

**Structural Studies of MCM-48 Derivatized with
(1,1'-Ferrocenediyl)dimethylsilane**

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The Editors
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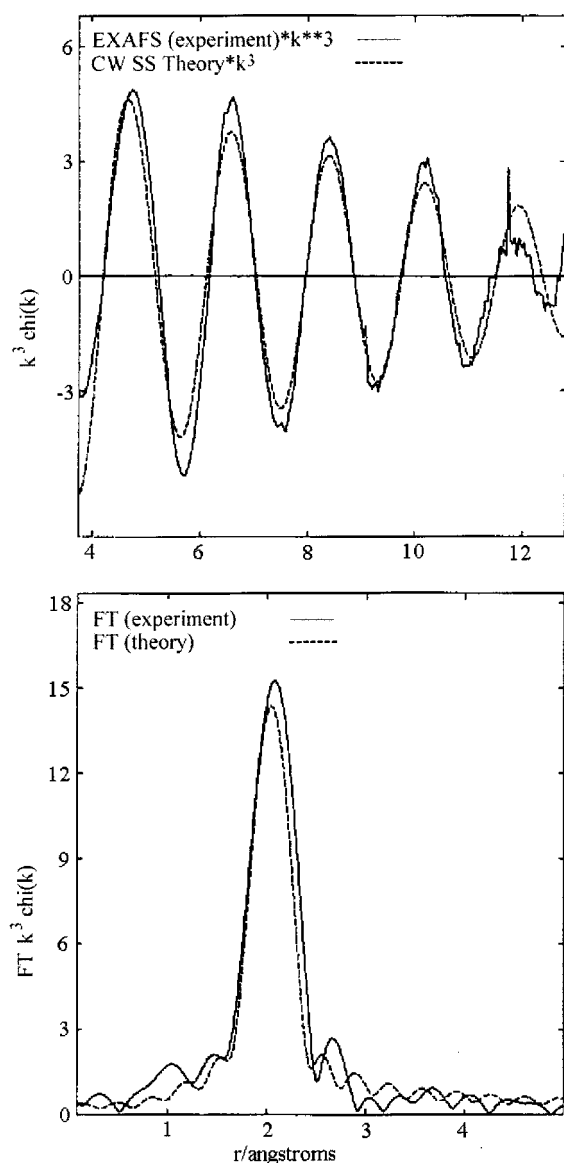


Figure 6. Fe K-edge k^3 -weighted EXAFS spectrum and Fourier transform, phase-shift corrected for carbon (— experimental; ----- curved wave theory, fit B in Table 1), of $[\text{Fe}\{\eta\text{-C}_5\text{H}_4\text{SiMe}_2\}]$ at 298 K

were very large: R factor 45.5%, E° -1.8 eV, $r(\text{Fe}-\text{C})$ $2.023(5)$ Å, $2 \sigma^2$ $0.0236(17)$ Å², $r(\text{Fe}\cdots\text{Si})$ $2.736(33)$ Å, $2 \sigma^2$ $0.0176(83)$ Å². A better fit to the experimental data was obtained by starting from fit A and refining the coordination number (fit B, Table 1, Figure 6). The final value was 4.3 but the error in this value must be much higher than 20% for the reasons outlined above.

Conclusion

The pore walls of mesoporous siliceous MCM-48 have been successfully derivatized with (1,1'-ferrocenediyl) dimethylsilane. The organometallic complexes react with the MCM-48 surface silanols (particularly of the Q³ type) to give a $\text{C}_5\text{H}_4\text{SiMe}_2\text{-O}$ linkage to the silica surface. Despite

the fact that MCM-48 and MCM-41 possess very different mesoporous surfaces, this process strongly resembles the process previously reported for the functionalization of the latter by strained ferrocenophanes.

Experimental Section

General: All preparations and manipulations were performed using standard Schlenk techniques under an oxygen-free and water-free argon atmosphere. Pentane was dried by reflux over Na/benzophenone ketyl, distilled under argon, and kept over 4-Å molecular sieves. — Powder X-ray diffraction (XRD) data were collected on a Philips Xpert diffractometer using Cu- K_α radiation filtered by Ni. — Microanalyses were performed at the TU Munich. — Infrared spectra were recorded on a Unicam Mattson Mod 7000 FTIR spectrophotometer using KBr pellets and/or solutions. — ^{29}Si - and ^{13}C -NMR spectra were recorded at 79.49 and 100.62 MHz, respectively, on a (9.4 T) Bruker MSL 400P spectrometer. ^{29}Si -MAS NMR spectra were recorded with 40° pulses, spinning rates of 5.0–5.5 kHz, and 60 s recycle delays. ^{29}Si -CP MAS NMR spectra were recorded with 5.5 μs pulses, a spinning rate of 5.0 kHz and 5 s recycle delays. Chemical shifts are quoted in parts per million relative to TMS. ^{13}C -CP MAS NMR spectra were recorded with 4.5 μs pulses, a spinning rate of 8 kHz, and a 4 s recycle delay. Chemical shifts are quoted in ppm relative to TMS. — Nitrogen adsorption isotherms were recorded using a CI electronics MK2-M5 microbalance connected to a vacuum manifold line. The as-made MCM samples (typically around 0.02 g) were dehydrated overnight at 723 K to an ultimate pressure of 10^{-4} mbar, and then cooled to room temperature prior to adsorption. Extra care with the functionalized materials was necessary and so the samples were dehydrated at 423 K to prevent the destruction of the functionalities. Nitrogen isotherms were then recorded at 77 K. Equilibration of each data point was monitored using CI electronics Labweigh software, and the pressure monitored using an Edwards Barocel pressure sensor. Specific surface areas, A_{BET} , were determined from the linear part of the BET equation ($P/P_0 = 0.05\text{--}0.3$). — Fe K-edge X-ray absorption spectra were collected at room temperature in transmission mode on station 9.2 [double crystal Si(220) order-sorting monochromator, 50% harmonic rejection] of the Synchrotron Radiation Source at the Daresbury Laboratory, operating at 2 GeV in single bunch mode, with typical currents of 13–19 mA. Solid samples, diluted if necessary with boron nitride, were held between layers of mylar film in 0.5 mm thick aluminium plates. Two spectra were recorded for each sample and summed using the program EXCALIB, available on the Daresbury computer XRSSERV1. The program EXBACK was used to extract the raw EXAFS, $\chi^E(k)$, and curve-fitting analyses, by least-squares refinement of the non-Fourier filtered k^3 -weighted EXAFS data, were carried out within EXCURVE (version EXCURV98^[13]) using spherical wave methods.^[14] Phase shifts were calculated using Von Bart ground state and H. Lundqvist exchange potentials.

$[\text{Fe}\{\eta\text{-C}_5\text{H}_4\text{SiMe}_2\}]$ was prepared by the method reported by Wrighton^[15] and purified by sublimation under vacuum.

MCM-41 was synthesized according to the literature employing $[(\text{C}_{14}\text{H}_{29})\text{NMe}_3]\text{Br}$ as a templating agent.^[16] After calcination (540 °C/6 h) and dehydration (200 °C under a vacuum 10^{-4} Torr for 8 h) the material was characterized by XRD, N_2 adsorption and IR spectroscopy.

MCM-41/ $[\text{Fe}\{\eta\text{-C}_5\text{H}_4\text{SiMe}_2\}]$ was prepared as described in the literature.^[4] Elemental analysis indicated 8.33 mass-% Fe. — IR

(KBr): $\tilde{\nu} = 3574$ vs cm^{-1} , 3096 m, 2963 m, 1645 s, 1365 m, 1234 vs, 1169 vs, 901m, 816 s, 798 s, 667 m. — (^1H , ^{13}C , ^{29}Si) NMR spectroscopic data are in agreement with ref.^[4]

MCM-48 was synthesized according to the literature employing $[(\text{C}_{16}\text{H}_{33})\text{NMe}_3]\text{Cl}$ as a templating agent.^[17,10b] After calcination (540°C/6 h) and dehydration (220°C at 10^{-4} Torr for 6 h) the material was characterized by XRD, N_2 adsorption and IR spectroscopy.

Preparation of MCM-48/[Fe $\{(\eta\text{-C}_5\text{H}_4)_2\text{SiMe}_2\}$]: A suspension of MCM-48 (0.5 g) in pentane (15 mL) was treated with a solution of $[\text{Fe}\{(\eta\text{-C}_5\text{H}_4)_2\text{SiMe}_2\}]$ (0.35 g) in pentane. After 24 h at room temperature, the resulting suspension was filtered off and the remaining orange solid was washed several times with pentane, and dried under an oil-pump vacuum. The pentane washings contained trace amounts of the starting material $[\text{Fe}\{(\eta\text{-C}_5\text{H}_4)_2\text{SiMe}_2\}]$ and ferrocene, identified by solution ^1H -NMR spectroscopy. — Elemental analysis indicated 8.18 mass-% Fe. — IR (KBr): $\tilde{\nu} = 3454$ vs cm^{-1} , 3103 m, 2960 m, 1637 s, 1423 m, 1234 vs, 1169 vs, 1081 vs, 968 m, 900 m, 822 s, 798 s, 667 m, 453 s.

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