Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 102–103 (2005) 154–159

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Copper(II) acetylacetonate anchored onto an activated carbon as a heterogeneous catalyst for the aziridination of styrene

Ana Rosa Silva [a], José Luís Figueiredo [b], Cristina Freire [a,*], Baltazar de Castro [a]

[a] REQUIMTE/Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
[b] Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia,
Universidade do Porto, 4200-465 Porto, Portugal

Abstract

Copper(II) acetylacetonate anchored onto a triamine functionalised activated carbon, [Cu(acac)$_2$*trien*]@AC, was tested in the aziridination of styrene, using PhI = NTs as nitrogen source and acetonitrile as solvent, at room temperature. The styrene conversion and total TON of the heterogeneous phase reaction are similar to those relating the same reaction catalysed in homogeneous phase by [Cu(acac)$_2$]; nevertheless, the initial activity decreases and reaction time increases due to substract and product diffusion limitations. The heterogeneous catalyst could be reused in further catalytic reactions for four times with successive increase in styrene conversion, initial activity and thus in the total turnover number (TON, better than in homogeneous phase reaction). No metal complex leaching was observed after the consecutive catalytic reactions.

Keywords: Copper(II) complexes; Schiff bases; Activated carbon; Anchoring; Aziridination

1. Introduction

The aziridination of alkenes is a reaction of great importance since aziridines are used as intermediates in organic synthesis for pharmaceuticals and agrochemicals [1]. Evans et al. reported that copper(II) acetylacetonate is a very efficient homogeneous catalyst for the aziridination of alkenes using [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane] (PhI = NTs) as nitrogen source [2]. Copper(II) Schiff base complexes have also been used as homogeneous catalysts in the aziridination of olefins [3], as well as in the cyclopropanation of olefins [4], oxidation of sulfides to sulfoxides [5] and in the peroxidative oxidation of phenol to dihydroxy benzynes [6]. Currently, transition metal complexes with Schiff base ligands, of *salen* type, are the object of intense research due to their high activity, chemoselectivity and enantioselectivity in a large range of catalytic processes [7].

Since homogeneous catalysts cannot be separated from the reaction media and, subsequently, cannot be recycled, the last decade has witnessed a growing interest in the heterogenisation of homogeneous metal complexes using several types of supports [7–11]. Initially the complexes were just ion exchanged or adsorbed on the porous supports and, consequently, could be susceptible to leaching [11–13]. More recently, several grafting and tethering procedures have been developed to covalently attach transition metal complexes to organic polymers [9], silica, zeolites and other micro and mesoporous inorganic materials [8,10,11].

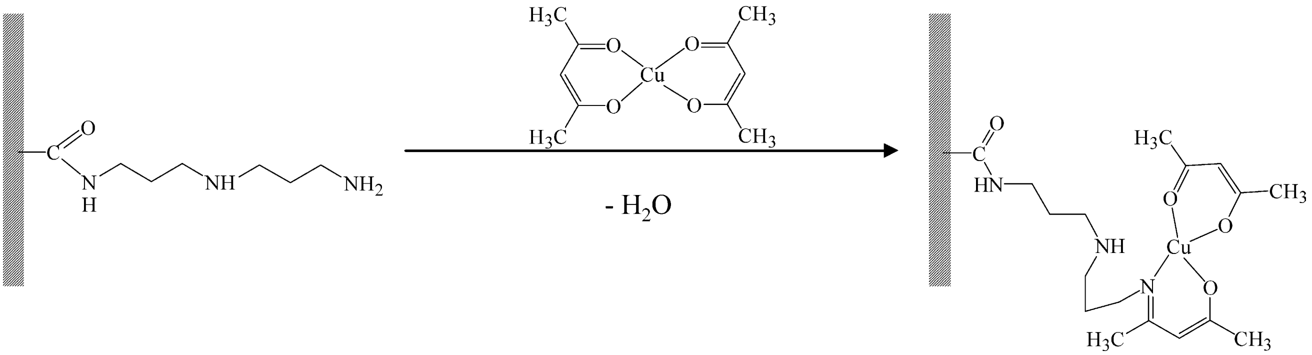
The use of activated carbons and other carbon materials as support for homogeneous catalysts is an untapped area, despite of their broad use as catalysts and as supports for metals in its reduced state [14,15]. Conversely, activated carbons present several advantages when compared to inorganic supports [14]; they are thermally stable, resistant to chemical attack in acid and basic media and, generally, of low cost [14]. Several thermal and chemical processes can be used to tailor the porous structure and the type and concentration of specific oxygen surface groups [14,16]. These groups can be used as building blocks to bridge the metal complex to the support, and their variety allows the use of various immobilisation procedures.

In this context, and with the aim of optimising procedures to prepare carbon-based heterogeneous catalysts, we have

---

* Corresponding author. Tel.: +351 22 6082890; fax: +351 22 6082959.
E-mail address: acfreire@fc.up.pt (C. Freire).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.02.016



Scheme 1. Anchoring copper(II) acetylacetonate onto *trien* functionalised activated carbon.

been developing several strategies for the immobilisation of Schiff base transition metal complexes onto activated carbons [17–20]. From our different methodologies, the direct complex anchoring was applied to the preparation of manganese(III) *salen*-based activated carbons. The resulting materials were shown to act as efficient and reusable heterogeneous catalysts in the epoxidation of styrene [21,22], with similar styrene epoxide chemoselectivities as the corresponding homogeneous phase reactions [21–23].

In the present work, we report the catalytic activity in the aziridination of styrene using PhI = NTs as nitrogen source at room temperature, of copper(II) acetylacetonate anchored onto a chemically oxidised activated carbon functionalised with *trien*; the complex was immobilised through Schiff condensation between the free amine groups of *trien* covalently attached to the activated carbon surface (Scheme 1) with the oxygen atoms of acetylacetonate coordinated to copper(II), as depicted in Scheme 1 [20].

2. Experimental

2.1. Materials

The starting carbon material was a NORIT ROX 0.8 activated carbon (rodlike pellets with 0.8 mm diameter and 5 mm length). The physical properties of the activated carbon, as well as the purification procedure used have been published elsewhere [17–22].

All reagents and solvents used in the modification of the activated carbon and in the anchoring of the copper(II) complex were purified by distillation, except for copper(II) acetylacetonate which was used as received. Copper(II) acetylacetonate and bis-(3-aminopropyl)amine (*trien*) were from Aldrich, and thionyl chloride, toluene and all other chemicals were from Merck (*pro analysi*). The nitrene donor [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane] (PhI = NTs) was synthesised using reported procedures [24].

2.2. Functionalisation of activated carbon

The procedures used in oxidation of the NORIT ROX 0.8 activated carbon activated carbon, reaction with thionyl chloride ($SOCl_2$) and carbon functionalisation bis-(3-aminopropyl)amine (*trien*) were described previously by us [20]. The anchoring of [Cu(acac)$_2$] onto the bis-(3-aminopropyl)amine functionalised carbon (trien@AC) was performed by refluxing a solution of [Cu(acac)$_2$] in toluene with this last carbon for 5 h, during which a progressive disappearance of the solution colour was observed. The resulting material [Cu(acac)$_2$*trien*]@AC was extensively washed with toluene, purified by Soxhlet with this solvent and dried in an oven at 150 °C, under vacuum [20].

2.3. Physico-chemical measurements

X-ray photoelectron spectroscopy was carried out at 'Centro de Materiais da Universidade do Porto' (Portugal), in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized Mg Kα radiation (1253.6 eV). The metal complex was compressed into a pellet prior to the XPS study. In order to correct for possible deviations caused by electric charge on the samples, the C 1 s line at 284.6 eV was taken as internal standard [25,26]. The textural characterisation of carbon-based materials was based on the N_2 adsorption isotherms, which were determined at 77 K with a Coulter Omnisorp 100 CX apparatus using the experimental conditions described elsewhere [17–20]. The volume (V_{micro}) and mesopore surface area (S_{me}) were determined by the *t*-method, using the standard isotherm for carbon materials proposed by Reinoso et al. [27]. Elemental analysis of C, H, and N were performed with a Carlo Erba EA 1108 Elemental Analyzer. Metal analysis was performed by Kingston Analytical Services, UK.

GC-FID chromatograms were obtained with a Varian CP-3380 gas chromatograph using helium as carrier gas and a fused silica Varian Chrompack capillary column CP-Sil 8 CB Low Bleed/MS (30 m × 0.25 mm i.d.; 0.25 μm film thickness). Conditions used: 60 °C (3 min), 5 °C min^{-1}, 170 °C (2 min), 20 °C min^{-1}, 200 °C (10 min); injector temperature, 200 °C; detector temperature, 300 °C.

^{1}H NMR spectra were recorded with a Bruker AC 200 at 25 °C, using $SiMe_4$ as internal reference.

Table 1
Selected characteristics of the [Cu(acac)$_2$*trien*]@AC and trien@AC[a]

Carbon	Cu (μmol g^{-1})		Elemental analysis (wt%)			textural properties[b]	
	ICP-AES	XPS	C	H	N	V_{micro} (cm^3 g^{-1})	S_{me}(m^2 g^{-1})
trien@AC			88.57	1.49	1.20	0.255	207
[Cu(acac)$_2$*trien*]@AC	123	492	87.57	1.08	1.17	0.222	74

[a] From Ref. [20].

[b] From the nitrogen adsorption isotherm at 77 K, calculated by the *t*-method.

2.4. Catalysis experiments

The activity of the catalysts in the aziridination of styrene was studied at room temperature using 1.22 mmol of styrene, 1.22 mmol chlorobenzene (internal standard), 0.100 g of [Cu(acac)$_2$*trien*]@AC, or 0.0122 mmol of [Cu(acac)$_2$] (catalyst), and 0.244 mmol of PhI = NTs (nitrogen source), in 5.00 cm^3 of acetonitrile, under stirring conditions. During the experiment 0.1 cm^3 aliquots were taken from solution with a hypodermic syringe, filtered through 0.2 μm PTFE filters and directly analysed by GC-FID. When all the PhI = NTs had disappeared from solution and the ratio of the areas of iodobenzene and of chlorobenzene in the chromatogram was constant, the solution was withdrawn with a hypodermic syringe and filtered through 0.2 μm PTFE filters to a new flask, to which 0.244 mmol of PhI = NTs were added. This procedure ensures that there was no leaching of the metal complex to the reaction medium and thus the aziridination of styrene was catalysed only heterogeneously. The solvent of the reaction mixture was withdrawn by vacuum and the presence of the aziridine was confirmed both by NMR and mass spectroscopy.

N-(*p*-tolylsulfonyl)-2-phenylaziridine: $C_{15}H_{15}NO_2S$. ^{1}H NMR (d_3-acetonitrile, 200 MHz, 297 K), δ/ppm: 7.87, 7.83 (d, 2H, aromatic), 7.42, 7.38 (d, 2H, aromatic), 7.32–7.24 (m, 5H, aromatic), 3.77–3.72 (dd, 1H, aliphatic), 2.95, 2.91 (d, 1H, aliphatic), 2.51, 2.49 (d, 1H, aliphatic), 2.41 (s, 3H, CH_3). EI-MS, *m*/*z*: 273 (M).

The heterogeneous catalyst was then washed sequentially by Soxhlet extraction with 100 cm^3 of methanol and 100 cm^3 of acetonitrile, for 1–2 h, and dried under vacuum in a horizontal oven at 120 °C for 13 h. This material was reused for further four times using the same experimental procedure.

To provide a framework for the results obtained using the heterogenised copper(II) complex, styrene aziridination was also carried out under experimental conditions comparable to those described above (a) in homogeneous media using the same amount of [Cu(acac)$_2$], and (b) using the trien@AC activated carbon, the precursor of [Cu(acac)$_2$*trien*]@AC.

3. Results and discussion

Immobilisation of copper(II) acetylacetonate onto the activated carbon was performed in four steps as described in Ref. [20]: (i) oxidation of the activated carbon with nitric acid; (ii) reaction with $SOCl_2$; (iii) functionalisation with *trien*, bis(3-aminopropyl)amine, and then (iv) anchoring of the complex onto the modified carbon. These materials have been extensively characterised by us and thus only the results from their characterisation that are relevant to the catalytic experiments will be discussed; data are summarised in Table 1.

Evidence for the effective anchorage of the copper(II) complex onto the surface of carbon trien@AC was first provided by noting that (a) the blue colour of complex solution disappears during the adsorption reaction, and (b) colourless solutions are obtained when the material is purified by Soxhlet extraction. The copper content obtained by ICP-AES of [Cu(acac)$_2$*trien*]@AC is 123 μmol g^{-1}, which corresponded to an 85% complex immobilisation efficiency.

Table 2
Aziridination of styrene catalysed by the [Cu(acac)$_2$] in homogeneous phase and anchored onto the amine functionalised activated carbon, at room temperature, using PhINTs as nitrogen source

Catalyst	Run	Molar ratio catalyst: PhINTs: styrene	*t* (h)[a]	%C[b]	Total TON[c]	Initial TOF[d]
[Cu(acac)$_2$]		1:20:97	0.5	41	8	16.5
trien@AC		20:100	24	30		
[Cu(acac)$_2$*trien*]@AC	1st	1:19:96	24	37	7	1.2
	2nd	1:20:97	24	52	10	3.6
	3rd	1:20:98	24	54	11	5.4
	4th	1:20:101	24	57	12	4.8
	5th	1:22:110	24	47	10	3.6

[a] Time needed for total consumption of PhI = NTs.

[b] Styrene conversion, corrected for the limiting reagent PhI = NTs.

[c] Based on the styrene conversion.

[d] Initial TOF for 1 h of reaction.

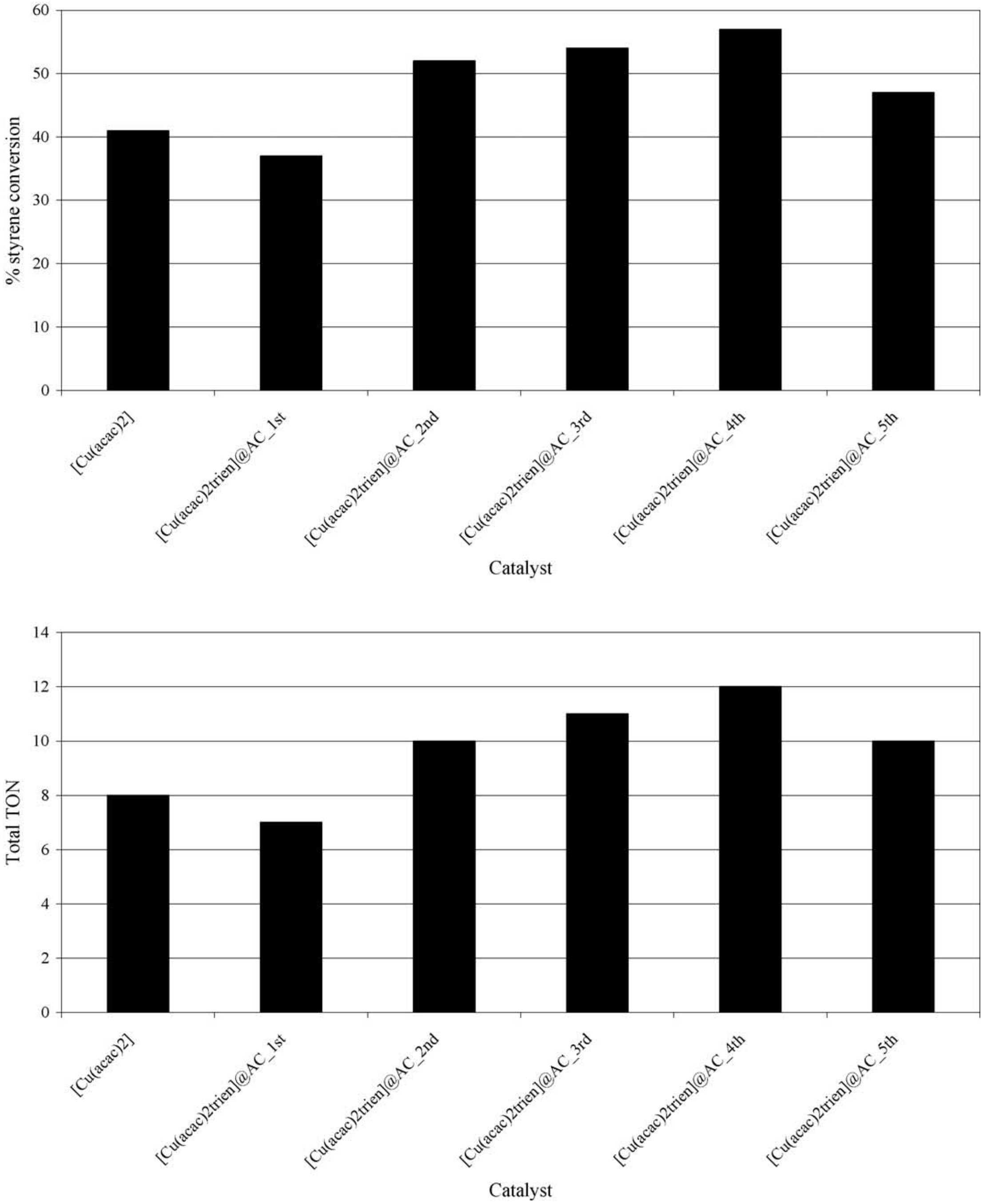


Fig. 1. Percentage styrene conversion and total TON of the [Cu(acac)$_2$] in homogeneous phase and heterogenised onto an amine functionalised activated carbon.

Nevertheless, the copper(II) complex did not anchored homogeneously throughout the trien@AC matrix, since a higher value of copper content was obtained by XPS (Table 1). Hence, the copper(II) complex is mainly anchored at the outer pores of the modified activated carbon. This indication was also provided by the differences between the textural properties of the trien@AC and [Cu(acac)$_2$*trien*]@AC (Table 1): a bigger decrease in the mesopore area than in the micropore volume was observed, suggesting that the copper(II) complex anchored preferentially onto the mesopore and macropore surface.

The indication that Schiff condensation took place between the free amine groups on the surface of the trien@AC material and the copper(II) complex is given by comparing the hydrogen elemental analyses of the trien@AC and [Cu(acac)$_2$*trien*]@AC (Table 1): a decrease of hydrogen content took place after complex anchorage, due to loss of water during the process (Scheme 1).

Nevertheless, the similarity of the N/Cu atomic ratios of 6.8 obtained by both XPS and elemental analysis provided an indication that the anchoring mechanism of [Cu(acac)$_2$] is the same within the matrix. This value is consistent with the presence of un-complexed *trien,* but does not provide any conclusive information on *trien* binding to copper.

Some insights on the copper(II) coordination sphere upon complex anchoring could be gathered from EPR. In fact, the spectrum of [Cu(acac)$_2$*trien*]@AC is similar to those of [Cu(acac)$_2$] in several solvents where axial coordination is incipient or nonexistent [20]. This result suggest that the majority of *trien*-based anchored complexes are four-coordinate (probably with some tetrahedral distortion) and with no axial coordination to the nitrogen of the secondary amine of *trien* (Scheme 1). However, direct anchoring of [Cu(acac)$_2$] by axial coordination to carbon surface groups can not be ruled out on basis of EPR data [20].

3.1. Catalytic experiments

Table 2 summarizes the results obtained for the aziridination of styrene catalysed by the [Cu(acac)$_2$] in homogeneous phase and immobilised onto the amine functionalised activated carbon, at room temperature, using PhI = NTs as nitrogen source.

The [Cu(acac)$_2$*trien*]@AC acted as a heterogeneous catalyst in the aziridination of styrene, with similar styrene conversion and total TON as the ones obtained with homogeneous phase reaction performed with [Cu(acac)$_2$], under comparable experimental conditions. However, a decrease in the initial activity and increase in reaction time was observed, which may be due to the inherent diffusion limitations within the activated porous structure, as the oxygen source is a solid with limited solubility in acetonitrile, and its solubilisation is controlled by its rate of consumption [2]. Besides the formation of *p*-toluenesulfanamide, due to competitive homolytic cleavage of the PhI = NTs [2], only very small amounts of benzaldehyde and epoxide were detected in the reaction media by gas chromatography.

After the catalytic reactions no further activity was found in the filtrates, suggesting that no metal complex leaching took place. The heterogeneous catalyst could be reused in further catalytic reactions for four times with successive increase in styrene conversion and thus in the total turnover number (TON, better than in homogeneous phase reaction) and initial activity (Table 1 and Fig. 1). After each consecutive reuse of [Cu(acac)$_2$*trien*]@AC no further activity was found in the filtrates.

The trien@AC also shows some activity in the conversion of styrene; by gas chromatography, benzaldehyde and styrene epoxide were detected in the reaction media; and by NMR or by mass spectroscopy, no aziridine was detected at the end of reaction: only *p*-toluenesulfanamide. Thus, the successive increase of catalytic activity of [Cu(acac)$_2$*trien*]@AC with reuse may be due to deactivation of some active site on the support surface that induced the homolytic cleavage of PhI = NTs.

4. Conclusion

Copper(II) acetylacetonate immobilised onto an amine functionalised activated carbon [20] acted as a heterogeneous catalyst in the aziridination of styrene, with similar catalytic parameters as the ones obtained with homogeneous phase reaction using [Cu(acac)$_2$] as catalyst. However, due to the inherent diffusion limitations promoted by the porous structure of the support, decrease in the initial activity (TOF) and an increase in reaction time was observed. Moreover, the heterogeneous catalyst could be reused in further catalytic reactions for four times with successive increase in styrene conversion and thus, in initial activity and total turnover number (TON, better than in homogeneous phase reaction). No metal complex leaching was observed after the catalytic reactions.

The present anchoring method allowed spacing of the catalytic active copper(II) centres from the carbon surface, but keeping the original copper(II) acetylacetonate coordination number (Scheme 1). This latter aspect is of crucial importance for the catalytic activity of the new heterogeneous catalyst, since the anchored copper(II) complex has kept the same free vacant sites for coordination of reactants.

Acknowledgements

The authors are indebted to NORIT N.V., Amersfoort, Netherlands, for providing the activated carbon. A.R.S. thanks ‘‘Fundação para a Ciência e Tecnologia’’ (Lisboa) and the European Social Fund for a post-doctoral fellowship.

References

[1] J. Gullick, S. Taylor, P. McMorn, D. Bethell, P.C. Bulman Page, F.E. Hancock, F. King, G. Hutchings, J. Mol. Catal. A: Chem. 180 (2002) 85.
[2] D.A. Evans, M.M. Faul, M.T. Bilodeau, J. Org. Chem. 56 (1991) 6744.
[3] Z. Li, K.R. Conser, E.N. Jacobsen, J. Am. Chem. Soc. 115 (1993) 5326.
[4] C.-M. Che, H.-L. Kwong, W.-C. Chu, K.-F. Cheng, W.-S. Lee, H.-S. Yu, C.-T. Yeung, K.-K. Cheung, Eur. J. Inorg. Chem. (2002) 1456.
[5] S. Bunce, R.J. Cross, L.J. Farrugia, S. Kunchandy, L.L. Meason, K.W. Muir, M. O'Donnell, R.D. Peacock, D. Stirling, S.J. Teat, Polyhedron 17 (1998) 4179.
[6] C.R. Jacob, S.P. Varkey, P. Ratnasamy, Microporous Mesoporous Mater. 22 (1998) 465.
[7] L. Canali, D.C. Sherrington, Chem Soc. Rev. 28 (1999) 85.
[8] Q.-H. Fan, Y.-M. Li, A.S.C. Chan, Chem. Rev. 102 (2002) 3385.
[9] N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217.
[10] C.E. Song, S. Lee, Chem. Rev. 102 (2002) 3495.

[11] D. Brunel, N. Belloq, P. Sutra, A. Cauvel, M. Laspéras, P. Moreau, F. Di Renzo, A. Galarneau, F. Fajula, Coord. Chem. Rev. 178–180 (1998) 1085.
[12] J.S. Rafelt, J.H. Clark, Catal. Today 57 (2000) 33.
[13] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175.
[14] F. Rodríguez-Reinoso, Carbon 36 (1998) 159.
[15] A.J. Bird, in: A.B. Stiles (Ed.), Catalyst Supports and Supported Catalysts, Butterworths, Boston, 1987, Chapter 5.
[16] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Òrfão, Carbon 37 (1999) 1379.
[17] A.R. Silva, C. Freire, B. de Castro, M.M.A. Freitas, J.L. Figueiredo, Microporous Mesoporous Mater. 46 (2001) 211.
[18] A.R. Silva, M. Martins, M.M.A. Freitas, A. Valente, C. Freire, B. de Castro, J.L. Figueiredo, Microporous Mesoporous Mater. 55 (2002) 275.
[19] A.R. Silva, C. Freire, B. de Castro, M.M.A. Freitas, J.L. Figueiredo, Langmuir 18 (2002) 8017.
[20] A.R. Silva, M. Martins, M.M.A. Freitas, C. Freire, B. de Castro, J.L. Figueiredo, Eur. J. Inorg. Chem. (2004) 2027.
[21] A.R. Silva, J. Vital, J.L. Figueiredo, C. Freire, B. de Castro, New J. Chem. 27 (2003) 1511.
[22] A.R. Silva, J.L. Figueiredo, C. Freire, B. de Castro, Microporous Mesoporous Mater. 68 (2004) 83.
[23] A.R. Silva, C. Freire, B. de Castro, New J. Chem. 28 (2004) 253.
[24] S. Taylor, J. Gullick, P. McMorn, D. Bethell, P.C. Bulman Page, F.E. Hancock, F. King, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (2001) 1714.
[25] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: J. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer, 1992.
[26] Y.M. Xie, P.M.A. Sherwood, Chem. Mater. 2 (1990) 293.
[27] F. Rodríguez-Reinoso, J.M. Martin-Martinez, C. Prado-Burguet, B. McEnaney, J. Phys. Chem. 91 (1987) 515.