Modification of MCM-41 *via* ring opening of a strained [1]ferrocenophane

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The walls of the mesoporous silicate MCM-41 can be functionalised with ferrocenyl end groups by reaction with an alkane solution of (1,1′-ferrocenediyl)dimethylsilane; the product is studied by solid-state NMR and EXAFS spectroscopies.

The synthesis, characterisation and potential uses of the new generation of mesoporous silicates has attracted considerable interest in recent years.[1,2] The size of the channels (diameters of 20–100 Å) allows the catalytic conversion of substrates much larger than previously possible using zeolites. The immobilisation of transition-metal catalysts on the surface is possible by utilising the reactivity of the hydroxy groups on the pore walls (an estimated 8–27% of the silicons are silanols in MCM-41[3,4]).

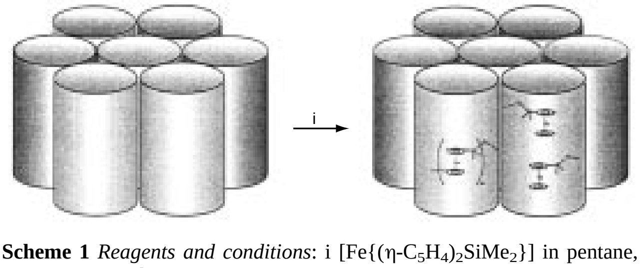
Bein and coworkers reported the surface attachment of a trimethylstannyl complex in MCM-41,[5] and Thomas and coworkers successfully achieved the inclusion of titanium dioxide nanoparticles inside the channels of MCM-41 using an organotitanium precursor.[6]

Here we report on the use of the ring-opening reaction of the strained metallocenophane $[Fe\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$[7,8] as a high-yield, low-temperature method of functionalising mesoporous silicates.

The functionalisation of a silica surface with (1,1′-ferrocenediyl)dimethylsilane, was first reported by Wrighton and coworkers[7] and utilises the susceptibility of [1]ferrocenophanes to nucleophilic attack by the hydroxy groups on the surface of the silica wall. It has been found previously that reaction of [1]ferrocenophanes with nucleophiles can lead, depending on the reaction conditions, to oligomeric and high molecular mass species[8,9] as well as stoichiometrically ring-opened species.

MCM-41 was prepared according to the published procedure.[10] It was activated at 540 °C for 8 h and then heated to 150 °C under a vacuum of 10^{-4} Torr for 6 h. Treatment with a pentane solution of $[Fe\{(C_5H_4)_2SiMe_2\}]$ for 24 h under nitrogen gave an orange powder (Scheme 1). The orange solid was then washed repeatedly with dry pentane until the pentane extracted remained colourless. Trace amounts of ferrocene were recovered from the pentane washings. The proportion of [1]ferroceneophane converted to ferrocene was 4–5%, while the rest was immobilised within the host. Elemental analysis indicated that a high loading of the organometallic guest into the silicate had been achieved, typical analysis gives 8.28 mass% Fe. XRD showed the product to be a slightly less well defined hexagonal phase than the original MCM-41 used, with a lattice constant, a = 45.8 Å. Reaction with iodine vapour under vacuum immediately turned the solid green, indicating facile oxidation of the ferrocenyl units.

The ferrocenyl-functionalised MCM-41 **1** was investigated using ^{13}C and ^{29}Si solid-state NMR and Fe K-edge EXAFS spectroscopy. The room-temperature solid-state CP MAS ^{29}Si NMR is shown in Fig. 1(*b*). Four resonances can be observed, the two closely spaced signals at δ −101.1 and −108.0 can be assigned as two convoluted broad signals representative of the silica framework, consisting mainly of Q_3 and Q_4 units with the presence of a very little Q_2 [where Q_n is defined as $Si(OSi)_n(OH)_{4-n}$]. A comparison with the ^{29}Si NMR of the original mesoporous silicate showed that the intensities of Q_2 and Q_3 had decreased significantly. This was confirmed by a significant decrease in the ν(OH) adsorptions in the IR spectrum. The signal at δ 7.0 can be assigned as an $(O)_3SiR$ (R = alkyl) in accordance with previously reported chemical shifts for such species.[1,11] The remaining narrow signal at δ −6.5 has a longer relaxation than its neighbours, and hence some ring-down can be observed at this acquisition time. This resonance has been assigned to the bridging silicon atoms present in small oligomeric units of poly(ferrocenylsilane) with the first unit



Scheme 1 *Reagents and conditions*: i $[Fe\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$ in pentane, room temp., 24 h

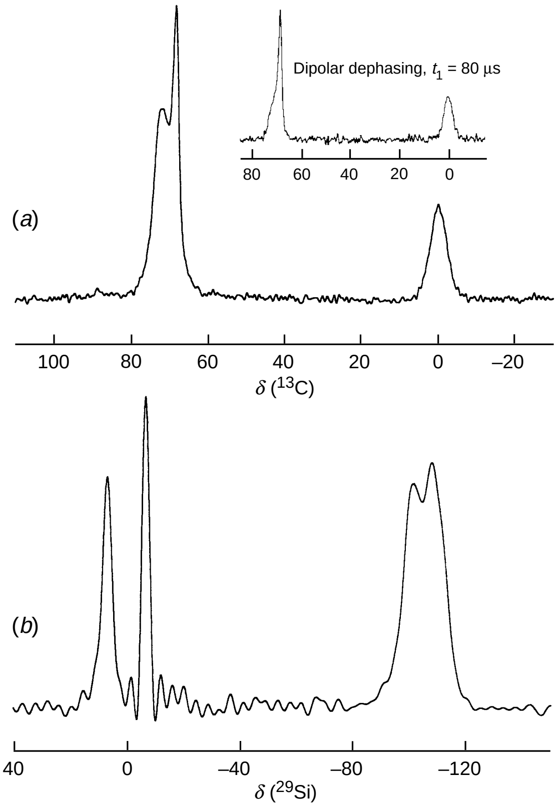


Fig. 1 (*a*) Room-temperature 50.32 MHz solid-state ^{13}C CP MAS NMR spectra of $[Fe\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$/MCM-41 **1** with spinning rate of 2.66 kHz. Contact times were 1 ms and recycle delay 2 s. (*b*) Room-temperature 39.76 MHz solid-state ^{29}Si CP MAS NMR spectrum of $[Fe\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$/MCM-41 **1** at a spinning rate of 2.47 kHz. Contact time 2 ms and recycle delay 3 s. Recorded on a Bruker MSL200.

bound to the channel wall by comparison to the value of δ −6.4 quoted for the shift of poly(ferrocenylsilane) in C_6D_6 solution.[8] The narrower linewidth, suggesting longer spin–spin relaxation time, is consistent with a model of a molecule that exhibits more motional averaging relative to its counterparts, and this would be possible through rotation about a bond to the silicon atom.

The room-temperature solid-state ^{13}C CP MAS NMR spectrum of **1** is shown in Fig. 1(*a*). Three broad resonances are observed, all of which are broader than those of the related crystalline ferrocene compounds. The broadness is due to the range of chemically different environments in which the molecules are located, giving rise to an envelope of peaks with very similar chemical shifts. The isotropic chemical shifts are at δ −0.1, 68.6 and 72.1 with full widths at half maximum (FWHM) of 234, 105 and 220 Hz respectively. The widths can be compared with those of the solid-state NMR of the [1]ferrocenophane which were measured as 180.7 Hz (δ 77–79.5, C_5H_4), 30.3 Hz (δ 34.4, cyclopentadienyl C–Si) and 58.3 Hz (δ −2.5, CH_3). The signal at δ −0.1 can be assigned to the methyl carbons attached to bridging silicon atoms, be they bonded to the wall of the silicate *via* an oxygen or to another ferrocenyl unit (expected chemical shifts of δ *ca.* 0.4 and −0.5, respectively). The set of peaks downfield is due to cyclopentadienyl carbons of the modified ferrocene analogue. The sharper, more clearly defined peak at δ 68.6 is the free C_5 ring comparable to the chemical shift observed for the cyclopentadienyl ring formed from the ring-opening reaction of (1,1′-ferrocenediyl)dimethylsilane with CD_3OD. Cross-polarization and dephasing techniques (described by Alemany *et. al.*[12]) were employed to discern between the carbon atoms in the system. These experiments showed that the broad peak at δ 72.1 exhibited rapid dephasing [see Fig. 1(*a*), inset] and so we assign this signal to the CH groups of the static cyclopentadienyl ring grafted to the walls. Dephasing was slower for the neighbouring signal, indicating an attenuated $^{13}C–^{1}H$ dipolar coupling, as a result of greater motional freedom in the form of ring rotation. The methyl carbons attached to the silicon demonstrated an attenuation of effective $^{13}C–^{1}H$ coupling owing to rapid rotational motion.

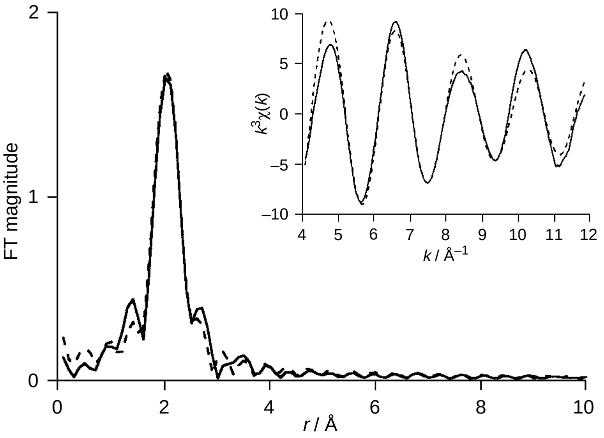


Fig. 2 Fourier transform of the K-edge transmission EXAFS spectrum (shown in inset) for the [Fe{(η-C_5H_4)$_2$SiMe_2}]/MCM-41 **1**, together with best fit (—) experiments, (---) theory. Data was collected on station 8.1 [equipped with a Si(220) monochromator and ion chambers for obtaining data in transmission mode] of the CLRC synchrotron radiation source, Daresbury (2 GeV with typical current ranging from 150 to 250 mA). Data analysis was carried out using curved-weight theory[13] to obtain the structural parameters outlined in Table 1.

Table 1 EXAFS structural parameters for [Fe{(η-C_5H_4)$_2$SiMe_2}]/MCM-41 **1**[a]

Atom type	N^b	r^c/Å	Error (%)	$\sigma^{2\,d}$/Å^2	Error (%)
C	10	2.045	0.1	0.0073	1
C	2	2.555	1	0.0098	4

[a] *R* factor for refinement = 22.0 defined as $R = \int|\chi^T - \chi^E|k^3dk / \int|\chi^E|k^3dk \times 100\%$ (T = theory, E = Experiment). [b] *N* = coordination number. [c] *r* = interatomic distance. [d] σ = Debye–Waller factor.

The Fe K-edge EXAFS of **1** was recorded on Station 8.1 at the SRS Daresbury Laboratory. Fig. 2 shows the observed and best fit to the model described below. The analysis was initially conducted by postulating a model of ferrocene for the Fe centre, and therefore selecting a single shell (coordination sphere) of ten carbon atoms using standard scattering treatment of the EXAFS data.[13] Refinement gave a bond distance appropriate and comparable to that observed in crystals of ferrocene (Fe–C_{av} 2.045 Å). The best fitting was achieved by including an additional second shell of two carbon atoms. This shell is thought to arise from neighbouring rather than bonding carbon atoms (most likely from methyl groups attached to the silicon atoms) or as result of multiple scattering complications due to collinearity of the cyclopentadienyl carbons.

In conclusion, we have demonstrated the use of strained ferrocenophanes to functionalise mesoporous silicates. Both solid-state NMR and EXAFS spectroscopy indicate that the organometallic guest has remained intact within the silicate structure and is tethered to the silicate wall *via* Si–O linkages.

We thank the EPSRC for access to the SRS, Daresbury Laboratory and Dr Mosselmans for his help with the EXAFS experiments. We also thank EPSRC for studentships (S. O'B., J. T., S. B.).

Footnote

† D. O'Hare is the Royal Society of Chemistry Sir Edward Frankland Fellow.

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Received, 8th January 1997; Com. 7/00176B