Synthesis of Iron-containing MCM-41

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A mesoporous crystalline iron-containing MCM-41 molecular sieve is prepared by direct hydrothermal synthesis; XRD, framework IR, ESR, UV–VIS and solid-state ^{29}Si MAS NMR spectroscopies provide evidence of iron(III) incorporation into framework positions.

Many groups have synthesized various kinds of *microporous* iron silicates (FeZSM-5,[1–3] FeNu-1,[4] *etc.*) and characterized their structural and catalytic properties. Here, we report the synthesis and partial characterization of *mesoporous* crystalline iron-containing MCM-41 molecular sieve. MCM-41 is a family of mesoporous non-layered crystalline aluminosilicate molecular sieves, characterized by pore diameters that can be adjusted between 18 and 100 Å, and an unusually large sorption capacity demonstrated by its benzene adsorption capacity > *ca.* 15% (*m*/*m*) at 50 Torr and 298 K, which is used as a sorbent and a catalyst component for the conversion of organic and inorganic compounds.[5,6]

An Fe-containing MCM-41 sample was prepared by the conventional crystallization method, hydrothermal synthesis. Ferric nitrate, fumed silica, sodium hydroxide and hexadecyltrimethylammonium bromide (CTMABr) were used as starting materials for the synthesis of the Fe-MCM-41 molecular sieve. The ferric nitrate was added to a dilute solution containing sodium hydroxide, CTMABr and fumed silica. The molar ratios of the components in the synthesis slurry were as follows: $SiO_2:Fe_2O_3 = 50–100:1$, $(CTMA)_2O:SiO_2 = 0.1:1$, $OH^-:SiO_2 = 0.5–1:1$.

The crystallization of the molecular sieves was performed hydrothermally under autogenous pressure within 7–10 d at 423 K. The as-synthesized product Fe-MCM-41 was white. The calcination of the Fe-MCM-41 sample was carried out at 773 K in nitrogen and air. The calcined Fe-MCM-41 was also completely white, indicating the absence of coloured oxides of iron, at least in bulk form, outside the zeolite crystals. The calcinated sample was shown to have a sorption capacity of 15% (*m*/*m*) cyclohexane ($p/p_0 = 0.5$, 293 K). The chemical analyses were performed using a ICP 9000 (N + m) spectrometer, the $SiO_2:Fe_2O_3$ ratio in Fe-MCM-41 ($SiO_2:Fe_2O_3$ in the gel was 100:1) was found to be 150:1. The sodium content in the protonic form of the sample was less than 0.05% (*m*/*m*). Because of the high purity of the silica used the concentration of Al in Fe-MCM-41 was negligible ($SiO_2:Al_2O_3 > 1000:1$). NMR experiments proved unable to detect the presence of any Al in Fe-MCM-41.

An X-ray powder diffraction pattern of the sample confirmed the presence of a highly crystalline ferrisilicate with the ultra-large pore molecular sieve MCM-41[5,6] structure (Fig. 1). There are two very strong intensity peaks at *ca.* 2θ 1.9 and 2.1°.

The structural arrangement of the iron species is easily detectable by ESR techniques.[7,8] As depicted in Fig. 2, two different signals occur in the spectrum of the as-synthesized sample. The signal with $g = 4.2$ is assigned to iron(III) ions in a distorted tetrahedral coordination, whereas the line with $g = 2.0$ belongs to iron(III) ions in a highly symmetric octrahedral environment.[7]

No adsorption bands in the 'crystal field' region were observed by UV–VIS spectroscopic studies, indicating the absence of d–d transitions.

The framework IR spectrum of the as-synthesized Fe-MCM-41 is shown in Fig. 3. On introduction of Fe, most of the bands are shifted to lower wavenumbers consistent with their incorporation in lattice positions. Additionally, an absorption band at *ca.* 660 cm^{-1} assigned to the vibration of Si–O–Fe linkages[9] is observed. Moreover, an absorption band at 960 cm^{-1} is also observed, which was not observed in Al-MCM-41 samples. This could be related to iron incorporation into framework positions. We believe that the 960 cm^{-1} band could

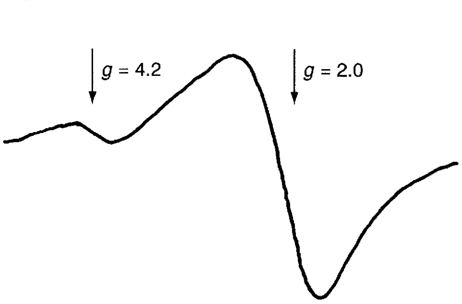

Fig. 2 ESR spectrum of FeMCM-41 (JES-FELIXG ESR spectrometer)

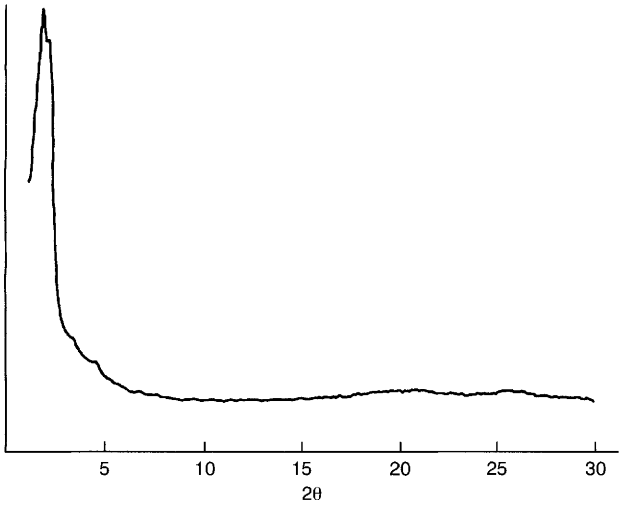

Fig. 1 X-Ray powder diffraction pattern of FeMCM-41 (Rigaku D/MAX rA, Cu-Kα radiation)

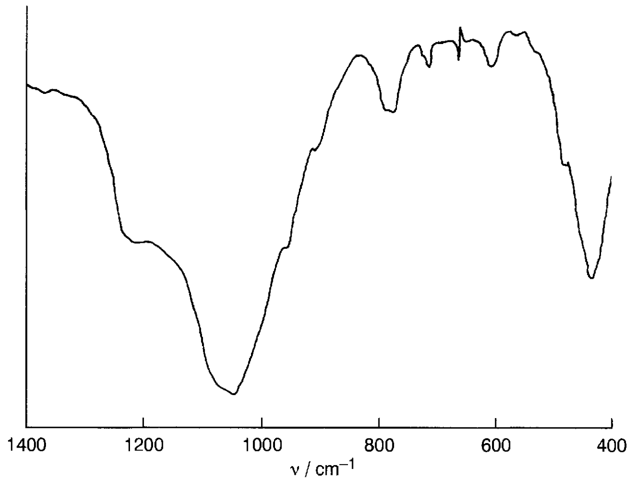

Fig. 3 Framework IR spectrum of FeMCM-41 (Perkin-Elmer 684 spectrometer)

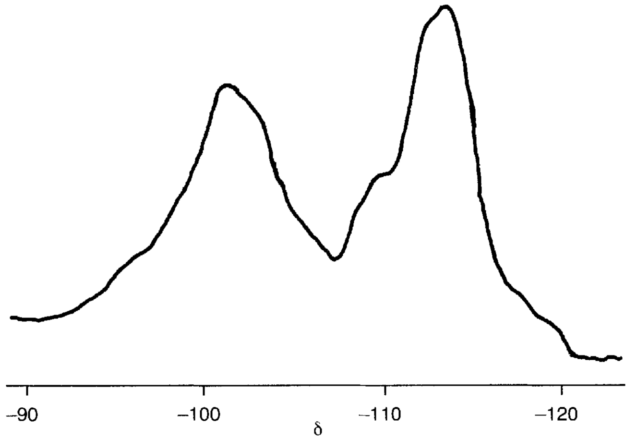

Fig. 4 ^{29}Si MAS NMR spectrum of FeMCM-41 (Varian UNITY plus 400 NMR spectrometer)

be assigned to Si–O–T (T = Fe) vibration in the Fe-silicate MCM-41 framework structure.

The ^{29}Si MAS NMR of the Fe-MCM-41 as-synthesized sample is shown in Fig. 4. In the NMR spectrum, the peak around δ −101 is assigned to silanol groups[10] and the peak around δ −113 is due to silicon atoms coordinated with four silicon atoms *via* oxygen [$Si(OSi)_4$]. A shoulder peak at δ −110, which may be assigned to the signal of tetrahedrally coordinated silicon distorted by the presence of iron, indicates that iron atoms are located in the framework structure.

In conclusion, XRD, framework IR, ESR, ^{29}Si MAS NMR and UV–VIS methods have confirmed the presence of iron in the lattice framework of Fe-MCM-41. A mesoporous molecular sieve with iron in the framework has been synthesized for the first time. Catalytic testing of Fe-MCM-41 is in progress.

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