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Mesoporous Metal Complex–Silica Aerogels for Environmentally Friendly Amination of Allylic Alcohols

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Two series of mesoporous hybrid iron(III) complex-silica aerogels were prepared in one-pot synthesis by using the sol-gel coordination chemistry approach. The use of the ligands 3-(2aminoethylamino)propyltrimethoxysilane and 2-(diphenylphosphino)ethyltriethoxysilane, both with terminal triethoxysilyl groups, were used to incorporate metal complexes in situ into the framework of silica, through their co-condensation with a silicon alkoxide during the aerogel formation. This methodology yielded optically translucent hybrid mesoporous gels with homogeneous metal incorporation and excellent textural properties. The catalytic performance of these materials was tested in the direct amination of allylic alcohols in water as a target reaction, with activities comparable or even higher than those corresponding to the homogeneous iron(III) complex. Furthermore, these catalysts were stable and maintained their catalytic activity after six reaction cycles.

Homogeneous catalysts exhibit high activity and selectivity but they are difficult to recover and reuse.^[1] Heterogenisation of metal complexes on mesoporous supports overcomes these limitations by easing catalyst separation and reuse, avoiding leaching and retaining the activity and selectivity of the homogeneous catalysts.^[2] Traditionally, mesoporous silicas have been used as a catalyst support.^[3] More recently, silica aerogels are becoming ideal candidates to be used as catalyst supports because their high specific surface area, high porosity, good accessibility and simple surface functionalisation.^[4,5] One of the properties that characterises an aerogel is the major accessibility of reagents and products to the catalyst when supported owing to the open-pore structures and interconnectivity in three dimensional networks.^[4f] So, they are widely used in nu-

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Herein, we report the synthesis of hybrid iron(III) complexsilica gels by using the sol-gel coordination approach, in which a metal complex with ligands containing terminal trialkoxysilane groups is hydrolysed either in the presence or absence of other silica sources to produce a coordination complex-silica network.^[5] The main advantages of this approach are that it does not require anaerobic or anhydrous environments, and it is performed under mild conditions, preserving the integrity of the metal complexes in the framework, ensuring an homogeneous dispersion along the support and avoiding the pore blocking.^[5] This methodology has already been used to incorporate metal nanoparticles and metal complexes in mesoporous silica and organosilica supports.^[5b-e] Monomer complexes have been prepared under the same reaction conditions and characterised fully before the formation of the mesoporous materials by spectroscopic (FTIR, Raman, UV/Vis) and spectrometric techniques. Once the gels containing 1 wt% Fe^{III} were synthesised and characterised, the activity of these materials as supported heterogeneous catalysts was evaluated. The catalytic performance of these materials has been tested in the direct amination of allylic alcohols in water as solvent as the target reaction.^[6] This transformation, which yielded allylic amines with water as the only by-product, has recently been described with FeCl₃·6H₂O as catalyst, obtaining the corresponding amination products in high yields.^[7] In addition, we have compared the results herein to those obtained with the homogeneous catalyst and the metal-free hybrid gels to elucidate which iron(III) species are the active phase in the reaction in aqueous media

Iron(III) complexes

Monomeric Fe^{III} complexes were obtained by stirring an $FeCI_3 \cdot 6H_2O$ solution with two different ligands, 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTS, L1) and 2-(diphenylphosphino)ethyltriethoxysilane (PPETS, L2), in 1:2 and 1:3 metal/ligand molar ratios under the same conditions as those used for the synthesis of the hybrid mesoporous metal complex-silica gels (i.e., by using a ethanolic aqueous solution at room temperature). The colour of the solution with L2 changed from yellow (initial ethanolic $FeCI_3 \cdot 6H_2O$ solution) to blue but that with L1 remained unchanged, according to the substitution of chloride ligands by L1 or L2 after the addition of the ligands. Both solutions with L1 and L2 in water were a yellow-orange colour, owing to the incorporation of water

merous application fields, including thermal insulators, drug release, drug delivery, catalysis and adsorption.^[4]

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Figure 1. UV/Vis spectra of a) Fe-L1 (1:2) $(-\cdot-\cdot)$ and b) Fe-L2 (1:2) $(-\cdot-\cdot)$ complexes in comparison with the UV spectra of the corresponding L1 (____) and L2 (____) ligands. The spectra were recorded in an ethanol solution.

molecules in the coordination sphere. Accordingly, matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF) analysis indicated that, in the complex with amine ligand L1, the ligand occupied two coor-

dination positions and, with phosphine ligand L2, one coordination position was occupied, independently of the ligand amount added, with water molecules filling up the hexacoordinated environment. Thus, non-coordinated ligand was present in the solution, as previously reported for Fe^{III}-amine complexes. $\ensuremath{^{[8a]}}$ UV/Vis spectra of $\ensuremath{\mathsf{Fe}^{\text{III}}}$ complexes with their respective ligands are shown in Figure 1. Both complexes displayed high energy bands ($\lambda = 203$, 224, 276 nm for Fe-L1 and $\lambda = 207$, 250 nm for Fe-L2) associated with the intraligand charge transfer transition $\pi \rightarrow \pi^*$. Low energy features (shoulder near $\lambda =$ 340 nm for Fe-L1 and $\lambda = 367$ nm for Fe-L2) were most likely a result of metal-perturbed intraligand transitions.^[8] Metal complex formation was confirmed further by FTIR and Raman measurements, as discussed later.

Mesoporous metal complex-silica catalysts

The preparation of the hybrid mesoporous metal complex–silica catalyst is illustrated in Scheme 1. Firstly, the Fe^{III} complex was obtained in tetraethylor-thosilicate (TEOS; silica precursor), then an ammonia fluoride solution was added to induce the co-condensation of the terminal trialkoxysilane groups of the ligands with the silica precursor. After 15 min under magnetic stirring at room temperature, an orange gel was formed. Optically transparent gels were obtained by this method with the two ligands in two different ligand/metal molar ratios (see Scheme 1). The nomenclatures, elemental composi-

Table 1. Nomenclature, metal and ligand incorporation, and BET surface area of the as-synthesised hybrid gels.									
Sample	Fe ^[a]	L ^[b] [w	t %]	L/Fe [™] ratio	$S_{BET}^{[h]}$				
	[wt %]	EA ^[c]	TGA ^[d]	in silica ^[e]	[m ² g ⁻¹]				
silica gel	-	-	-	$\begin{array}{c} -\\ 1:1 & (1.4^{[f]}/1.8^{[g]})\\ 1:1 & (1.2^{[f]}/2.0^{[g]})\\ 1:1 & (1.7^{[f]}/2.2^{[g]})\\ 1:1 & (2.4^{[f]}/3.3^{[g]}) \end{array}$	820				
gel-Fe- L1 (1:2)	0.82	4.4	5.8		660				
gel-Fe- L1 (1:3)	1.00	4.8	7.9		550				
gel-Fe- L2 (1:2)	0.62	7.2	5.5		810				
gel-Fe- L2 (1:3)	0.42	6.8	5.6		830				
[a] From ICP-OES analysis after treatment of the samples with aqua regia. [b] Ligand content in the hybrid gels from [c] elemental analysis (based on N and C contents for L1 and L2, respectively) and [d] TGA. [e] From MALDI-TOF. [f] From elemental analysis. [g] From TGA. [h] BET surface area estimated by using a multipoint BET method with adsorption data in the P/P_0 range 0.05–0.30 after supercritical drying of the samples.									

tions, incorporation yields and BET surface areas of the synthesised samples are shown in Table 1.

The loadings of Fe^{III} in the mesoporous hybrid materials determined by using inductively coupled plasma optical emission spectrometry (ICP-OES) were 0.82–1 wt% for the amine ligand L1 and slightly lower for the phosphine ligand L2. The rates of incorporation of the organic moieties calculated by thermogra-



Scheme 1. Formation of Fe^{III} complex and incorporation into the framework of the silica aerogel. L=L1 or L2 (L1 is shown in the reaction).

vimetric analysis (TGA) were 65–85% for L1 and 60–80% for L2, very similar to the results obtained by elemental analysis, which confirmed the presence of the different ligands in the siliceous materials.

MALDI-TOF measurements of gel suspensions confirmed that the Fe^{III} complexes maintained their coordination sphere after incorporation into the silica framework (Table 1, column 4). The preservation of the structure and the effective incorporation of Fe^{III} complexes into the silica network was confirmed further by diffuse-reflectance UV/Vis, FTIR and RAMAN analyses. Diffuse-reflectance UV/Vis spectra of the gels, both air-dried (gel-Fe-L) and supercritically dried (aerogel) in comparison with the corresponding metal complex spectra are shown in Figure 2. The broad band centered around



Figure 2. Diffuse reflectance UV/Vis spectra of hybrid mesoporous gels containing a) Fe-L1 (1:2) and b) Fe-L2 (1:2) complexes before (gel; -----) and after (aerogel; -----) supercritical drying in comparison with the diffuse reflectance UV/Vis spectra of the corresponding metal complexes (----) and complex-free wet silica gel (----).

 $\lambda = 400$ nm, attributed to ligand-to-metal charge transfer absorptions owing to phosphine and amine–Fe^{III} (3d) transitions in metal complexes, appeared also in silica materials, thus confirming the presence of these complexes in the silica framework after their incorporation.^[2c,8]

Raman spectra of hybrid mesoporous gels show the band characteristics of the metal complexes, independently of the amount of ligand added. As an example, the spectra of the Fe-L1 (1:2) and Fe-L2 (1:2)-based systems are shown in Figure 3 (top) and Figure S1, respectively. In addition to the bands corresponding to the silica network, SiO–H at $\tilde{\nu} \approx 2900 \text{ cm}^{-1}$, Si–OH tension at $\tilde{\nu} = 970 \text{ cm}^{-1}$, Si–O–Si network symmetric bond stretching vibration at $\tilde{\nu} = 790 \text{ cm}^{-1}$, and the rocking motion of the bridging oxygen atoms and stretching motions in the Si–O–Si backbone centred at $\tilde{\nu} \approx 490 \text{ cm}^{-1}$, ^[5,9] absorptions corresponding to metal complexes can be clearly observed. Stretching vibrations of both the hydrocarbon chains (v(CH)) and the aromatic rings (v(=CH)) appear at $\tilde{\nu} = 2895$ and 2935 cm⁻¹, respectively (not shown). The band at $\tilde{\nu} = 1083 \text{ cm}^{-1}$ owes to the vibrations of the v(C–N) bond in the amine ligand. In all cases,



Figure 3. a) Raman spectra in the $\tilde{\nu} = 1500-100 \text{ cm}^{-1}$ range and b) FTIR spectra of hybrid mesoporous aerogels containing Fe-L1 (1:2) complex (____) compared to spectra of metal complex-free silica aerogel (____), monomer complex Fe-L1 (1:2) (____) and ligand L1 (____).

v(Fe–Cl) and v(Fe–N) vibrations are masked by the wide band at $\tilde{v} = 490 \text{ cm}^{-1}$ due to the silica.^[10] The same features have been observed for Fe-L2-based systems (see Figure S1). Bands characteristic of aromatic groups appear at $\tilde{v} = 1585 \text{ cm}^{-1}$ (v(C=C)) and at $\tilde{v} = 983$, 1022 and 1100 cm⁻¹, corresponding to deformations of the plane in the ring formed by CH bonds, and v(Fe–P) are masked by the wide band at $\tilde{v} = 490 \text{ cm}^{-1}$ due to the silica,^[10] thus confirming the presence of the metal complexes in the silica gels.

Finally, FTIR spectra of the materials show the characteristic bands of the respective ligands (see Figure 3, bottom and Figure S2). Several absorptions appear in the high energy region ($\tilde{\nu} = 2965-2840 \text{ cm}^{-1}$) associated to the v(C–H) stretching vibration of the aromatic rings in complexes with **L2** and CH₂ units. In this zone, the absorptions observed at $\tilde{\nu} = 3274$ and 3231 cm^{-1} (v(N–H)) for the gel-Fe-**L1** or at $\tilde{\nu} = 3074$ and 3060 cm^{-1} (v(C–H)Ph) for the gel-Fe-**L2** are hidden by a broad band centred at $\tilde{\nu} \approx 3400 \text{ cm}^{-1}$ (v(O–H)) in the spectra of the corresponding metal complex–mesoporous silica materials. The signal corresponding to the N–H vibrations in the spectrum of the complex with the ligand **L1** is very weak but it should show four bands assigned as N–H vibrations ($\tilde{\nu} = 3408$,

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3339, 3254 and 3212 cm⁻¹) and two bands due to the free ligand ($\tilde{\nu}$ = 3353 and 3195 cm⁻¹). Generally, the NH₂ group produces only two bands in this region.^[Ba]

The complex with the ligand L2 exhibits peaks at $\tilde{\nu} \approx 632$ and 1384 cm⁻¹ corresponding to δ (C–H) and v(C–H) vibrations of the benzene ring, respectively. A weak absorption at $\tilde{\nu} \approx 1465$ cm⁻¹, which could be assigned to a δ (C–H) deformation vibration, is also observed for the four materials. The peaks at $\tilde{\nu} = 1050$ and 1066 cm⁻¹ are assigned to the v(Si–O) and v(Si–C) vibrations.^[1,5b,8b] The spectrum of the Fe-L2 (1:2)based system also displays a weak signal at $\tilde{\nu} = 1417$ cm⁻¹ characteristic of the v(P–C) stretching vibration. v(Fe–Cl) ($\tilde{\nu} =$ 308, 290 cm⁻¹) and v(Fe–N) ($\tilde{\nu} = 420$ cm⁻¹)^[11] or v(Fe–P) ($\tilde{\nu} =$ 544 cm⁻¹)^[8b] stretching absorptions are not observed in the FTIR spectra.^[1,8,11] These results demonstrated the successful incorporation of the Fe complexes into the network of the silica materials.

The mesoporous nature of the as-synthesised gels was investigated by using N_2 adsorption-desorption isotherms at 77 K and TEM. N_2 physisorption experiments were also performed to investigate the influence of the incorporation of the Fe^{III} complexes on the textural properties of the hybrid gels after supercritical drying. For comparison purposes, the isotherm of the metal complex-free silica gel is also included in Figure 4. After the supercritical drying of the wet gels, all sam-



Figure 4. N₂ adsorption-desorption isotherms at 77 K of hybrid mesoporous gels containing a) Fe-L1 and b) Fe-L2 complexes after supercritical drying. ■: Silica aerogel, □: aerogel-Fe-L (1:2), ▼: aerogel-Fe-L (1:3).

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ples showed type IV isotherms, typical of mesoporous materials, in agreement with an aerogel structure.^[4f] The incorporation of the metal complexes into the silica materials enhanced the adsorption process at $P/P_0 > 0.6$, which was characteristic of the interparticle meso-macroporosity. Based on the isotherms, the textural parameters of the samples were calculated. BET surface area values are listed in Table 1. Interestingly, BET surface area was not affected by the incorporation of the complexes and was in some cases even higher than in the complex-free material, probably due to the additional interparticular mesoporosity caused by the incorporation of the metal complexes with terminal trialkoxysilane groups. The samples possess a broad pore size distribution including mesopores and macropores.^[4f]

TEM analyses revealed that all the hybrid catalysts comprised an amorphous and highly porous silica network in which the Fe^{III} complexes were homogeneously dispersed (see Figure 5 and Figure S3). Representative TEM images of the



Figure 5. Representative TEM images of the silica gels containing 1 wt% Fe-L2 (1:3) a) before and b) after supercritical drying. Scale bars = 10 nm.

silica gel before and after supercritical drying—optically translucent gels were obtained after supercritical drying—clearly showed that the silica gels preserved their pore structure (see Figure 5 and Figure S3) after supercritical drying. This observation supports the concept that the as-synthesised metal complex silica hybrids were aerogels. The absence of any contrast caused by metal clusters corroborated that no agglomeration of the Fe^{III} complexes occurred upon immobilisation, thus confirming the incorporation of these complexes into the framework of the mesoporous silica gel,^[2b] which, taking into account their textural properties, made them ideal candidates for catalytic applications.

Catalytic activity

Once the mesoporous silica gels were characterised, they were evaluated as heterogeneous catalysts. For this purpose, the direct amination of allylic alcohols was chosen as the target reaction.^[6] This transformation has been recently described by using FeCl₃·6 H₂O as catalyst in water as solvent, obtaining the corresponding amination products in high yields.^[7] Taking advantage of this strategy, we decided to emulate the reported reaction conditions by using our wet aerogels instead of the FeCl₃·6 H₂O (Table 2). Firstly, the reaction was performed with

Table 2. Catalyst sc OH Ph Ph + 1a	reening. ^[a] TsNH ₂ 2a	Catalyst (10 mol% Fe) H ₂ O, 90 °C 24 h	NHTs Ph Ph 3aa		
Entry	Sample		Conv. ^[b]		
1 2 3 4 5 6 7 8 9	silica-FeCl gel-Fe-L1 gel-Fe-L2 gel-Fe-L2 silica gel silica-L2 g silica-L2 g FeCl ₃ -6 H ₂ !	₃ -6 H ₂ O (ligand-free) (1:2) (1:3) (1:2) (1:3) (1:3) (1:3) (complex-free) (el (1:3) (complex-free) (el (1:3) (complex-free) (c)	< 10 95 36 95 77 42 23 ≈ 10 86		
[a] Reaction conditions: 1a (42 mg, 0.2 mmol), 2a (68 mg, 0.4 mmol, 2 equiv) and catalyst (525 mg) in H_2O (1 mL). [b] From ¹ H NMR analysis of the reaction crude.					

the ligand-free Fe^{III}–silica gel sample, obtaining poor conversions at best to the product (*E*)-*N*-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (**3 aa**, Table 2, entry 1). This result could suggest a poor accessibility of the reactants to the active phase in the heterogeneous catalyst. The low yield obtained for the ligand-free catalysts suggested negligible leaching; otherwise, the reaction would have worked in the homogeneous phase as previously reported in the case of FeCl₃-6 H₂O.^[7]

Next, Fe-L complex–silica gels were tested. To our delight, the results improved considerably (Table 2, entries 2–5). Especially good were the results achieved with Fe-L1 (1:2) and Fe-L2 (1:2)-gels containing 2 units of AEAPTS and PPETS ligand per Fe^{III} atom, respectively (Table 2, entries 2 and 4). These results corroborated the stability of the Fe^{III} complexes after incorporation into the silica gel network, resulting in high accessibility to the active phase due to the ligands, which acted as spacers that created mesoporous active regions.

We also ran control experiments employing the supports in the absence of Fe^{III} to test if the reaction was promoted by them alone. When the silica gel without ligand or Fe^{III} was employed, a 42% yield of the corresponding amination product was obtained (Table 2, entry 6). When the other supports containing only the ligands (silica–AEAPTS and silica–PPETS) were used, even lower results were achieved (Table 2, entries 7 and 8).

Notably, results obtained with Fe-L1 (1:2) and Fe-L2 (1:2) catalysts are slightly superior to those obtained with FeCl₃·6H₂O in water^[7a] and close to those obtained with FeCl₃·6H₂O in organic solvents.^[7b] A possible explanation for this behaviour could be the presence of EtOH in the wet aerogel, which would increase the solubility of the organic reactants.

With gel-Fe-L1 (1:2) and gel-Fe-L2 (1:2), we decided to further optimize the reaction conditions. To learn about the reaction kinetics, the above mentioned reaction was monitored by measuring the conversion at different reaction times, catalysed by these two heterogeneous catalysts and homogeneous FeCl₃·6 H₂O. This study revealed that gel-Fe-L2 (1:2) had a comparable or slightly superior activity to homogeneous $FeCI_3$ - $6H_2O$ as its reaction was complete after 6 h rather than 24 h, which was necessary with gel-Fe-L1 (1:2).

To make this transformation even more attractive from the environmental point of view, we decided to study the recyclability of these hybrid gels. In the allylic amination reaction in water catalysed by FeCl₃•6 H₂O, attempts to recycle the catalyst were performed but were unsuccessful due to the formation of the corresponding hexaaquo complex.^[7] This limitation made the recycling procedure tedious and difficult and it was thus discarded. The heterogeneity of the catalysts herein made them more suitable for recycling. The gel-Fe-L2 (1:2) sample, which showed the better catalytic performance, was chosen (Table 3) for recycling experiments. Following the standard pro-

Table 3. Recyclability OH Ph Ph +	of catalyst g TsNH ₂	el-Fe- L2 (1:2). ^[a] Gel-Fe- L2 (1:2) (10 mol% Fe) H ₂ O, 90 °C	NHTs	
1a	2a	6 h	3aa	
Cycle		Yie	ld ^[b]	
1		9	1	
2		8	9	
3		9	3	
4		6	1	
5		10	7	
6		8	7	
[a] Reaction conditions: 1a (42 mg, 0.2 mmol), 2a (68 mg, 0.4 mmol, 2 equiv) and catalyst (525 mg) in H_2O (1 mL). [b] Isolated yield after flash chromatography.				

cedure and after the 1st reaction cycle, ethyl acetate (3×3 mL) was added and the organic layer decanted, after which residual traces of organic solvent were removed under vacuum. As shown in Table 3, the heterogeneous catalyst contained in the reaction water was thus reused up to 6 times without apparent activity loss. The discordant values observed in cycles 4 and 5 can be ascribed to a change in the gel-Fe-L2 catalyst morphology; after the 4th cycle the structure became more colloidal, thus inhibiting proper decantation of the organic layer. As a consequence, a drop in the yield was obtained. This situation was overcome after the 5th cycle; after the addition of ethyl acetate the reaction tube was centrifuged, allowing perfect decantation of the organic phase. The extremely high "107%" yield resulted from the incomplete extraction of the amination product in the previous cycle. This centrifugation procedure was also followed in the 6th cycle, which yielded similar results to the 1st cycle.

Finally, we analysed the Fe content in the reaction solvent (water) to discard any catalytic activity derived from Fe^{III} leaching. This was measured by using ICP-MS after the first and last cycles and we observed total Fe contents of 80 ppb and 4.02 ppm, respectively. These small quantities would not have been enough to catalyse the reaction, thus we concluded that the reaction was catalysed exclusively by the Fe^{III} complex-silica mesoporous gels.

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In summary, hybrid iron(III) complex-silica mesoporous gels with homogeneous metal incorporation and excellent textural properties were obtained through the sol-gel coordination chemistry approach. These hybrid mesoporous gels were applied in the direct amination of allylic alcohols as heterogeneous catalysts in water as the solvent with a comparable or slightly superior activity than previously described with iron(III) chloride hexahydrate in water, obtaining the corresponding amination products in high yields in less than 6 h. The results obtained with the silica aerogel-iron(III)-2-(diphenylphosphino)ethyltriethoxysilane hybrid as the catalyst were particularly positive. In addition, these heterogeneous catalysts were recovered and reused over at least 6 cycles without any apparent loss of catalytic activity, having demonstrated that this activity resulted exclusively from the heterogeneous catalyst and not from iron(III) leaching.

Experimental Section

Synthesis of Fe^{III} complexes

Two series of Fe^{III} complexes were synthesised by using FeCl₃·6H₂O (Aldrich, 97%) as the Fe^{III} source and the ligands AEAPTS (L1, Aldrich, \geq 80%) and PPETS (L2, Gelest, 97%). In a typical synthesis, yellow solutions of FeCl₃·6H₂O (65 mg, 0.240 mmol) in a mixture of ethanol/water (7.5:7.0 mL) were treated with the corresponding quantity of the ligand and the mixtures stirred for 10 min to yield yellow–orange solutions. Fe^{III} complexes were labelled as Fe-L1 (M/L) and Fe-L2 (M/L), in which M/L represented ligand/metal molar ratios of 1:2 or 1:3.

Synthesis of mesoporous hybrid Fe^{III} complex-silica aerogels

Catalysts were synthesised by co-condensation of the Fe^{III} complexes with the silica source TEOS (Aldrich, 98%). NH₄F (Aldrich, 98%) and NH₄OH (Aldrich, 30 wt% in water) were used as nucleophilic catalysts for the condensation of the silica network (see Scheme 1).

In a typical synthesis, TEOS (5 mL, 0.022 mmol), FeCl₃·6H₂O (65 mg, 0.240 mmol) and ligand **L1**or **L2** (160 mg) were stirred magnetically in absolute ethanol (4 mL) for 10 min. To induce the silica gel formation, $0.5 \,\text{M}$ NH₄F (0.028 mL, 0.014 mmol) and $30 \,\%$ NH₄OH (0.122 mL, 0.857 mmol) in a water/ethanol (2.4:1) solution (11 mL) were added to the above solution. The mixture was reacted at RT for 15 min under vigorous stirring. The pore fluids of the gels were exchanged (multiple times) into acetone. Wet gels were dried by using the critical point drying method at 8.6 MPa and 35 °C. The Fe^{III} concentrations in the silica gels were kept at 1 wt% and the metal/ligand molar ratios used were 1:2 and 1:3.

Complex-free silica gel and Fe^{II} -free gel samples, both of them colourless, were prepared following the same procedure without addition of Fe^{III} salt and/or ligands. For comparison purposes, a ligand-free Fe^{III} -silica gel (orange in colour) was also prepared under the same conditions.

Physicochemical characterisation

To characterise the as-synthesised hybrid materials, samples were dried by using the supercritical drying process, resulting in optically translucent gels in all cases. Chemical compositions of the silica ${\sf Fe}^{III}$ complex hybrid materials were characterised by using FTIR, Raman and UV/Vis spectroscopies and MALDI-TOF and ICP-OES spectrometries. The morphologies of the mesoporous materials were investigated by using TEM and the porous texture was characterised by N_2 adsorption–desorption isotherm analysis at 77 K. See the Supporting Information for details.

Catalytic measurements

To an open-air flask containing hybrid gels (525 mg, equivalent to 10 mol% of Fe^{III}), (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**, 42 mg, 0.2 mmol), *p*-toluenesulfonamide (**2a**, 68 mg 0.4 mmol, 2 equiv) and H₂O (1 mL) were added. The tube was sealed and the reaction mixture stirred at 90 °C for 6 h. After this time, the mixture was cooled to RT, then ethyl acetate (3×3 mL) was added and the solution stirred vigorously for 5 min. The organic phase was then decanted (note: this can be performed on a centrifuge stirring the mixture for 3 min at 2500 rpm), dried over MgSO₄ and evaporated to afford crude (*E*)-*N*-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (**3aa**), which was purified by using flash chromatography. To reuse the synthesised hybrid gels in water, traces of organic phase were gently evaporated under vacuum.

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Mesoporous Metal Complex-Silica Aerogels for Environmentally Friendly Amination of Allylic Alcohols



The incredible hybrid: Hybrid mesoporous iron(III) complexes-silica gels are an excellent catalyst for the environmentally friendly amination of allylic alcohols in water.