ligand molecules between 1590 and $1622\ \text{cm}^{-1}$, associated to the C=N, confirms the presence of schiff-base moiety, whereas the absence of bands in the region between 1590 and $1622\ \text{cm}^{-1}$, associated with the N–H bonds, were also observed. Typical Si–O lattice vibration bonds were observed around $1095–1160\ \text{cm}^{-1}$ [26]. The mass spectra of Cu(II) complexes were characterized by an intense molecular ion, which was the most abundant ion in the spectrum, as well as relatively abundant doubly charged parent molecular ions. There were no polymeric species found which suggests that only monomeric species of complexes were formed. The hyperfine splits were clearly observed in EPR spectra for the paramagnetic ^{63}Cu($I = 3/2$) between $g_{||} = 2.1481–2.0921$ and $g_{\perp} = 2.0522–1.9834$ for **III-a** and **III-b**, thus confirming the presence of monomeric species of Cu(II) complex [27].

Supported catalysts **Catal.-1** to **Catal.-4** were anchored by the reaction of surface silanol (–OH) of supports (Al_2O_3 and SiO_2) with methoxysilane (OCH_3–Si) of metal complexes by a condensation process, overnight refluxing in toluene (Scheme 1: *Step. B*). All the manipulations were performed under N_2, since these complexes contain sensitive methoxysilane groups. To the best of our knowledge, these supported Cu catalysts are being described for the first time.

The FT-IR spectra of **Catal.-1** to **Catal.-4** show that few changes occurred in the range, $3620–3290\ \text{cm}^{-1}$ and $1550–1075\ \text{cm}^{-1}$ can be assigned due to the presence of the support (Al_2O_3 or SiO_2). However, the main characteristic were observed for C–H bands between, s, $2920–2946\ \text{cm}^{-1}$, C=N band between; s, $1582–1610\ \text{cm}^{-1}$ and Si–O bond between: s, $1123–1155\ \text{cm}^{-1}$. The catalysts EPR results exhibited the values $g_{||} = 2.1013$, $g_{\perp} = 2.0205$ for **Catal.-1**, $g_{||} = 2.1001$, $g_{\perp} = 1.9943$ for **Catal.-2**, $g_{||} = 1.9721$, $g_{\perp} = 1.9930$ for **Catal.-3** and $g_{||} = 1.9661$, $g_{\perp} = 1.9711$ for **Catal.-4**. The principal g values were calculated by the published method [27]. These values also strongly support the metal complex anchoring on support matrix.

Thermal analysis results show an initial weight loss, most likely due to absorbed atmospheric moisture (Fig. 1). These complexes have melting point, 213 °C for **III-a** and 208 °C for **III-b**. After the anchoring, they showed improve thermal stability (*ca.* 245 and 275 °C for **Catal. 1** to **Catal. 4)** in compare to unsupported complexes. Beyond it, rapid weight losses were observed in all the catalysts. An absolute decay was observed above 375 °C up to 550 °C (wt. loss *ca.* 5.2%). Such results suggest that the supported catalysts were stable in the range of oxidation reaction temperatures.

Morphological study of the most active **Catal.-2** was shown in two different magnifications (Fig. 2). Brighter particles on the surface of the dark SiO_2 indicate the presence of the Cu complex (Fig. 2b). Same area was analysed in the SEM-EDS detector and

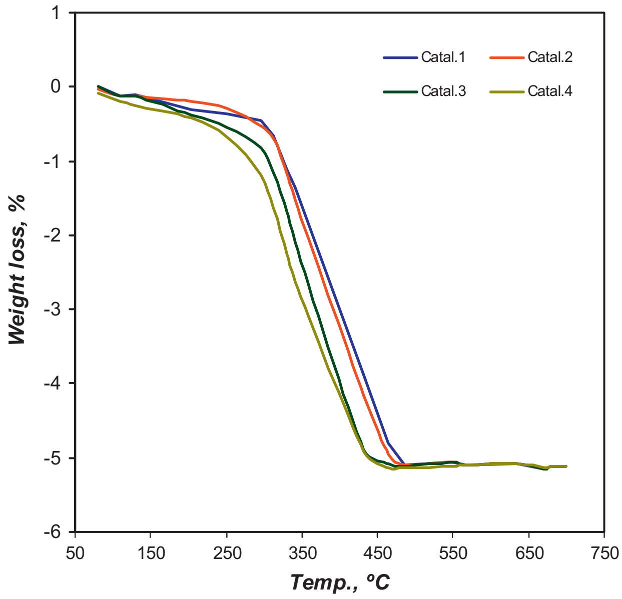


Fig. 1. Thermogravimetric analysis of supported hybrid Cu catalysts **Catal.-1** to **Catal.-4**.

the presence of Cu (peaks at 8.10 and 8.8 keV) was confirmed on the surface support (Fig. 2c). The occurrence of Cu was further confirmed by the ICP analysis (0.19 weight% of fresh **Catal.-2** and one time used catalyst 0.17 and 0.16 weight% for *n*-hexane and *n*-heptane, respectively). It shows only a negligible amount of metal loss for both the *n*-alkanes reactions (under the same condition Table 1).

3.2. Catalytic n-alkanes O_2 oxidation

We have applied all the supported catalysts (**Catal.-1** to **Catal.-4)** and their soluble derivatives (**III-a** and **III-b**) for selective O_2 oxidation of *n*-alkanes, under relatively mild conditions in batch process without requiring any solvents and additives. First tests were conducted with soluble derivatives *i.e.* **III-a** and **III-b** (2×10^{-2} mmol, each) in homogeneous conditions. Low conversions were obtained with **III-a** (8.3% for *n*-hexane and 7.1% for *n*-heptane) and with **III-b** (10.2% for *n*-hexane and 8.4% for *n*-heptane), under the analogous condition (Table 1). In second place we tested the Al_2O_3 and SiO_2 supports, and obtaining low conversions too (for *n*-hexane *ca.* 4.6% by Al_2O_3 and 4.1% by SiO_2 and for *n*-heptane, *ca.* 4.3 by Al_2O_3 and 3.8% by SiO_2). The blank experiments (absence of catalyst) provided the lowest conversions *ca.* 2.2 and 1.6% for *n*-hexane and *n*-heptane, respectively.

Remarkably, very high TONs from 1468 up to 2422 with overall conversions 12% up to 25% were obtained when supported catalysts (**Catal.-1** to **Catal.-4**) were used (Table 1). The most effective result was provided by **Catal.-2**, leading to an overall conversion 25.2% for *n*-hexane and 20.1% for *n*-heptane. We have obtained hexane-ol selectivity 60.3% (hexane-2-ol *plus* hexane-3-ol) as main products and other products in less amounts (24.6%, hexane-2-one and 7.9% caproic acid). In *n*-heptane reaction, it gives good selectivity of heptane-ol 74.6% (at 2nd and 3rd positions) with heptane-2-one selectivity of 13.9% and heptanoic acid of 7.0%. Minor amount (less then 1.0%) of by-products were also detected in the GC/MS analysis (hexanal, heptan-4-one, hexane-3-one *etc.*). There were no isomerization and dehydrocyclization product detected on both the *n*-alkanes. Concerning the mass balance for *n*-hexane in typical conditions (Table 1, catalyst 2, 150 °C, 12 atm), the *n*-hexane (2.051 g, 23.8 mmol) reacted with O_2 (0.754 g, 23.56 mmol) producing hexan-2-ol (0.248 g, 2.43 mmol), hexan-3-ol (0.122 g, 1.19 mmol), hexan-2-one (0.148 g, 1.48 mmol), caproic acid (0.055 g, 0.48 mmol). Some by products were also produced *i.e.* hexanal (0.012 g, 0.12 mmol), H_2O (0.003 g, 0.19 mmol) and unidentified product (≈0.05 mmol). The unreacted *n*-hexane (1.534 g, 17.80 mmol) and O_2 (0.651 g, 20.34 mmol) are also present in the final mixture. In the case of *n*-heptane in typical conditions (Table 1, catalyst 2, 160 °C, 10 atm), the mass balance gives that the *n*-heptane (1.764 g, 17.6 mmol)

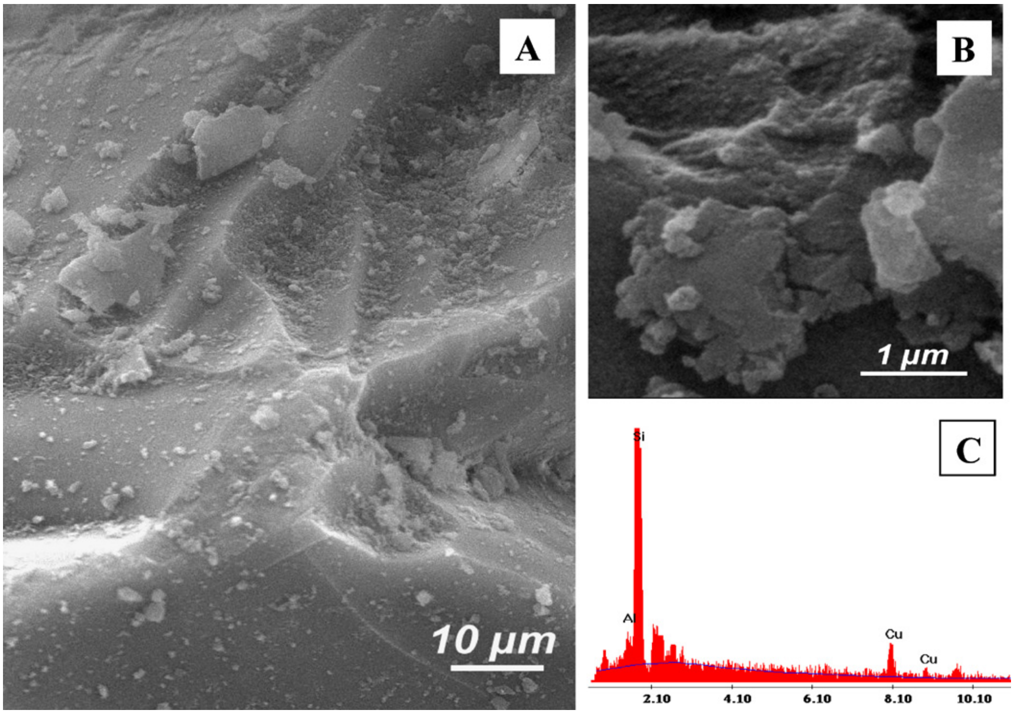


Fig. 2. Scanning electron microscopy images 2 and EDS spactra of **Catal. 2**.

Table 1
Oxyfunctization of *n*-alkanes catalyzed by supported Schiff-base trialkoxysilane pentacoordinate Cu(II) catalysts.[a]

Substrate	Catalyst	TONs[b]	Yield (%)				
			Overall[c]	hex-2-ol	hex-3-ol	hex-2-one	hex-acid
n-hexane	**Catal.-1**	2203	23.3	8.6	5.1	6.3	1.6
	Catal.-2	2422	25.2	10.2	5.0	6.2	2.0
	Catal.-3	1882	17.7	6.8	4.0	3.9	1.0
	Catal.-4	1931	20.6	7.9	4.2	5.3	1.2
			Overall[c]	hept-2-ol	hept-3-ol	hept-2-one	hept-acid
n-heptane	**Catal.-1**	1753	18.2	10.1	3.3	2.3	1.0
	Catal.-2	1968	20.1	11.0	4.0	2.8	1.4
	Catal.-3	1468	12.0	6.2	2.3	2.1	0.6
	Catal.-4	1597	14.5	8.1	2.4	2.0	0.8

[a] Reaction conditions: supported catalyst = 25 mg, *n*-hexane = 23.8 mmol; 150 °C; 12 atm for 8 h and *n*-heptane = 17.6 mmol; 160 °C; 10 atm for 8 h (measured at RT; 1 atm = 1.01 bar = 101 kPa).
[b] TONs = alcohols + ketones.
[c] Overall yield = main products + by products.

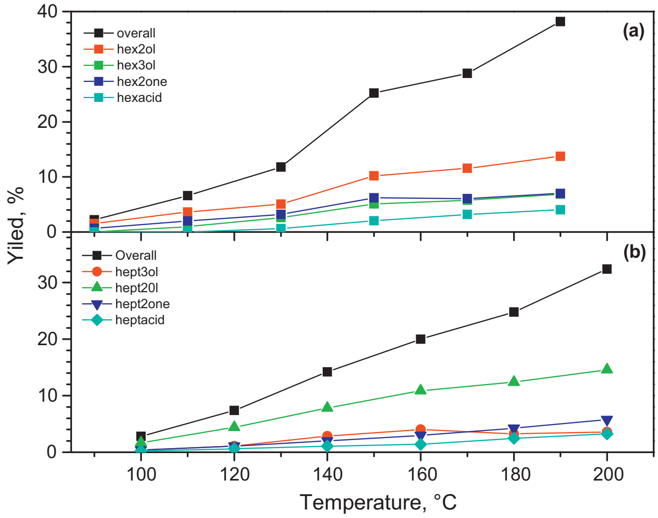


Fig. 3. Effect of temperature on percentage yield in the course of *n*-alkanes oxidation catalyzed by **Catal.-2**.

reacted with O_2 (0.628 g, 19.63 mmol) and produced heptan-2-ol (0.225 g, 1.94 mmol), heptan-3-ol (0.082 g, 0.70 mmol), heptane-2-one (0.056 g, 0.49 mmol), heptanoic acid (0.032 g, 0.25 mmol). The by products were heptan-4-ol (0.012 g, 0.11 mmol), H_2O (0.001 g, 0.05 mmol) and unidentified product (≈0.04 mmol). The unreacted *n*-heptane (1.406 g, 14.03 mmol) and unreacted O_2 (0.568 g, 17.74 mmol) are also present in the final mixture. Various effecting factors such as temperature, O_2 pressure, time and catalyst amount affect the oxidation reaction and were investigated towards the optimization conditions for best activity and selectivity, with most active **Catal.-2**. The details of these reactions, including recycle tests and effect of co-catalysts were summarized in Figs. 3–7, Tables 1 and 2.

3.2.1. *Effect of temperature*

The temperature effect was studied between 90 and 200 °C for *n*-alkanes oxidation under constant conditions: catalyst amount of 25 mg; reaction time of 8 h; $p(O_2) = 10$ atm for *n*-hexane and $p(O_2) = 12$ atm for *n*-heptane (Fig. 3a and b). An increase in the reaction temperature leads to an enhancement of the overall yields, which reaches 38.2% yield for *n*-hexane (main product yield, 13.8% hexane-2-ol) at 190 °C and 32.4% for *n*-heptane (main product yield, 14.6% heptan-3-ol) at 200 °C. The other *n*-hexane products yields were obtained in lesser amount *i.e.* hexane-3-ol; 6.88%, hexane-2-one; 6.99% and hexanoic acid; 4.0% (Fig. 3a). In the case of *n*-heptane, other products yields were obtained like heptane-3-ol; 3.6% (11% selectivity), heptane-2-one; 5.8% (18% selectivity) and hexanoic acid; 3.2% (10.1% selectivity) (Fig. 3b). However, the reaction temperature was not allowed to go beyond this temperature, since an unidentified black charring material appears under deep oxidation. Moreover, the best selectivity results towards the main products (hexane-2-ol; 40.5%, hexane-3-ol; 20.2%, hexane-2-one; 24.6%) were obtained at 150 °C. At the same moment, the hexanoic acid was observed in a small amount (8.0%). On the other hand, a best selectivity result of *n*-heptane was obtained at 160 °C, *i.e.* heptan-3-ol; 20%, heptan-3-ol; 54.7%, heptan-2-one; 15.0%). Heptanoic acid; 7.0% was also observed in as small amount. Temperature study shows that the higher temperatures lead to higher *n*-alkanes conversions but lower selectivities to main products, whereas lower temperatures correspond to lower conversions with good selectivities.

3.2.2. *Effect of O_2 pressure*

The study of the effect of molecular O_2 pressure on *n*-alkanes oxidation was performed between 6 and 20 atm, under constant conditions: catalyst amount of 25 mg; reaction time of 8 h; temperature of 150 °C for *n*-hexane and 160 °C for *n*-heptane (Fig. 4a and b). The maximum overall yields values 41.6% and 33.6% were reached at the highest $p(O_2)$ pressure (20 atm), for *n*-hexane and *n*-heptane, respectively. At same point, highest *n*-hexane products

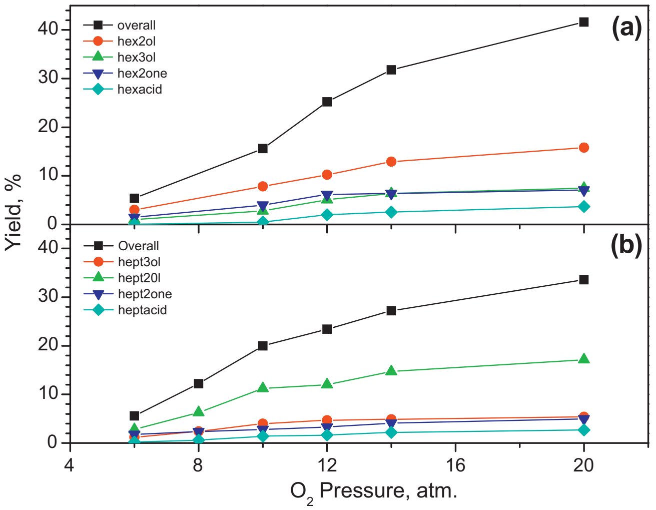


Fig. 4. Effect of O_2 pressure on percentage yield in the course of *n*-alkanes oxidation catalyzed by **Catal.-2**.

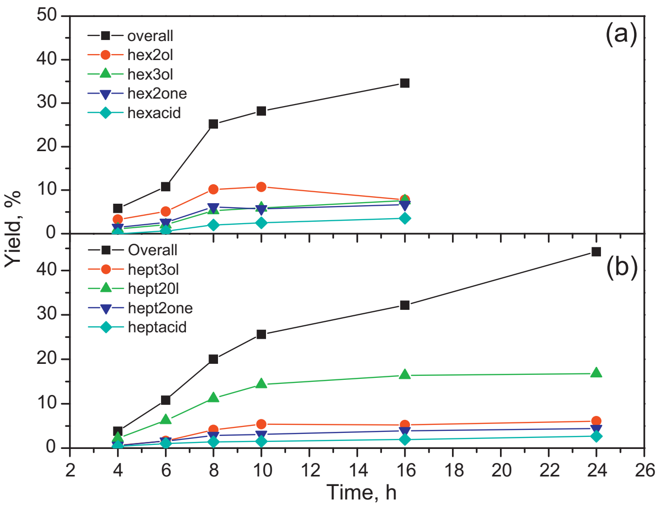


Fig. 5. Effect of reaction time on percentage yield in the course of *n*-alkanes oxidation catalyzed by **Catal.-2**.

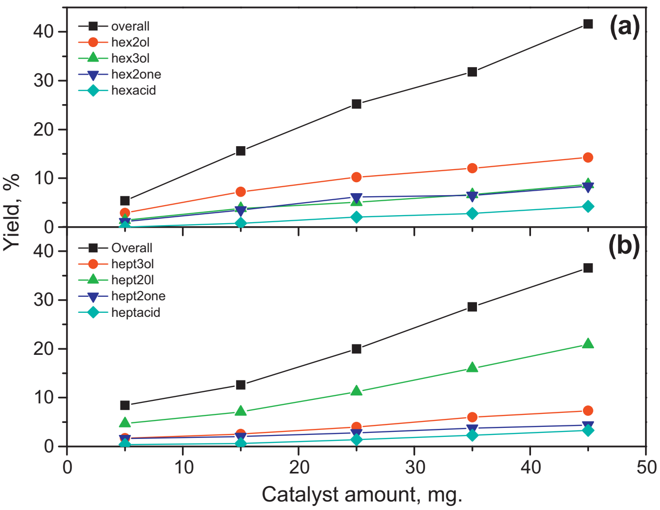


Fig. 6. Effect of **Catal.-2** amount on percentage yield in the course of *n*-hexane oxidation by O_2.

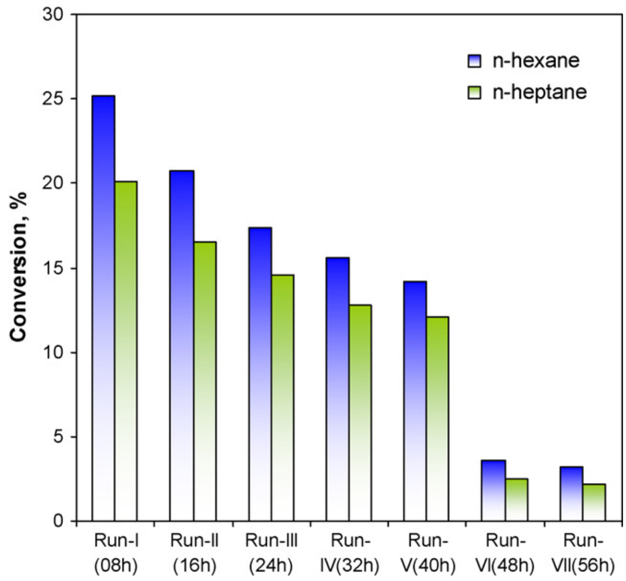


Fig. 7. **Catal.-2** recycle tests for *n*-alkanes oxidation under analogous conditions as Table 1.

yield were obtained *i.e.* hexane-2-ol; 15.8%, hexane-3-ol; 7.49%, hexane-2-one; 7.07% and hexanoic acid; 3.7% (Fig. 4a). However, the best selectivity values for main products of *n*-hexane were obtained at 10 atm (50.1% hexan-2-ol and 25.5% hexane-2-one). For *n*-heptane (Fig. 4a), the best selectivities result was achieved at 12 atm (57% heptan-2-ol, 20% heptan-3-ol and 14.1% heptan-3-one). Above these pressures (10 atm for *n*-hexane and 12 atm for *n*-heptane), the yields of major products were increased but the selectivities decreased. Hence, the O_2 pressure is an essential factor to maintain a high conversion and best selectivity.

3.2.3. *Effect of time*

The reaction time was studied from 4 to 24 h for both *n*-alkanes oxidation, under constant condition: catalyst; 25 mg, $p(O_2)$; 10 atm, temperature;150 °C for *n*-hexane and $p(O_2)$ 12 atm, 160 °C for *n*-heptane (Fig. 5a and b). The overall yield increases with increase of reaction time in both *n*-alkanes reaction. The maximum yields were reaches for *n*-hexane, 16 h (overall 34.6%) and for *n*-heptane 24 h (44.2%); beyond these times, the overall yields were significantly reduces due to the formation of black charring material. At maximum time, the main *n*-alkanes products yields (7.8% hexan-2-ol, 7.6% hexan-3-ol, 6.7% hexan-2-one, 16.8% heptan-2-ol, 6.0% heptan-3-ol and 4.4% heptane-2-one) were achieved. However, the best product selectivities results were observed at 8 h reaction time for both *n*-alkanes. Therefore, time is an essential factor to maintain the best conversion and products selectivities.

3.2.4. *Effect of catalysts amount*

The amount of catalyst was studied for *n*-alkanes oxidation under constant condition: $p(O_2)$ 10 atm, 8 h, 150 °C for *n*-hexane and $p(O_2)$ 12 atm, 8 h, 160 °C for *n*-heptane. The increasing amount **Catal.-2** from 5 to 45 mg, leads to a growth of overall yields from 5.2 to 34.2% for *n*-hexane (Fig. 6a) and from 8.4 to 36.8% for *n*-heptane. The yields of main *n*-hexane products with 45 mg catalyst (*i.e.* 14.3% hexan-2-ol, 8.7% hexan-3-ol and 8.4% hexane-2-one) were much higher than that obtained with 5 mg catalyst (*i.e.* 2.1% hexan-2-ol, 1.4% hexan-3-ol and 1.1% hexane-2-one). Same enhance effect was observed in *n*-heptane case (Fig. 6b). The best selectivity was obtained with 25 mg of catalyst amount in both the *n*-alkanes reactions. Therefore, catalyst amount is also an essential factor for maintaining the high yield and products selectivities.

3.2.5. *Effect of co-catalysts*

A significantly improved yield for *n*-hexane oxidation were obtained with some heteroaromatic carboxylic acids (as possible co-catalysts) [22] *i.e.* 25.7% PA, 27.2% APCA, 28% DPCA, 28.8% HPCA and 30.6% PCA. For *n*-heptane, same improvement effect was observed with these carboxylic acids, *i.e.* 20.6% PA, 21.0% APCA, 21.6% DPCA, 22.3% HPCA and 23.8% PCA (Table 2). Highest enhancement effect was exhibited with PCA for *n*-hexane (30.6%) and for *n*-heptane (23.8%) under the same conditions (Table 1). Same enhancement effect with PCA was observed previously, when the vanadate anions combine with PCA-H_2O_2 [28–30] and with O_2 [31].

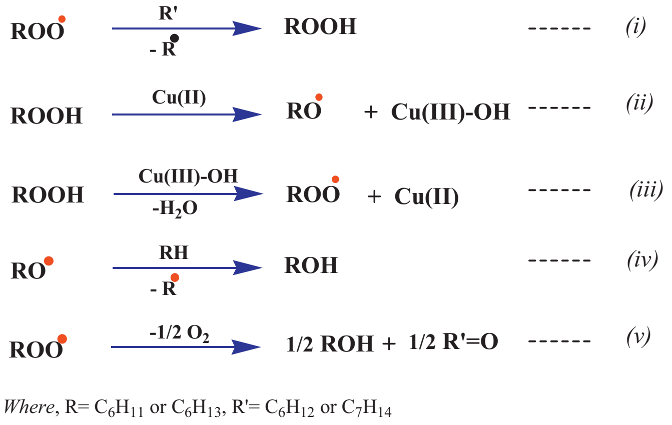
3.2.6. *Effect of catalyst recycles*

The most effective **Catal.-2** shows that the reaction system still presents a significant catalytic activity after recycling. Hence, it could be reused for further oxidation cycles, after some reactivation. The overall yields of *n*-alkanes then decried after 2nd cycle, relatively to the first runs, from 25.2 to 22.2% for *n*-hexane and from 20.1 to 16.8% for *n*-heptane, showing that the reaction system still presents a significant catalytic activity. Thus, the catalytic experiments were extended further more experiments up to 7th cycles for 56 h. Until 5th cycle, the catalyst showed some catalytic activity (14.8% for *n*-hexane and 12.1% for *n*-heptane), however after 6th cycle the catalytic power was completely ceased (Fig. 7).

Table 2
Co-catalysts effects on oxyfunctization of *n*-alkanes catalyzed by **Catal.-2**.[a]

Co-catalyst	Yield (%)							
	n-hexane				*n*-heptane			
	Overall	hex-ol[b]	hex-one	hex-acid	Overall	hept-ol[b]	hept-one	hept-acid
PCA	30.6	18.4	7.7	2.9	23.8	17.8	3.9	1.9
HPCA	28.8	17.5	7.2	2.7	22.3	16.4	3.5	1.6
DPCA	28.0	17.1	7.0	2.5	21.6	16.0	3.3	1.6
APCA	27.2	16.6	6.7	2.4	21.0	15.7	3.0	1.5
PA	25.7	15.5	6.3	2.2	20.6	15.5	2.9	1.4

[a] Experimental conditions as those indicated in Table 1.
[b] hex-ol = hex-2-ol + hex-3-ol, hept-ol = hept-2-ol + hept-3-ol.



Scheme 2. Proposed metal catalyzed reaction mechanism for *n*-alkanes oxidation.

We believe that metal loss was not the sole responsible factor for decrease of the catalytic activity but some other factors were also responsible as well. A possible structural change of the catalyst, as suggested by the observed change of colour upon use, and the black charring material deposition on the catalyst surface, which may also act as pore-blocking of catalyst, should probably account for it.

3.3. *Mechanistic considerations*

Generally, three types of mechanisms for the metal catalyzed alkanes oxidation have been known, *viz.* oxidation *via* a free-radical process, oxidation through substrate coordination and catalytic oxygen transfer [32–35]. These are mainly depends upon the reaction conditions and available metal oxidation states, *e.g.* Co(II/III), Cu(II/III), V(IV/V), Mn(II/III), Fe(II/III). In the current system, it was conformed by the EPR analysis and observed some splitting for fresh and no splitting for used catalyst (see Section 3.1). Two liquid radical traps (*i.e.* $CBrCl_3$ and Ph_2NH) were tested for both the *n*-alkanes and we obtained relatively low conversions. These lower conversions indicate that the radicals are presence in the reaction mixture.

Even though, the mechanistic facts are still unclear, one can consider that the reactions proceed *via* formation of alkyl radicals ($R^•$), initially obtained by reaction of the *n*-alkanes (RH) with molecular O_2 upon homolytic C–H bond cleavage. The $R^•$ radicals again reacts with O_2 forming the alkylperoxy radicals ($ROO^•$), which is further reacting with $R^•$ forming and formed alkyl hydroperoxide (ROOH), Scheme 2(i). H-abstraction from the RH would produce the ROOH (Scheme 2(i)). Subsequently homolytic decomposition of $ROO^•$ and alkyloxy ($RO^•$) (O–O bond cleavage) and alkyl peroxy ($ROO^•$) (O–H bond cleavage) can catalyzed by supported Cu catalyst (Scheme 2(ii) and (iii)). The alcohol (ROH) could be derived by H-abstraction form *n*-alkane by $RO^•$ (Scheme 2(iv)). Decomposition of $ROO^•$ form alcohol (ROH) *plus* can also be the precursor for the formation of ketone (R(–H)=O) and 1/2 O_2 (Scheme 2(v)).

Hexan-2-ol, hexan-3-ol, heptan-2-ol and heptan-3-ol could be formed either by H-abstraction from the *n*-alkanes (RH) by $RO^•$ or by decomposition of $ROO^•$ to yield hexan-2-one and heptan-2-one. The ROOH involvement is evident by the promotion of the detected amount of ROH, with a decrease of that of the R(–H)=O. When the final reaction mixture is treated with excess of PPh_3 (20 min. before by the GC analysis) which reduces ROOH to ROH, as a result eliminating the ROOH [36].

4. Conclusions

The main idea was to use potentially active Cu complexes as supported and recyclable catalysts for *n*-alkanes oxidation under relatively mild conditions. Therefore, $-N_3$ and $-O_2$ coordinated trialkoxysilane Cu(II) complexes (*i.e.* **III-a** and **III-b**) were synthesized and well characterized. These novel complexes were covalently anchored into Al_2O_3 and SiO_2 surface as supported catalysts. Supported catalysts (**Catal.-1** to **Catal.-4**) and their soluble derivatives (**III-a**, **III-b**) were tested for *n*-alkanes selective oxidation with O_2 (chipper and "green" oxidant) in batch reactor.

Higher TONs from 1468 to 2422 were achieved with the supported catalysts in comparison with the soluble derivatives. Among them, **Catal.-2** was the best catalyst with an overall yield 25.2% and TON 2422 for *n*-hexane and overall yield 20.1% and TON 1968 for *n*-heptane. Best selectivity for main products of *n*-hexane (50.1% hexan-2-ol and 25.5% hexane-2-one) was obtained under optimized condition (150 °C, 10 atm, for 8 h). For *n*-heptane, the best selectivity (57% heptan-2-ol, 20% heptan-3-ol and 14.1% heptan-3-one) were achieved at 160 °C, 12 atm, for 8 h. A 20% increase in the total yields was achieved with PCA as co-catalyst. The radical traps and PPh_3 experiments suggested that these oxidation reactions proceed *via* free radicals. Recycle studied showed that these catalysts could be used at least for 40 h reaction time.

Acknowledgements

The authors express gratitude to Foundation for Science and Technology (FCT), Portugal for the financial support under the Ciência 2007 program, Research projects PTDC/EQE-ERQ/110825/2009 and PEst-C/QUI/U10616/2011. We also thank for the analytical analysis to Centro de Apoio Científico e Tecnolóxíco á Investigación, Universidade de Vigo, Spain and Unidade de Microscopia Electrónica at UTAD.

References

[1] B.K. Hodnett, Heterogeneous Catalytic Oxidation: Fundamental and Technological Aspects of the Selective and Total Oxidation of Organic Compounds, John Wiley & Sons, New York, 2000.
[2] D.J. Cole-Hamilton, Science 299 (2003) 1702–1706.

[3] E.G. Derouane, V. Parmon, F. Lemos, F. Ramôa Ribeiro (Eds.), Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities, NATO Science Series, vol. 191, Springer, Dordrecht, The Netherlands, 2005.

[4] G. Centi, F. Cavani, F. Trifiro, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic/Plenum Publishers, New York, 2001.

[5] J. Fan, Y. Gao, J. Exp. Nanaosci. 1 (2006) 457–475.

[6] (a) S.E. Wanke, P.C. Flynn, Catal. Rev. 12 (1975) 93–135;
(b) D.E. de Vos, B.F. Sels, P.A. Jacobs, Adv. Catal. 46 (2001) 1–87.

[7] T.F.S. Silva, G.S. Mishra, M.F.G. da Silva, R. Wanke, L.M.D.R.S. Martins, A.J.L. Pombeiro, Dalton Trans. 42 (2009) 9207–9215.

[8] B.C. Bales, P. Brown, A. Dehestani, J.M. Mayer, J. Am. Chem. Soc. 127 (2005) 2832–2833.

[9] K.T. Queeney, D.A. Chen, C.M. Friend, J. Am. Chem. Soc. 119 (1997) 6945–6946.

[10] (a) A. Corma, V.G.B. Alfaro, A.V. Orchillks, Catal. Appl. A: Gen. 129 (1995) 203–215;
(b) G.S. Mishra, A. Kumar, Chem. Eng. Sci. 1 (2011) 1224–1231;
(c) G. Siddiqi, P. Sun, V. Galvita, A.T. Bell, J. Catal. 274 (2010) 200–206;
(d) N.Ph. Toktabaeva, G.D. Zakumbaeva, L.V. Gorbacheva, Stud. Surf. Sci. Catal. 100 (1996) 483–488;
(e) P. Mériaudeau, Y. Ben Taarit, A. Thangaraj, J.L.G. Almeida, C. Naccache, Catal. Today 38 (1997) 243–247;
(f) J. Joubert, F. Delbecq, P. Sautet, J. Catal. 251 (2007) 507–513;
(g) P. Yarlagadda, C.R.F. Lund, E. Ruckenstein, Appl. Catal. 62 (1990) 125–139;
(h) G.A. Olah, A. Molnár, Hydrocarbon Chemistry, 3rd ed., Wiley, New York, 2003, p. 10.

[11] M.H. Valkenberg, W.F. Hölderich, Catal. Rev. 44 (2002) 321–374.

[12] V. Ayala, A. Corma, M. Iglesias, J.A. Rincón, F. Sánchez, J. Catal. 224 (2004) 170–177.

[13] R. Ferreira, M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, Micro. Meso. Matl. 38 (2000) 391–401.

[14] T.J. Mc Neese, T.E. Mueller, Inorg. Chem. 24 (1985) 2981–2985.

[15] G.S. Mishra, A. Kumar, S. Mukhopadhyay, P.B. Tavares, Appl. Catal. A: Gen. 384 (2010) 136–146.

[16] S.V. Kudryashov, A.Y. Ryabov, G.S. Shchegoleva, E.E. Sirotkina, L.M. Velichkina, Petroleum Chem. 44 (2004) 438–443.

[17] R.P. O'Connor, L.D. Schmidt, Chem. Eng. Sci. 55 (2000) 5693–5703.

[18] B. Zhan, B. Modén, J. Dakka, J.G. Santiesteban, E. Iglesia, J. Catal. 245 (2007) 316–325.

[19] K.S. Anisia, A. Kumar, J. Mol. Catal. A: Chem. 219 (2004) 319–326.

[20] G.S. Mishra, A. Kumar, J. Mol. Catal. A: Chem. 192 (2003) 275–280.

[21] T.Y. Stoylkova, C.D. Chanev, H.T. Lechert, C.P. Bezouhanova, Appl. Catal. A: Gen. 203 (2000) 121–126.

[22] G.S. Mishra, A.J.L. Pombeiro, Appl. Catal. A: Gen. 304 (2006) 185–194.

[23] F. Carré, R.J.P. Corriu, E.L. Beltran, A. Mehdi, C. Reyé, R. Guilard, J. Sýkora, A. van der Lee, Dalton Trans. (2003) 3211–3215.

[24] D. Kumar, C.C. Landry, Micropor. Mesopor. Mater. 98 (2007) 309–316.

[25] (a) P. Sutra, D. Brunel, Chem. Commun. (1996) 2485–2486;
(b) M. Nowotny, L.N. Pedersen, U. Hanefeld, T. Maschmeyer, Chem. Eur. J. 8 (2002) 3724–3731;
(c) A.M. Thayer, Chem. Eng. News 10 (70) (1992) 27–49.

[26] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edition, Wiley, 1978, p. 266.

[27] E. Kwiatkowski, T. Ossowski, A. Jankowska, Polyhedron 4 (1985) 1191–1196.

[28] G.B. Shul'pin, Y.N. Kozlov, G.V. Nizova, G. Süss-Fink, S. Stanislas, A. Kitaygorodskiy, V.S. Kulikova, Perkin Trans. 2 (2001) 1351–1371.

[29] G. Süss-Fink, S. Stanislas, G.B. Shul'pin, G.V. Nizova, H. Stoekli-Evans, A. Neels, C. Bobillier, S. Claude, Dalton Trans. (1999) 3169–3175.

[30] R.Z. Khaliullin, A.T. Bell, M. Head-Gordon, J. Phys. Chem. B. 109 (2005) 17984–17992.

[31] G.S. Mishra, E.C.B. Alegria, L.M.D.R.S. Martins, J.J.R.F. da Silva, A.J.L. Pombeiro, J. Mol. Catal. A: Chem. 285 (2008) 92–100.

[32] M. Hartman, S. Ernst, Angew. Chem. Int. Ed. 39 (2000) 888–890.

[33] R. Pohorecki, J. Badyga, W. Moniuk, W. Podgorska, A. Zdrojkowski, P. Wierzchowski, Chem. Eng. Sci. 56 (2001) 1285–1391.

[34] (a) C.A. Tolman, J.D. Druliner, M.J. Nappa, N. Herron, in: C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989, pp. 303–360;
(b) G.S. Mishra, S. Sinha, Catal. Lett. 125 (2008) 139–144.

[35] C.A. Tolman, J.D. Druliner, P.J. Krisic, M.J. Nappa, W.C. Seidel, I.D. Williams, S.D. Ittel, J. Mol. Catal. 48 (1988) 129–148.

[36] (a) G.B. Shul'pin, Y.N. Kozlov, L.S. Shul'pina, A.R. Kudinov, D. Mandelli, Inorg. Chem. 48 (2009) 10480–10482;
(b) G.B. Shul'pin, Y.N. Kozlov, L.S. Shul'pina, P.V. Petrovskiy, Appl. Organometal. Chem. 24 (2010) 464–472.