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Amine-Functionalised Hexagonal Mesoporous Silica as Support for Copper(II) Acetylacetonate Catalyst

Ana Rosa Silva,[a] Karen Wilson,[b] Adrian C. Whitwood,[c] James H. Clark,[b] and Cristina Freire*[a]

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Copper(II) acetylacetonate was anchored onto a hexagonal mesoporous silica (HMS) material using a two-step procedure: (i) functionalisation of the surface hydroxy groups with (3-aminopropyl)triethoxysilane (AMPTSi) and then (ii) anchoring of the copper(II) complex through Schiff condensation with free amine groups, using two different metal complex loadings. Upon the first step, nitrogen elemental analysis, XPS and DRIFT showed the presence of amine groups on the surface of the HMS material, and porosimetry indicated that the structure of the mesoporous material remained unchanged, although a slight decrease in surface area was observed. Atomic absorption, XPS and DRIFT showed that copper(II) acetylacetonate was anchored onto the amine-functionalised HMS by Schiff condensation between the free amine groups and the carbonyl groups of the copper(II) complex; using EPR an NO_3 coordination sphere was proposed for the anchored copper(II) complex. The new $[Cu(acac)_2]$-AMPTSi/HMS materials were tested in the aziridination of styrene at room temperature, using PhI=NTs as nitrogen source and acetonitrile as solvent. The styrene conversion and total TON of the heterogeneous phase reaction are higher than those of the same reaction catalysed in homogeneous phase by $[Cu(acac)_2]$; nevertheless, the initial activity decreases and the reaction time increases due to substrate and product diffusion limitations. The heterogeneous catalyst showed a successive slight decrease in catalytic activity when reused for two more times.

Introduction

Currently, transition-metal complexes with Schiff-base ligands of the salen type are the object of intense research due to their high activity, chemoselectivity and enantioselectivity in a large range of catalytic processes.[1–3] One of the best-known examples are (salen)manganese(III) complexes, that catalyse the epoxidation of alkenes,[1–3] and lead (by direct atom transfer to olefins) to epoxides, which are of great utility in organic synthesis.[1–3,4] The equivalent nitrogen-atom-transfer process catalysed by transition-metal complexes has been less exploited,[4,5] despite aziridines being valuable products as intermediates in organic synthesis,[4–7] efficient chiral auxiliaries and ligands in asymmetric catalysis.[6] Evans et al. reported that copper(II) acetylacetonate is a very efficient homogeneous catalyst for the aziridination of alkenes using 4-methyl-*N*-(phenyl-λ^3-iodanylidene)benzenesulfonamide (PhI=NTs) as nitrogen source;[4] (salen)copper(II) complexes have also been applied as homogeneous catalysts for the alkene aziridination using the same nitrogen source.[7]

However, homogeneous catalysts can not be separated from the reaction media and, subsequently, can not be reused. Thus, one way to improve the homogeneous chemical processes, preventing the requirement for laborious and inefficient extraction processes, is to immobilise the (sometimes) expensive homogeneous catalyst on solid supports.[8] In fact, the last decade has witnessed a growing interest in the heterogenisation of homogeneous metal complexes using several types of supports and several immobilisation strategies.[9–13] Initially, the complexes were just ion-exchanged or adsorbed on the porous supports and, consequently, could be susceptible to leaching.[14,15] More recently, several grafting and tethering procedures have been developed to covalently attach transition-metal complexes to organic polymers,[13] silica, zeolites and other micro- and mesoporous inorganic materials.[9–12]

Copper(II) acetylacetonate has already been immobilised in a polymer[6] and activated carbon,[16,17] and the new materials have acted as recoverable and reusable heterogeneous catalysts for the aziridination of olefins using PhI=NTs as nitrogen source.[6,17] In the first case, the copper(II) complex was microencapsulated in polystyrene, and in the latter it was anchored onto an amine-functionalised activated car-

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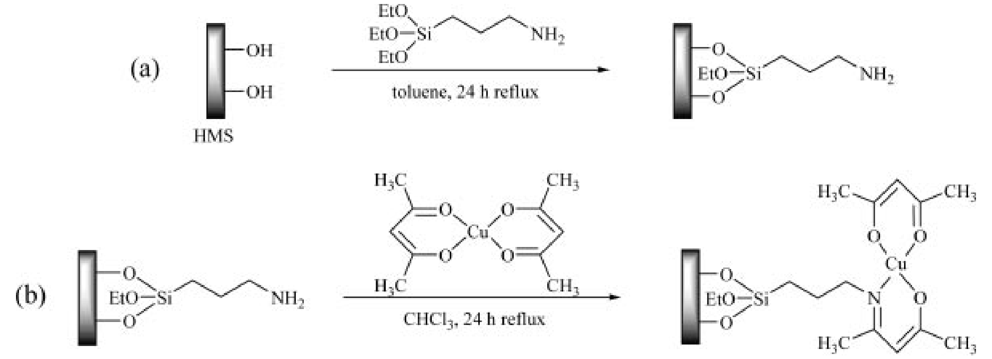
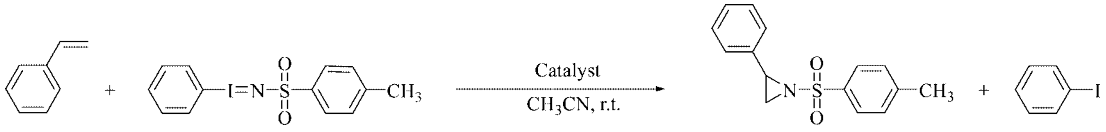
[a] REQUIMTE/Departamento de Química, Faculdade de Ciências, Universidade do Porto,
4169-007 Porto, Portugal
Fax: +351-226082959
E-mail: acfreire@fc.up.pt
[b] Department of Chemistry, Green Chemistry Group, University of York,
Heslington, York YO10 5DD, UK
[c] Department of Chemistry, University of York,
Heslington, York YO10 5DD, UK



Scheme 1. Anchoring procedure: (a) functionalisation of the HMS with (3-aminopropyl)triethoxysilane and (b) anchoring copper(II) acetylacetonate onto AMPTSi-functionalised HMS.



Scheme 2. Aziridination of styrene using PhI=NTs as nitrogen source.

bon,[16] through Schiff-base condensation between the free amine group, covalently attached to the activated carbon surface with the carbonyl groups of the acetylacetonate ligand coordinated to copper(II). Both heterogeneous catalysts presented similar catalytic parameters as those obtained in homogeneous-phase reaction using [Cu(acac)$_2$], under similar experimental conditions, and no significant metal complex leaching was observed after the catalytic reactions.[6,17] However, in the case where activated carbon was used as support, inherent diffusion limitations were observed due to the porous structure of the support, and thus a decrease in the initial activity (TOF), and an increase in the reaction time was observed.[17] Furthermore, the spectroscopic characterisation by DRIFT and UV spectroscopy of the new carbon-based heterogeneous catalysts proved to be difficult and impossible, respectively, due to the highly absorbing carbon matrix, which limited the gathering of information about the copper(II) complex formed on the surface of the amine-functionalised activated carbon. Immobilisation on several porous supports of (Schiff base)copper(II) complexes previously synthesised[18] or prepared in situ on the porous structure,[19,20] have also been reported in the literature.

The silica-based inorganic mesoporous materials which offer pore sizes in the range 20–100 Å, are more suitable for liquid-phase reactions, because they allow easy diffusion of reactants to the active sites.[8,21] Their surface silanol groups can also be easily functionalised by using trialkyloxysilanes, with amine, thiol, carboxylic acid, phenyl, cyano, sulfonic acid and vinyl groups, hence allowing subsequent chemical attachment of the catalytic active species, namely inorganic coordination compounds.[8,21] Furthermore, they can be easily characterised by several spectroscopic techniques. Despite of the hexagonal mesoporous silicas (HMS) being less ordered than MCM-41 and SBA-15 materials, they are much easier and straightforward to synthesise due to the use of a cheap and neutral template, which does not require the need of strongly acidic conditions.[22]

In the present work, a new and simpler route to obtain immobilised (Schiff base)copper(II) complexes is presented. A hexagonal mesoporous silica (HMS), organically functionalised with (3-aminopropyl)triethoxysilane, was chosen to anchor copper(II) acetylacetonate. The anchoring process was done through Schiff condensation between the free amine group, covalently attached to the HMS surface (Scheme 1), with the carbonyl groups of the acetylacetonate ligand, coordinated to copper(II), as depicted in Scheme 1. All the materials were characterised by nitrogen elemental analysis, FTIR-DRIFT, nitrogen isotherms at 77 K and XPS, and those with immobilised copper(II) complex were also characterised by copper atomic absorption, UV diffuse reflectance spectroscopy and EPR. The catalytic activity of this new materials in the aziridination of styrene at room temperature using PhI=NTs as nitrogen source was studied (Scheme 2).

Results and Discussion

Characterisation of the HMS and Amine Functionalisation

The nitrogen adsorption isotherm at 77 K of the calcined HMS material is of type IV (Figure 1), and therefore is typical of mesoporous materials, although the presence of micropores can be detected in the lower relative pressure region. The material has a BET surface area of 1158 m^2 g^{-1} (Table 1).

The infrared spectrum of the calcined HMS shows the typical Si–O lattice vibrations: two broad bands between 2100 and 1750 cm^{-1}, with medium intensity, a strong and broad band with two peaks in the region 1450–900 cm^{-1}, and two strong bands between 900 and 500 cm^{-1}. Furthermore, a very broad band centred at 3450 cm^{-1}, due to the

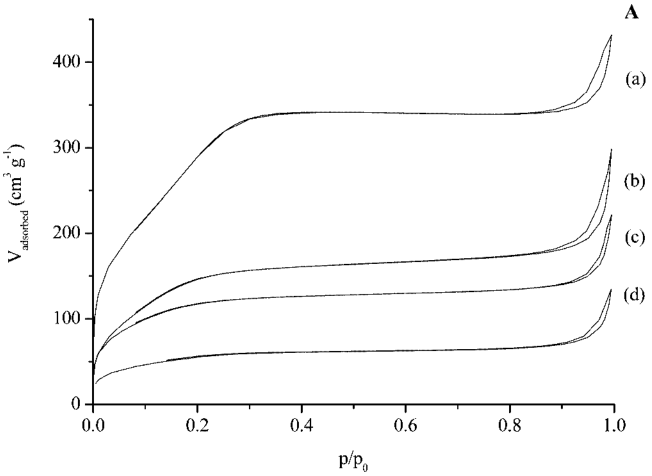


Figure 1. Nitrogen adsorption isotherms at 77 K of (a) calcined HMS, (b) AMPTSi/HMS, (c) [Cu(acac)$_2$]AMPTSi/HMS_A and (d) [Cu(acac)$_2$]AMPTSi/HMS_B.

Table 1. Selected characteristics of the modified HMS materials.

Sample	Cu [mmol g^{-1}] AA	XPS$^{[a]}$	N/Cu EA/AA	XPS	$A_{BET}$$^{[b]}$ [m^2 g^{-1}]
HMS					1158
AMPTSi/HMS					561
[Cu(acac)$_2$]AMPTSi/ HMS_A	0.362	0.269	3.9	4.6	436
[Cu(acac)$_2$]AMPTSi/ HMS_B	0.068	0.036	23	27	201

[a] mol Cu/weight of HMS (from XPS data in Table 2) ≈ atom-% Cu/[atom-% C × Ar(C) + atom-% O × Ar(O) + atom-% N × Ar(N) + atom-% Si × Ar(Si) + atom-% Cu × Ar(Cu)]. [b] From the nitrogen adsorption isotherm at 77 K.

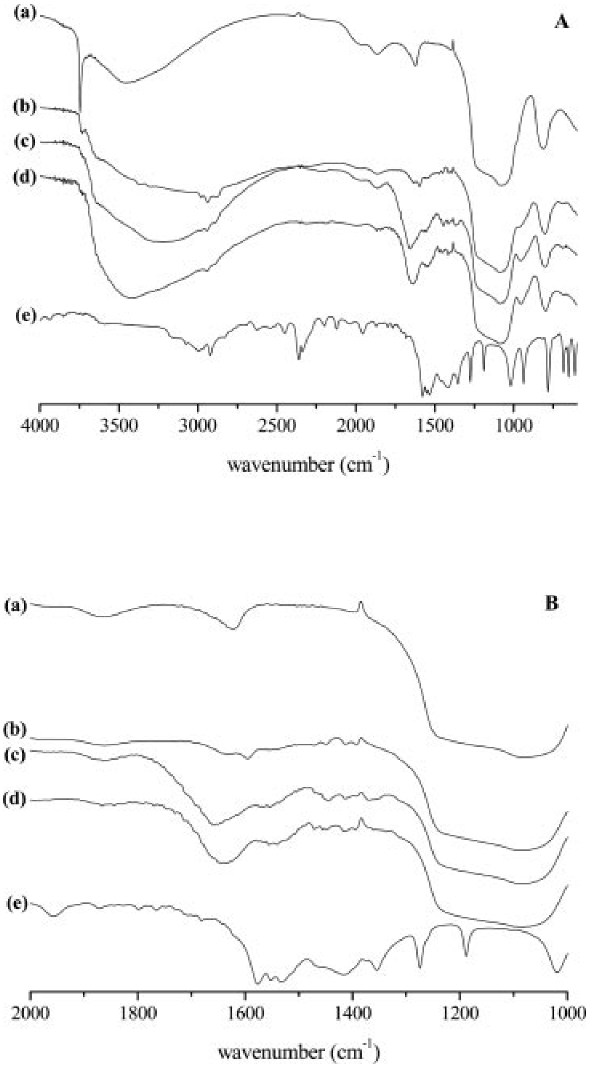


Figure 2. FTIR-DRIFT spectra of (a) calcined HMS, (b) AMPTSi/HMS, (c) [Cu(acac)$_2$]AMPTSi/HMS_A, (d) [Cu(acac)$_2$]AMPTSi/HMS_B and (e) [Cu(acac)$_2$] in the regions (A) 4000–500 cm^{-1} and (B) 2000–1000 cm^{-1}.

Table 2. XPS elemental analysis [atom-%] of the modified HMS materials.

Sample	C	O	N	Si	Cu
AMPTSi/HMS	18.3	57.1	1.8	22.9	–
[Cu(acac)$_2$]AMPTSi/HMS_A	17.9	53.7	2.3	25.6	0.5
[Cu(acac)$_2$]AMPTSi/HMS_B	13.7	51.1	1.9	33.2	0.07
[Cu(acac)$_2$]	66.9	26.0	–	–	7.0

O–H stretching vibrations, and a very sharp band at 3745 cm^{-1}, with medium intensity, which is assigned to the stretching vibrations of isolated surface SiO–H groups, are observed. A band at 1622 cm^{-1} is also observed in the spectrum and is attributed to the H–O–H bending vibrations of physisorbed water (Figure 2).

The HMS material was functionalised with (3-aminopropyl)triethoxysilane (AMPTSi) and both nitrogen elemental and XPS analyses show that nitrogen (Tables 1 and 2) was introduced on the surface of the material: 1.34 mmol g^{-1} and 0.999 mmol g^{-1}, respectively. From the former value and taking into account the AMPTSi used in the functionalisation reaction (3.00 mmol g^{-1}), the anchoring efficiency of the amine derivative onto the support was 44.7 %.

Upon amine functionalisation, a decrease in the intensity of the band at 3745 cm^{-1} is observed (Figure 2A), indicating that the reaction between the isolated silanol groups of the surface of the HMS with the ethoxy groups of the silane derivative took place. The N–H and C–H stretching vibrations of AMPTSi are observed in the region 3400–3000 cm^{-1} and 3000 cm^{-1}, respectively, and the corresponding H–N–H and H–C–H bending vibrations can also be observed in the regions 1700–1500 cm^{-1} and 1500–1300 cm^{-1}, respectively, as weak intensity bands (Figure 1B).

No changes in the isotherm profile were observed upon surface functionalisation of HMS with AMPTSi, suggesting that the structure of the parent material was unaffected after this step (Figure 1); however, a decrease in the HMS surface area (Table 1), as well as some blockage of the micropores and a slight decrease in the mean mesopore size (Figure 1) are observed, as expected.

Anchoring of Copper(II) Acetylacetonate onto the Amine-Functionalised HMS

Two chloroform solutions containing different quantities of copper(II) acetylacetonate were refluxed for 24 h with the amine-functionalised HMS. Evidence for the effective anchorage of the copper(II) acetylacetonate complex onto the surface of AMPTSi/HMS was first provided by noting that (a) the blue colour of the complex solution disappears during the adsorption reaction, and (b) colourless solutions are obtained when the materials were purified by Soxhlet extraction.

Atomic absorption analysis (Table 1) of the materials revealed that the [Cu(acac)$_2$]AMPTSi/HMS_A material contains 362 µmol of copper/g of material and the [Cu(acac)$_2$]-AMPTSi/HMS_B material contains 68 µmol of copper/g. Relatively to the copper(II) complex quantity initially present in each solution, these values correspond to an anchoring efficiency of 73% and 82%, respectively, suggesting the presence of some diffusion control in the metal complex immobilisation reactions.

The N/Cu ratios obtained by elemental analysis and XPS have similar magnitudes (Table 1) suggesting that the anchored copper(II) species have the same chemical environment throughout the HMS matrix. Nevertheless, in both materials the spacer AMPTSi is always in excess relative to complex (larger excess in [Cu(acac)$_2$]AMPTSi/HMS_B).

No change in the isotherm profile was observed upon complex immobilisation (Figure 1), suggesting that the functionalised HMS structure was unaffected by complex anchoring; however, a further decrease in the material surface area (Table 1 and Figure 1), and a slight decrease in the mean mesopore size are observed, confirming indirectly the presence of the complex within the matrices. Surprisingly, the material with lower copper loading, [Cu(acac)$_2$]-AMPTSi/HMS_B, shows a larger decrease in the surface area, specially in the mesopore region, than the material with higher copper loading, [Cu(acac)$_2$]AMPTSi/HMS_A.

The IR spectra of [Cu(acac)$_2$AMPTSi]/HMS_A and [Cu(acac)$_2$AMPTSi]/HMS_B show, with respect to the parent material, some changes in the regions where vibration from AMPTSi occur: 3500–3000 cm^{-1} region, due to N–H stretching vibrations and 1700–1300 cm^{-1}, weak absorptions due to the H–N–H and H–C–H bending vibrations, suggesting that some molecular changes in the spacer took place. On the other hand, new broad bands are observed at about 1658 and 1555 cm^{-1} (Figure 2), which may be attributed to a C=N stretching vibration and to the acetylacetonate ring vibrations of the metal complex, respectively. Furthermore, in the region between 1700 and 1300 cm^{-1}, where the fingerprint bands of [Cu(acac)$_2$] are usually detected, the DRIFT spectra of both [Cu(acac)$_2$AMPTSi]/HMS_A and [Cu(acac)$_2$AMPTSi]/HMS_B materials are different from that of free [Cu(acac)$_2$] (Figure 2), contrasting with a previous report for silica-supported [Cu(acac)$_2$], which shows a very similar DRIFT spectrum to that of the free complex.[23] These results clearly indicate that there was a Schiff condensation between the free amine groups on the surface of the HMS material and the oxygen atoms coordinated to copper(II), and that therefore the anchoring procedure occurred as depicted in Scheme 1.

The electronic spectrum of free [Cu(acac)$_2$] presents a large and asymmetric band with a maximum at λ = 558 nm and a shoulder lying lower in energy at about λ = 642 nm (Figure 3); this spectrum is typical of Cu$^{\mathrm{II}}$ complexes with a square-planar geometry.[16] In this context the band at lower energy is assigned to the $d_{xy} \leftarrow d_{z^2}$ transition and the band at higher energies is attributed to the envelop of two other allowed d–d transitions: $d_{xy} \leftarrow d_{x^2-y^2}$ and $d_{xy} \leftarrow d_{xz} \approx d_{yz}$, which have very close energies.[24]

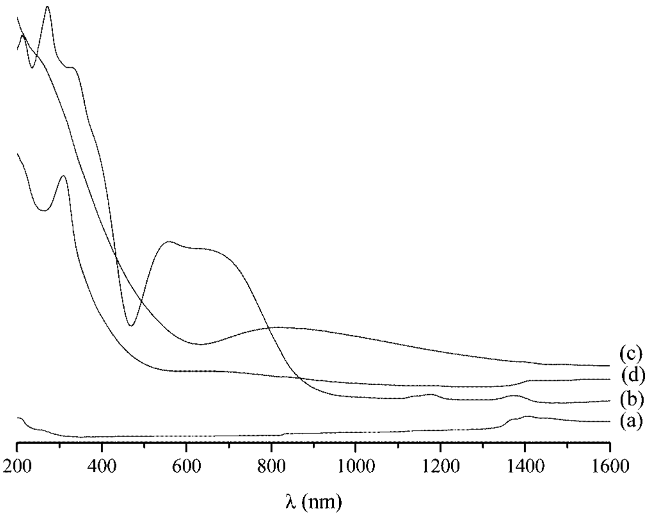


Figure 3. UV diffuse reflectance spectra of the HMS materials: (a) calcined HMS, (b) [Cu(acac)$_2$], (c) [Cu(acac)$_2$]AMPTSi/HMS_A and (d) [Cu(acac)$_2$]AMPTSi/HMS_B.

The electronic spectrum of the [Cu(acac)$_2$]AMPTSi/HMS_A material shows a broad asymmetric band at λ = 823 nm tailoring to lower energies, which corresponds to the envelop of the three allowed d–d transitions ($d_{xy} \leftarrow d_{z^2}$, $d_{xy} \leftarrow d_{x^2-y^2}$ and $d_{xy} \leftarrow d_{xz} \approx d_{yz}$) with close energies. In comparison to the spectrum of free [Cu(acac)$_2$], the maximum of the band is shifted towards lower energy (Figure 3); this type of changes in the electronic spectrum of Cu$^{\mathrm{II}}$ complexes can be interpreted as suggesting a tetrahedral distortion in the equatorial plane or axial coordination of a new ligand.[24] Although the first explanation could justify the proposed complex anchoring model, on the basis of electronic data alone, no choice between the two hypotheses can be made. The profile spectrum of [Cu(acac)$_2$]AMPTSi/HMS_B is similar to the previous one, but its low intensity, due to the lower copper content in this material, prevents any further interpretation (Figure 3).

Further insights into the copper(II) coordination sphere upon complex anchoring can be gathered from EPR spectroscopy. The EPR spectrum of [Cu(acac)$_2$]AMPTSi/HMS_B at 120 K, depicted in Figure 4 (b), is typical of copper(II) species: it is of the axial type and shows hyperfine couplings due to the interaction of the unpaired electron with the copper nucleus (^{65}Cu/^{63}Cu, I = 3/2) in the low magnetic field region (Figure 4b). The EPR spectrum of [Cu(acac)$_2$]AMPTSi/HMS_A (Figure 4a) shows band broadening due to the high local copper(II) concentration (2.30 %, Table 1), which prevents any further analysis. In contrast, the EPR spectrum of the [Cu(acac)$_2$]AMPTSi/HMS_B shows smaller band-broadening effects, and thus could be analysed in detail.

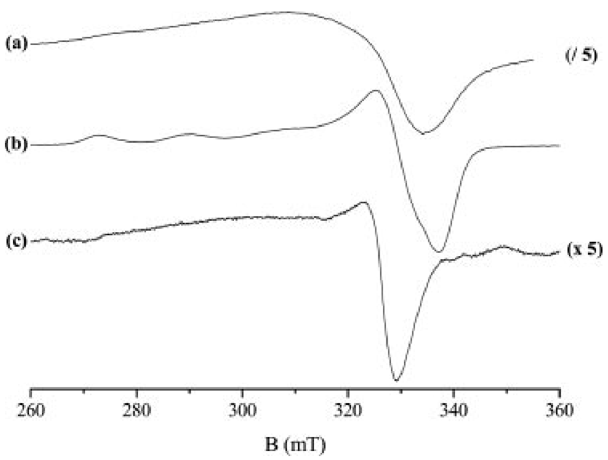


Figure 4. EPR spectra of the copper(II) acetylacetonate complexes, free and anchored onto HMS at 120 K: (a) [Cu(acac)$_2$]AMPTSi/HMS_A, (b) [Cu(acac)$_2$]AMPTSi/HMS_B and (c) [Cu(acac)$_2$]/HMS.

The EPR band profile of this material suggests that there is one major Cu^{II} species within the HMS matrix[20] and its similarity with the EPR of analogous free Cu^{II} complexes[18–20,25–28] allows the same orientation scheme for the tensor axes: $g_1 = g_2 = g_\perp$, $g_3 = g_\parallel$ (or $g_1 = g_x$, $g_2 = g_y$, $g_3 = g_z$), where g_1 and g_3 refer to the lowest and highest magnetic fields g values (obviously, $A_1 = A_2 = A_\perp$, $A_3 = A_\parallel$ or $A_1 = A_x$, $A_2 = A_y$, and $A_3 = A_z$). In this context, as $g_x = g_y < g_z$ the ground state of Cu^{II} in the immobilised complex has been kept and is d_{xy}; the values of the tensors g and A of the [Cu(acac)$_2$]AMPTSi/HMS_B were obtained by simulation and are compiled in Table 3, which also summarises the values for similar copper(II) acetylacetonate/salen-based complexes with O_4, NO_3 and N_2O_2 coordination spheres, as free complexes and immobilised onto other supports found in the literature.

Tetracoordinated copper(II) complexes with an equatorial O_4 coordination sphere generally possess higher $g_\parallel$ values (2.26–2.29)[26–28] relative to copper(II) complexes with an equatorial N_2O_2 coordination sphere (2.19–2.24),[18,29] because the introduction of nitrogen atoms into the equatorial plane increases the in-plane covalence. This can be confirmed by the data extracted from literature and compiled in Table 3. An NO_3 coordination sphere would give rise to intermediate g values, with some overlap with the intervals given above, but confirmation with experimental data is quite difficult due not only to the failure of the preparation the free counterpart of the anchored complex (all synthetic attempts resulted in oils which we were unable to fully characterise), but also to the almost nonexistent EPR data for compounds with these coordinating atoms: only Murphy et al. reported a silica-anchored [Cu(salicylaldimine)] species with an NO_3 coordinating sphere, which showed a $g_\parallel = 2.29$[20] and Talzi et al. reported Cu^{II} complexes with an equatorial NO_3 coordination sphere with $g_\parallel = 2.27–2.28$.[30] Nevertheless, some insights into the coordination sphere of the anchored complex can be gathered indirectly by comparison with g and A values of the parent copper complex and those with mixed NO_3 coordination spheres shown in Table 3.

Comparing the g values of [Cu(acac)$_2$]AMPTSi/HMS_B with those of the free copper(II) acetylacetonate in a non-coordinating solvent ($CHCl_3$, Table 3) a decrease in $g_\parallel$ and $g_\perp$; values, with consequent decrease in the g_{av} value, is observed; these g factors tendencies suggest that the anchored copper(II) complex has a different coordination sphere with higher equatorial covalence,[28] which is typical of the involvement of nitrogen atoms in the direct coordination with Cu^{II}.[20,28] As $g_\parallel = 2.275$ is higher than the typical values observed for copper(II) complexes with an N_2O_2 coordinating sphere and similar to those observed by Talzi et al.,[30] we propose that the major Cu species immobilised in [Cu(acac)$_2$]AMPTSi/HMS_B have an NO_3 coordinating sphere as shown in Scheme 1 (other species, for example, with an N_2O_2 coordination sphere and present in low quantities, cannot be unambiguously excluded because of the solid-state broadening effects in the EPR spectra). Although

Table 3. EPR parameters of the free and immobilised [Cu(acac)$_2$].

Sample (coordination sphere)	$g_\parallel$	$g_\perp$	g_{av}[a]	$\lvert A_\parallel\rvert$[b]	$\lvert A_\perp\rvert$[b]	Ref.
[Cu(acac)$_2$]AMPTSi/HMS_A[c,d]	[d]	[d]	[d]	[d]	[d]	
[Cu(acac)$_2$]AMPTSi/HMS_B[c]	2.275	2.057	2.130	180.0	12.0	[e]
[Cu(acac)$_2$]/$CHCl_3$ (O_4)	2.285	2.060	2.135	180	12	[25]
[Cu(acac)$_2$]/MeHO (O_4)	2.290	2.067	2.141	165.0	15.4	[19]
[Cu(salimine)]/SiO_2 (NO_3)	2.290	2.065	2.140	155	13	[20]
[Cu(salimine)]/SiO_2 (N_2O_2)	2.243	2.065	2.124	183	13	[20]
[Cu(4-OHsalen)]/MeHO (N_2O_2)	2.213	2.062 2.055	2.111	192.2	16.8 36.5	[18]

[a] $g_{av} = 1/3(2\times g_\perp + g_\parallel)$. [b] The values are expressed in 10^{-4} cm^{-1}. [c] At 120 K. [d] Not simulated due to band-broadening effects. [e] This work.

the spectrum was taken at low temperature, the bandwidths of the signals are still large to detect the nitrogen superhyperfine splittings (typically 14–25 G), due to the interaction between the copper unpaired spin and the nitrogen nuclear spin ($I = 1$), hence hindering the direct confirmation of nitrogen atoms coordinated to the copper(II) centre in the equatorial plane. Further confirmation of the proposed NO_3 coordination sphere for Cu species in [Cu(acac)$_2$]-AMPTSi/HMS_B and the exclusion of complex immobilisation through axial coordination to the free amines of the support can be gathered from the $A_{\parallel}^{Cu}$ values. Axial coordination to a square-planar complex usually leads to a decrease of the metal hyperfine couplings:[26–29] in our case, upon immobilisation of the complex onto the support, no change in the $A_{\parallel}^{Cu}$ value was observed, suggesting that no effective axial coordination took place with the functionalised matrix.

Despite the band-broadening effects in the [Cu(acac)$_2$]-AMPTSi/HMS_A spectrum that prevented its simulation and detailed analysis, the same coordinating sphere is proposed, because the N/Cu ratio is much lower than in [Cu(acac)$_2$]AMPTSi/HMS_B (Table 1), and thus the in situ formation of an anchored copper(II) complex with an N_2O_2 coordinating sphere is less likely to occur.

It is noteworthy that in a control experiment, where a [Cu(acac)$_2$] solution in chloroform was refluxed with the unfunctionalised HMS for 24 h, a very low copper content (see Figure 4) was obtained after purification. This indicates that the functionalisation of the support with amine groups leads to higher metal loadings, as observed by us when activated carbon was used as the heterogeneous support.[16] The anchoring process of the copper(II) acetylacetonate onto the calcined HMS must occur through axial coordination of the Cu^{II} centre to the isolated hydroxy groups of the HMS surface. The confirmation was achieved by the observation in the FTIR spectrum of a decrease in the intensity of the band at 3745 cm^{-1}, which is due to the isolated silanol groups. Taking into account that upon amine functionalisation of HMS there is a significant decrease in the intensity of this band (vide supra, Figure 2), it may be concluded that the axial coordination of the Cu^{II} centre to the isolated hydroxy groups of the surface of the HMS is hindered in the amine-functionalised HMS material.

The EPR spectrum of this material, [Cu(acac)$_2$]/HMS, was also recorded and is shown in Figure 4c. Although the spectrum could not be simulated due to the low intensity of the signal, some qualitative information relating to the anchored complex can be gathered from the spectrum profile. With respect to the spectrum of [Cu(acac)$_2$]AMPTSi/HMS_B (Figure 4b), that of [Cu(acac)$_2$]/HMS shows the parallel region at higher magnetic field values as a broad band, which corresponds to the envelope of the unresolved four features due to the Cu hyperfine splittings. The main consequence of this is an increase in $g_{\parallel}$ and a decrease in $A_{\parallel}^{Cu}$. By using the data from analogous Cu complexes[26–29] and those referred to in Table 3, it can be clearly shown that in the unfunctionalised HMS, the Cu centre lies in an equatorial O_4 plane and possesses axial coordination to the matrix hydroxy groups. On the contrary, in the NH_2-functionalised HMS, the Cu centre has a coordination sphere which involves the nitrogen atoms of the modified matrix and no significant axial coordination takes place.

Catalytic Experiments

The results obtained for the aziridination of styrene, catalysed by the [Cu(acac)$_2$] in homogeneous phase, and immobilised onto the amine-functionalised HMS are collected in Table 4, at room temperature, using PhI=NTs as nitrogen source.

Both [Cu(acac)$_2$]AMPTSi/HMS_A and [Cu(acac)$_2$]-AMPTSi/HMS_B materials acted as heterogeneous catalysts in the aziridination of styrene. As it was not possible to prepare the free counterparts of the anchored complexes, the catalytic activity of the heterogeneous copper complexes were compared with the parent free complex [Cu(acac)$_2$]. In this context, the former heterogeneous catalyst showed improved catalytic efficiency (styrene conversion and total TON, Figure 5) with respect to free [Cu(acac)$_2$] in the homogeneous phase, under similar experimental conditions. This is an important result, as the modification of the coordination sphere of the parent complex upon immobilisation

Table 4. Aziridination of styrene catalysed by the [Cu(acac)$_2$] in the homogeneous phase and heterogenised using PhI=NTs as nitrogen source.[a]

Catalyst	Run	t [h][b]	% C[c]	Total TON[d]	Initial TOF [h^{-1}][e]
[Cu(acac)$_2$]		0.5	69	11	21
AMPTSi/HMS		24	21		
[Cu(acac)$_2$]AMPTSi/HMS_A	1st	4	92	21	8
	2nd	24	79	24	7
	3rd	24	40	14	5
[Cu(acac)$_2$]AMPTSi/HMS_B	1st	24	15	3	0.5
	3rd	24	12	13	0

[a] Catalyst/styrene/chlorobenzene (internal standard)/PhI=NTs (1:100:100:20), in CH_3CN, at room temperature. [b] Time needed for total consumption of PhI=NTs. [c] Corrected for limiting reagent (PhI=NTs). [d] TON = mmol converted styrene/mmol Cu. [e] Initial TOF calculated for 1 h of reaction.

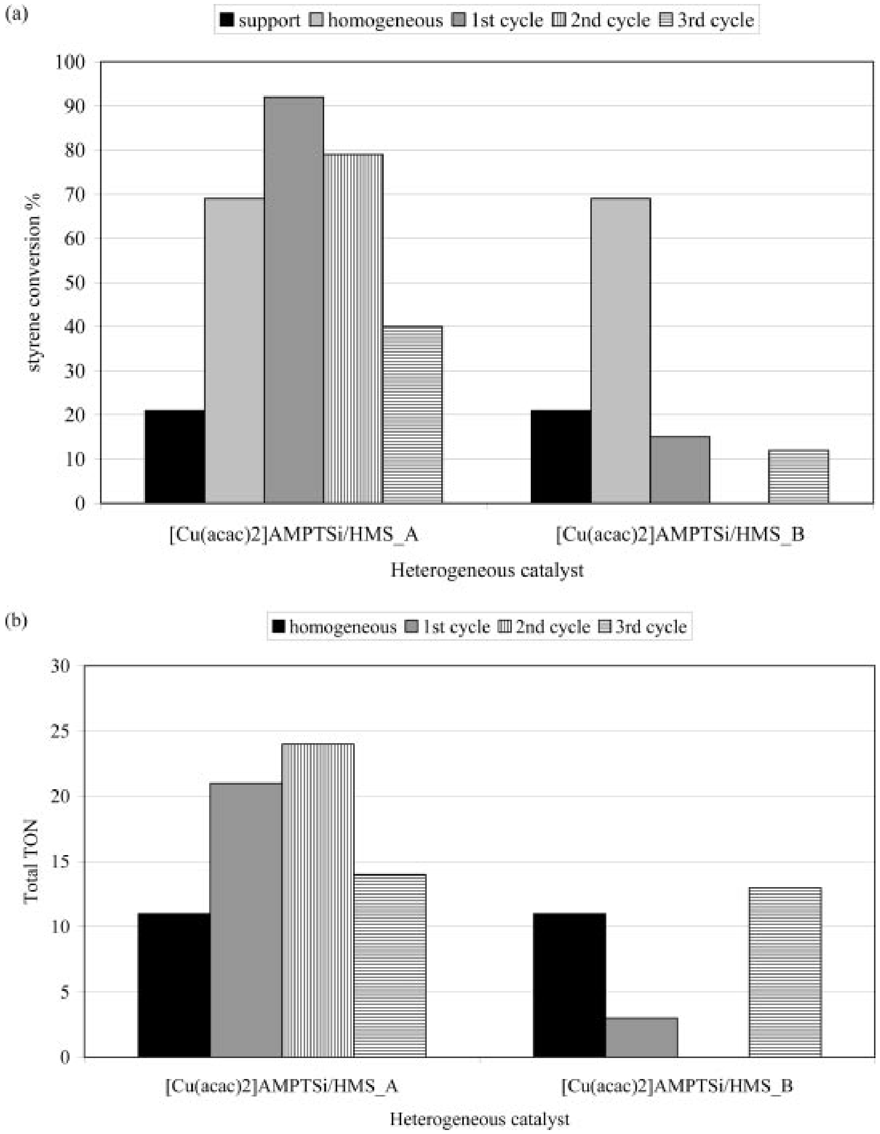


Figure 5. (a) Styrene conversion (%) and (b) total TON of the [$Cu(acac)_2$] in the homogeneous phase and heterogenised onto an amine-functionalised HMS.

led to an increase in the catalytic activity, contrasting with usual decrease observed in the majority of the anchorage procedures, which involve the coordination sphere of the catalytic centres.

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 HMS porous structure, as the nitrogen source is a solid with limited solubility in acetonitrile, and its solubilisation is controlled by its rate of consumption.[4] Besides the formation of *p*-toluenesulfanamide, due to competitive homolytic cleavage of the PhI=NTs,[4] only very small amounts of benzaldehyde and epoxide were detected in the reaction media by gas chromatography.

The AMPTSi/HMS support also shows some catalytic activity in the conversion of styrene, but much smaller compared with the new heterogeneous catalysts. Nevertheless, the amount of the benzaldehyde by-product observed in the product mixture, can be related with residual catalytic activity of the support.

The materials could be reused at least in two other catalytic reactions with formation of aziridine. However, the catalyst [$Cu(acac)_2$]AMPTSi/HMS_A showed a loss of the catalytic activity with reuse, giving, nevertheless, better catalytic efficiency (total TON) than the reaction run in homogeneous phase with the [$Cu(acac)_2$], under similar experimental conditions. The catalyst [$Cu(acac)_2$]AMPTSi/HMS_B showed improved catalytic efficiency in the 2nd reutilisation, and then a small drop in the 3rd cycle, which may be explained by a considerable decrease in the catalyst mass during the recycling procedure.

Nonetheless, the typical IR bands of the immobilised (Schiff base)copper(II) complex and silica backbone of both catalysts after the catalytic cycles remained unchanged, indicating the stability of the catalytic active species and support itself under the catalysis experimental conditions.

Hence, the loss of catalytic activity with reuse of the new heterogeneous catalyst may be due to slight leaching of active species, promoted by some degradation of the bond between the support and the spacer.

The [Cu(acac)$_2$]AMPTSi/HMS_A heterogeneous catalyst reported herein, which consists of copper(II) acetylacetonate anchored onto an amine-functionalised hexagonal mesoporous silica, presents higher catalytic activity in the aziridination of styrene, at room temperature, using PhI=NTs as nitrogen source, than [Cu(acac)$_2$] anchored onto a triamine-functionalised activated carbon.[17] However, it is not as stable and reusable as the latter heterogeneous catalyst, because this could be reused at least for 4 times with successive increase in styrene conversion, and thus in the total turnover number (TON) and initial activity (TOF).

Conclusion

Copper(II) acetylacetonate was anchored onto an HMS material using a two-step procedure: (i) functionalisation of the surface hydroxy groups with (3-aminopropyl)triethoxysilane and then (ii) anchoring of the copper(II) complex through Schiff condensation with free amine groups, using two different metal loadings.

Nitrogen elemental analysis, XPS and DRIFT showed the presence of amine groups on the surface of the HMS material and porosimetry indicated that the structure of the mesoporous material remained unchanged after this step.

Atomic absorption and XPS data showed that the copper(II) acetylacetonate could be irreversibly immobilised onto the amine-functionalised HMS through Schiff condensation between the surface amine groups and the oxygen atoms of the copper(II) ligand, leading to an NO_3 coordination sphere for the anchored metal complex. This was confirmed by the combination of data extracted from FTIR and EPR spectra of the materials.

The new [Cu(acac)$_2$]AMPTSi/HMS materials were 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 higher than those of the same reaction catalysed in homogeneous phase by [Cu(acac)$_2$]; nevertheless, the initial activity decreases and reaction time increases due to substrate and product diffusion limitations. The heterogeneous catalyst showed a successive slight decrease in catalytic activity when reused for two more times.

Experimental Section

Materials and Reagents: All reagents and solvents used in the preparation and modification of the hexagonal mesoporous silica (HMS) were used as received. Copper(II) acetylacetonate, 1-dodecylamine and (3-aminopropyl)triethoxysilane (AMPTSi) were from Aldrich; tetraethoxysilane was from Lancaster; toluene and other solvents used in the synthesis procedures were from Fischer Scientific (analytical reagent grade) and those used in the catalytic experiments and as eluents were from Romil or Fischer Scientific (HPLC grade). The nitrene donor 4-methyl-*N*-(phenyl-λ^3-iodanylidene)benzenesulfonamide (PhI=NTs) was synthesised using reported procedures.[31]

Synthesis and Modification of Hexagonal Mesoporous Silica (HMS)

Synthesis of Hexagonal Mesoporous Silica (HMS): The HMS was synthesised using a reported procedure;[22] tetraethoxysilane (37.0 mL, 0.166 mol) was added to a stirred solution of ethanol (88.1 mL, 1.51 mol), water (88.5 mL, 4.91 mol) and 1-dodecylamine (10.3 mL, 0.0448 mol). The mixture was stirred at room temperature for 24 h. The white precipitate obtained was vacuum-filtered, washed with deionised water (100 mL) and ethanol (100 mL). In order to remove the template (1-dodecylamine), the precipitate was calcined at 600 °C for 24 h.

Functionalisation of the HMS with (3-Aminopropyl)triethoxysilane (AMPTSi/HMS): A mixture of calcined HMS (3.00 g) in dry toluene (50.0 mL) and (3-aminopropyl)triethoxysilane (9.00 mmol, 2.10 mL) was refluxed for 24 h. The material was vacuum-filtered, washed with toluene (3 × 50 mL) and dried overnight in an oven at 85 °C.

Anchoring of Copper(II) Acetylacetonate onto Amine-Functionalised HMS: A solution of copper(II) acetylacetonate (0.1304 g, 498 µmol) in chloroform (100 mL, light blue solution) was refluxed with AMPTSi/HMS (1.02 g) for 24 h. At the end of the process, the colour of the solution was sligthtly blue. The solid was vacuum-filtered, washed with chloroform (3 × 20 mL), and then Soxhlet-extracted with chloroform for 6 h. Finally, the solid was dried overnight in an oven at 85 °C. This material will be referred to as [Cu(acac)$_2$]AMPTSi/HMS_A. Another material with lower complex loading was also prepared: [Cu(acac)$_2$]AMPTSi/HMS_B. In this case AMPTSi/HMS (0.35 g) was refluxed with copper(II) acetylacetonate (0.0077 g, 29 µmol) in chloroform (10 mL, light blue solution) for 24 h, after which an almost colourless solution was obtained after filtration of the material. The material was washed with chloroform (3 × 20 mL) and then Soxhlet-extracted with chloroform (150 mL) for 6 h. The blue solid was dried in an oven at 100 °C, after which it was light brown.

Physico-Chemical Measurements: Nitrogen elemental analysis and copper atomic absorption were performed by Microanalytical Services, University of Manchester, U. K. Surface area measurements were performed monitoring the N_2 adsorption isotherms at 77 K with a Micrometrics ASAP 2010 apparatus. Surface areas were calculated using the BET equation over the pressure range p/p_0 = 0.02–0.2. X-ray photoelectron spectroscopy was carried out with a Kratos AXIS His instrument equipped with a charge neutraliser and an Mg-K_α X-ray source. Spectra were recorded at normal emission with an analyser pass energy of 20 eV and an X-ray power of 225 W. The FTIR-DRIFT spectra of the powered materials were obtained with a Bruker Equinox 55 spectrophotometer in the region 400–4000 cm^{-1}. The UV diffuse reflectance spectra were obtained with a Shimadzu UV-3101 PC in the range 1600–200 nm, using barium sulfate as reference. EPR spectra were recorded with a Bruker ESP300 EPR spectrometer equipped with an X-band microwave bridge. Temperature control was achieved with a Bruker ER-4111 variable-temperature controller, the temperature at the centre of the EPR cavity was calibrated using a separate thermocouple. The spectra were taken at 120 K with the following typical experimental conditions: modulation frequency: 100 kHz; modulation amplitude: 5 G; microwave power: 1–5 mW. The EPR parameters were obtained by simulation using the program Win EPR Simfonia (Bruker) assuming axial or rhombic spin Hamiltonians. The reported values of $g_\perp$ (or g_x and g_y) and $A_\perp$ (or A_x and A_y) are less accurate because of their dependence on the used line widths (50–60 G). 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: 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. HPLC chromatograms were obtained with a Merck Hitachi Lachrom apparatus consisting of a pump L-7100, UV detector L-7400, interface D-7000, autosampler L-7200 and a column oven L-7300 equipped with a Phenomenex Luna 5u C18(2), 250 × 4.6 mm column. The eluent used was a mixture of 85% of acetonitrile and 15% of water with a flow rate of 1 mL min^{-1}.

Catalysis Experiments: The activity of the catalysts in the aziridination of styrene was studied at room temperature using a molar ratio of metal catalyst/alkene/chlorobenzene (internal standard)/PhI=NTs = 1:100:100:20 in acetonitrile (5.00 mL), whilst stirring. For the experiments with the catalyst $[Cu(acac)_2]$AMPTSi/HMS_A, styrene (1.22 mmol), chlorobenzene (1.22 mmol, internal standard), heterogeneous catalyst (0.0300 g) and PhI=NTs (0.244 mmol, nitrogen source) were used; for the experiments with catalyst $[Cu(acac)_2]$AMPTSi/HMS_B, styrene (0.20 mmol), chlorobenzene (0.20 mmol, internal standard), heterogeneous catalyst (0.0300 g) and PhI=NTs (0.041 mmol, nitrogen source) were used. During the experiment, 0.05-mL aliquots were taken from the solution with a hypodermic syringe, filtered through 0.2-µm PTFE syringe filters and directly analysed by GC-FID. When the entire PhI=NTs had disappeared from the solution and the ratio of the areas of iodobenzene and chlorobenzene in the chromatogram was constant, the solution was centrifuged at 3500 rpm for 15 min, and then to the decanted solution another portion of PhI=NTs (0.244 mmol) was added. This procedure checks the eventual existence of metal complex leaching to the reaction medium. The presence of the aziridine at the end of the reaction was confirmed by HPLC. The heterogeneous catalysts were then washed/centrifuged sequentially with acetonitrile (3 × 10 mL) and methanol (1 × 10 mL) and oven-dried at 90 °C overnight. These materials were reused for further two 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 AMPTSi/HMS material, the precursor of both heterogeneous catalysts.

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