Synthesis and characterization of vanadosilicate mesoporous molecular sieves MCM-41

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A range of mesoporous vanadosilicate molecular sieves with the MCM-41 structure and the atomic ratio Si/V = 10–160 have been synthesized using vanadyl sulfate as the source of vanadium. The products were characterized by XRD and ^{51}V and ^{29}Si MAS NMR spectroscopy. The increase of the unit-cell parameter (monitored by XRD) and the decrease of the Q^3/Q^4 ratio (determined from the ^{29}Si spectra) with increasing vanadium content indicate the incorporation of vanadium into the MCM-41 structure. In as-synthesized [Si,V]-MCM-41, vanadium is in an octahedral environment and is located mainly on the surface of the channels. The amount of octahedral vanadium decreases and tetrahedral V is increasingly created as the calcination temperature increases.

Microporous (pore diameter <20 Å) and mesoporous (20–100 Å) molecular sieves admit molecules below a certain size into their extensive internal volume, which makes them potentially important as shape-selective heterogeneous catalysts and sorbents. Much attention has recently been given to the mesoporous material known as MCM-41, a member of the M41S family.[1,2] Substitution of elements such as Ti,[3,4] V,[5,6] Ga,[7] Mn,[8] B[9,10] and Fe[11] into MCM-41 is of interest in view of the likely catalytic properties of the products and the prospect of being able to introduce large molecules into the mesopore system. We shall refer to the purely siliceous MCM-41 as [Si]-MCM-41 and to its variants containing vanadium as [Si,V]-MCM-41-*n*, where *n* is the Si/V ratio.

The established importance of vanadium compounds as oxidation catalysts has made the introduction of vanadium into the MCM-41 structure particularly desirable. Vanadium-containing molecular sieves are highly catalytically active in the ammoxidation of propane and xylenes,[12,13] oxidation of butadiene to furane[14] and oxidative dehydrogenation of propane to propene.[15] Their catalytic performance is different from, and in some case superior to, that of supported vanadium oxide catalysts used for the selective oxidation of large organic molecules with hydrogen peroxide.[5,6] We will show that in [Si,V]-MCM-41 vanadium resides in the molecular sieve framework on the relatively exposed sites on the surface of the channels. We have prepared a series of vanadosilicate MCM-41 with a wide range of compositions (Si/V = 10–160), as well as [Si,V]-MCM-41 with Si/V = 27 of particularly high quality. The chemical environment of vanadium was characterized using ^{51}V and ^{29}Si MAS NMR spectroscopy. The aim was to acquire a better understanding of the properties of [Si,V]-MCM-41 in order to be able to modify and improve its catalytic performance.

Experimental

[Si,V]-MCM-41 was synthesized as follows. Fused silica (6 g; Cab-O-Sil M5, BDH) was gradually added to an NaOH solution of 1.36 g NaOH (Fisons) in 58 g H_2O with stirring over 2 h. A vanadyl sulfate ($VOSO_4 \cdot 3H_2O$; 99%, Aldrich) solution, the concentration of which was dependent on the target Si/V ratio, in 25 g H_2O was then added with stirring for 3 h. Surfactant CTABr (cetyltrimetylammonium bromide; 99%, Aldrich; 18.2 g) dissolved in 25 g H_2O was then added with stirring for 2 h. The resulting reaction mixture with molar composition $SiO_2 : xVO_2 : 0.17Na_2O : 0.5CTABr : 60H_2O$ ($x \leqslant 0.06$) was aged overnight and poured into a PTFE-lined stainless-steel autoclave to crystallize at 100 °C without stirring. The product was filtered, washed with deionized water and ethanol, dried at 70 °C and finally calcined in air in three steps (120 °C for 3 h; 400 °C for 5 h; 550 °C for 5 h).

X-Ray diffraction (XRD) patterns were recorded using a Philips 1710 powder diffractometer with Cu-Kα radiation (40 kV, 40 mA), 0.02° step size and 1 s step time.

Solid-state MAS NMR spectra were recorded at 9.4 T using a Chemagnetics CMX-400 spectrometer and zirconia rotors, 7.5 mm in diameter, spun in air at 3 kHz for ^{29}Si, and 4 mm rotors spun at 10–12 kHz for ^{51}V. Various spinning rates were used to identify isotropic ^{51}V resonances. ^{29}Si spectra were acquired at 79.4 MHz with 30° pulses and 600 s recycle delays, and ^{51}V spectra at 105.2 MHz with <7° pulses and 25 ms recycle delays. The chemical shifts for ^{29}Si are given relative to external tetramethylsilane and for ^{51}V relative to external $VOCl_3$.

Results and Discussion

Because the atomic arrangement in MCM-41 is not crystalline, we shall refer to 'crystallinity' in the sense of the regular disposition of the channels, the only element of order in the material. All references to a unit cell, *etc*., should be interpreted accordingly. Thus the XRD patterns of as-synthesized and calcined [Si,V]-MCM-41 with Si/V = 27 (*i.e.* [Si,V]-MCM-41-27) are typical of MCM-41 (Fig. 1, Table 1).[1,2] The as-synthesized sample gives a very strong (100) peak and four

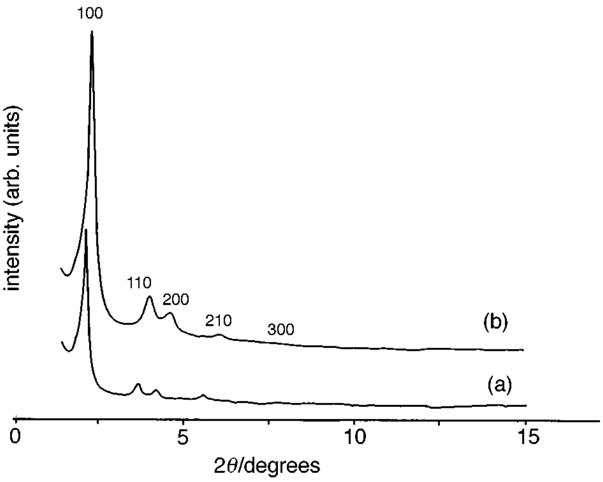

Fig. 1 XRD patterns of (a) as-synthesized and (b) calcined [Si,V]-MCM-41-27

Table 1 XRD data for as-synthesized and calcined [Si,V]-MCM-41-27

as-synthesized			calcined		
hkl	*d*/Å	I/I_o	*hkl*	*d*/Å	I/I_o
100	39.8	100	100	35.7	100
110	23.7	12.2	110	21.5	16.1
200	20.7	8.7	200	18.8	10.4
210	15.8	5.7	210	14.4	3.4
300	14.0	1.3	300	12.8	1.4

lower intensity peaks. All five reflections can be indexed on a hexagonal lattice.[2] The absence of peaks above $2\theta = 20°$ indicates that the as-synthesized sample is free from crystalline V_2O_5. Upon calcination the *d* spacings are smaller, and the d_{100} distance is reduced from 39.8 to 35.7 Å (Fig. 1, Table 1). This is accompanied by a reduction of the density of silanol Si—OH groups *via* condensation[16] and the decrease of the crystallite size, indicated by the broadening of the peaks. The intensity of the XRD pattern increases significantly upon calcination as a result of the removal of intercalated organic molecules.[7]

The d_{100} spacing in [Si,V]-MCM-41 is significantly larger than in the purely siliceous [Si]-MCM-41 (both as-synthesized and calcined) and unit-cell parameters increase with the vanadium content, indicating that V is incorporated into the structure. The d_{100} values for as-synthesized samples vary from 36.9 to 41.3 Å and those for calcined samples from 28.8 to 37.1 Å (Table 2).

While the precise structure of the vanadium-containing silicate matrix is unknown, the presence of similar distinct reflections in the XRD patterns (Fig. 2) suggests the presence of long-range order in the framework of as-synthesized [Si,V]-MCM-41, similar to that in purely siliceous [Si]-MCM-41.

In particular, the pattern of [Si,V]-MCM-41–27 gives the best resolved (110), (200), (210) and (300) peaks, indicating the particularly high crystallinity of this sample. It is thought that in zeolites vanadium resides at sites with a high concentration of Si—OH groups.[17] However, while zeolites contain only a moderate amount of silanol groups associated with crystal defects, the surface of MCM-41 is rich in Si—OM and Si—OH groups, where M is the template cation.[16] We could thus prepare [Si,V]-MCM-41 with more vanadium than other vanadium-containing molecular sieves such as [Si,V]-silicalite and [Si,V]-NCL-1,[18] because the highly concentrated silanol groups in MCM-41 stabilise the surface vanadium.

Even though the structure of [Si,V]-MCM-41 with $Si/V < 20$ is destroyed upon calcination, the (100) peak is present in the XRD pattern of as-synthesized samples even at $Si/V = 10$. While the purely siliceous MCM-41 gives a good quality XRD pattern, the addition of a very small amount of vanadium does affect the process of nucleation and/or crystallization. Thus the intensity and resolution of the peaks are affected severely even in the pattern of the sample [Si,V]-MCM-41-160.

Table 2 Interplanar d_{100} spacings and unit-cell parameters ($a_0 = 2d_{100}/\surd 3$) of purely siliceous [Si]-MCM-41 and samples of [Si,V]-MCM-41 with different Si/V ratios

	d_{100} spacing/Å		unit-cell parameter/Å	
Si/V ratio in gel	as-synthesized	calcined	as-synthesized	calcined
purely siliceous	36.9	28.8	42.6	33.3
160	37.3	30.0	43.1	34.6
67	38.6	32.1	44.6	37.1
27	39.9	35.7	46.1	41.2
23	41.3	37.1	47.7	42.8
20	41.6	—[a]	48.0	—[a]

[a] Crystallinity is destroyed upon calcination.

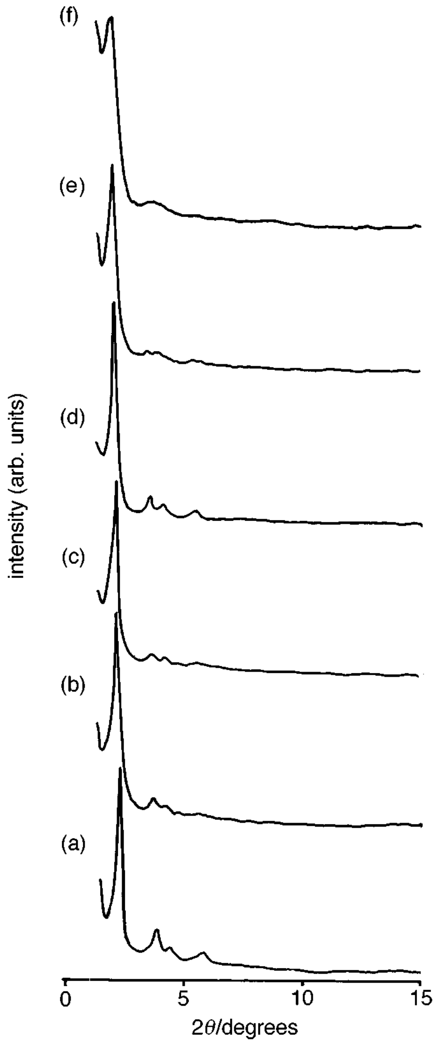

Fig. 2 XRD patterns of (a) purely siliceous [Si]-MCM-41, and as-synthesized [Si,V]-MCM-41 with Si/V ratios of (b) 160; (c) 67; (d) 27; (e) 23 and (f) 20

Interestingly, while the resolution of the XRD pattern of [Si,Al]-MCM-41 deteriorates rapidly as the aluminium content increases,[19] the quality of the XRD pattern improves with the vanadium content increasing up to $Si/V = 27$, and then deteriorates. The pattern of the [Si,V]-MCM-41-27 is the best resolved of all the [Si,V]-MCM-41 samples.

The ^{29}Si NMR spectra of [Si,V]-MCM-41 (Fig. 3) are very broad and the lines overlap, which indicates the presence of a wide range of T—O—T bond angles. On the basis of the chemical shift, the peak at δ −110 in the ^{29}Si MAS NMR spectra of as-synthesized [Si,V]-MCM-41 must be assigned to the central Si atom (in bold type) in $\mathbf{Si}(OSi)_4$ (Q^4) sites. The ^{29}Si peaks at δ *ca.* −91 and −100 are assigned to $\mathbf{Si}(OSi)_2(OH)_2$ (Q^2) and $\mathbf{Si}(OSi)_3(OH)$ (Q^3) sites, respectively.[20] The $\mathbf{Si}(OSi)_2(OM)_2$ and $\mathbf{Si}(OSi)_3(OM)$ sites (M is the template cation) should have very similar chemical shifts to those for $\mathbf{Si}(OSi)_2(OH)_2$ and $\mathbf{Si}(OSi)_3(OH)$, respectively.

The ^{29}Si spectra demonstrate clearly that the concentration of the silanol groups, reflected in the Q^3/Q^4 ratio, decreases with increasing vanadium content, and the intensity of the δ −100 peak decreases progressively. It follows that at higher vanadium contents more $\mathbf{Si}(OSi)_3(OH)$ and $\mathbf{Si}(OSi)_3(OM)$ units are converted to $\mathbf{Si}(OSi)_3(OV)$ (Q^4) units. This indicates that vanadium is being incorporated into the surface of the channel wall at the expense of the silanol sites. The increase of the unit-cell parameter with the vanadium content again indicates the incorporation of vanadium. It was suggested that

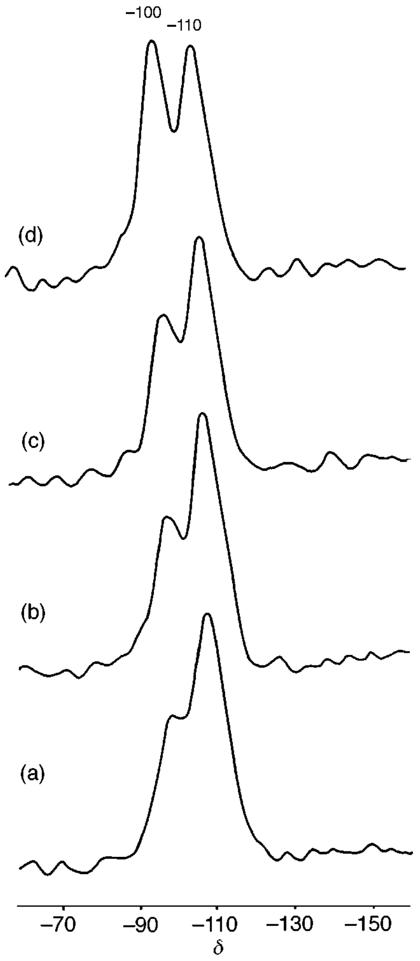

Fig. 3 ^{29}Si MAS NMR spectra of as-synthesized [Si,V]-MCM-41 with Si/V ratios of (a) 23, (b) 27 and (c) 67; (d) purely siliceous [Si]-MCM-41

in vanadium-impregnated MCM-48[21] and in as-synthesised MEL,[17] vanadium resides on the surface of the channels. Our ^{29}Si results show that vanadium in [Si,V]-MCM-41 is indeed bonded to Si on the internal surface *via* linking Si—OH groups to form mainly $(SiO)_3V{=}O$ units, leading to a decrease in the content of Q^3 groups with increasing vanadium content in the structure. This amounts to direct NMR proof that vanadium exists on the internal surface, which could well be the case with other [Si,V] molecular sieves.

Since the chemical shifts of ^{51}V in compounds containing both four- and six-coordinate vanadium are generally in the range δ −400 to −700, the chemical shift alone cannot be used to determine the coordination of vanadium, in contrast to other quadrupolar nuclei such as ^{27}Al and ^{71}Ga. Fortunately, the chemical shift anisotropy of ^{51}V is very sensitive to the type of environment provided by oxygen atoms, particularly as concerns the coordination number and the distortion of the local environment.[22] The ^{51}V MAS NMR spectrum of as-synthesized [Si,V]-MCM-41-27 in Fig. 4(a) (static spectrum not shown) consists of an isotropic peak at δ −627 with numerous broad sidebands. The large chemical shift anisotropy value corresponds to the six-coordinate range.[22] It follows that the vanadium atom in an $(SiO)_3V{=}O$ unit in the as-synthesized sample links water molecules, thus becoming six-coordinate.[23,24] The spectrum changes markedly upon calcination of the sample, and the chemical shift anisotropy pattern becomes narrower with increasing calcination temperature. Thus the MAS spectrum of the sample calcined at 550 °C contains only a main resonance at δ −514 with very weak spinning sidebands [Fig. 4(*b*)]. The chemical shift anisotropy shows clearly that vanadium becomes four-coordinate as a result of the loss of adsorbed water molecules upon calcination.

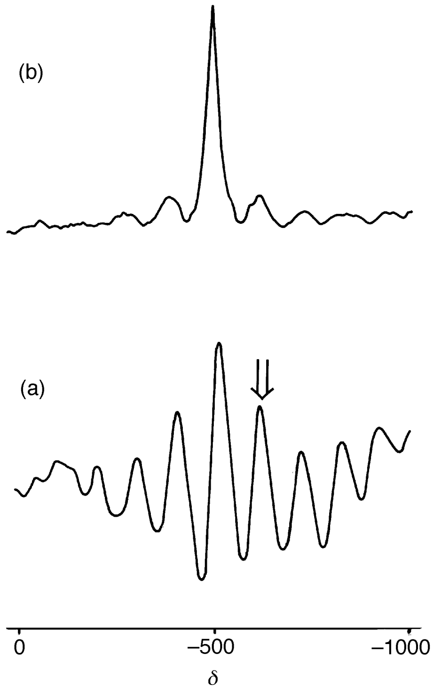

Fig. 4 ^{51}V MAS NMR spectra of (a) as-synthesized [Si,V]-MCM-41-27, and (b) after calcination at 550 °C. The arrow marks the isotropic line.

The nature of vanadium in [Si,V]-MCM-41 was further investigated by washing the sample [Si,V]-MCM-41–27 with a 1 mol dm^{-3} aqueous solution of ammonium acetate for 24 h. It is thought that ammonium acetate extracts the vanadium species from non-framework positions.[18] The NMR spectrum of washed [Si,V]-MCM-41–27 further calcined at 500 °C is almost identical to the spectra in Fig. 4. The results further prove that the vanadium resides in the framework.

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