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ORIGINAL CONTRIBUTION

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Vanadium(V)-doped MCM-41 synthesised by a novel one-step procedure

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Abstract A novel procedure to synthesise V-doped surfactant–templated mesoporous materials in one step using a V(V) complex is described. The resulting V(V)–MCM-41 material had a bimodal pore size distribution.

Keywords MCM-41 synthesis · Vanadium MCM-41 · Mesopores · Doped materials

Introduction

Much attention has been paid to MCM-41 molecular sieves with a unidimensional hexagonal mesopore structure since this was developed by researchers in the Mobil Oil Corporation [1, 2]. It was attempted to incorporate many different metals into the MCM-41 framework to add new character [3].

Molecular sieves containing redox active metals, like Ti, V, Cr, Fe or Co, are increasingly used as heterogeneous catalysts for selective oxidation of organic compounds. Such heterogeneous catalysts exhibit advantages over organometallics used as homogeneous catalysts, since the latter contaminate the effluents [4, 5] As an example, V-containing MCM-41 was claimed to be active in the oxidation of cyclododecene and other cyclic alkenes with H_2O_2 [6] and tetrahydropyrane borane complex [7]. In particular, there is great interest in the synthesis of V-doped mesoporous materials [8, 9] owing to their applications as catalysts [10–14].

The usual methods for the incorporation of V in MCM-41 are:

1. In situ incorporation of V during hydrothermal synthesis (V–MCM-41-syn) [4],
2. Chemical vapour deposition of $VOCl_3$ on siliceous MCM-41 (V–MCM-41-cvd) [15, 16].
3. Impregnation of siliceous MCM-41 with vanadyl acetylacetonate (V–MCM-41-imp), which was made by adsorption of a vanadyl acetylacetonate complex on silica in the liquid phase and the gas phase [17, 18].

The inclusion of V by adsorption of a vanadyl acetylacetonate complex on the surface of siliceous MCM-41 did not practically affect its structure, whereas the loading of dry siliceous MCM-41 with $VOCl_3$ resulted in slight damage of the mesoporous material structure [4]. All three previously mentioned methods reduced the surface area of the V-doped MCM-41 with respect to that of pure siliceous MCM-41, in the order $S_{\text{Si–MCM-41}}$ (1,023 m^2g^{-1}) > $S_{\text{V–MCM-41-imp}}$ (966 m^2g^{-1}) > $S_{\text{V–MCM-41-cvd}}$ (938 m^2g^{-1}) > $S_{\text{V–MCM-41-syn}}$ (821 m^2g^{-1}). The diameter of the mesopores was also slightly affected by the inclusion of V: $D_{\text{V–MCM-41-imp}}$ (3.68 nm) > $D_{\text{MCM-41}}$ (3.67 nm) > $D_{\text{V–MCM-41-cvd}}$ (3.65 nm) > $D_{\text{V–MCM-41-syn}}$ (3.48 nm) [4].

Luan et al. [19] asserted that only V located on the wall surface can undergo reversible redox cycles between the V(IV) and V(V) states, which is important for catalytic uses. Thus, it is of great interest for the production of V-doped mesoporous materials in which the metal is on the surface of the pore walls. The synthesis of these materials in a one-step method, which avoids further treatments, has obvious advantages with more complicated methods of metal grafting.

Some metal complexes react with cationic surfactants giving water-insoluble three-component complexes, which are solubilised by micelles. In particular, the V(V)–alizarine red (AR)–cetyltrimethylammonium bromide (CTAB) complex locates at the surface of CTAB micelles, with the V(V) ion situated at the outer limit of the Stern layer [20]. The V(V)–AR–CTAB complex has limited solubility in CTAB micelles. The maximum solubility is 3.7 complex molecules per spherical micelle (about one complex each 24 micellised surfactant molecules), occupying 17 nm^2 of the micelle surface. [20]. This information suggested to us that V(V) could be inserted on the mesoporous inner surface, while making the siliceous matrix, via its inclusion on the template surface by adsorption of the V(V)–AR–CTAB complex.

Experimental

Pure MCM-41 synthesis

Pure siliceous MCM-41 was prepared by addition of 6.2 g sodium silicate to a solution of 0.2 ml H_2SO_4 (Carlo Erba, 96%) in 13.3 ml distilled water. After stirring for 10 min, a solution of 5.59 g CTAB in 16.75 ml water was added, followed by 30 min of stirring. Then, 6.6 ml water was added and the gel was stirred for 30 min. The mixture was then autoclaved at 140 °C for 48 h. The resulting gel was filtered, washed and calcined at 540 °C for 6 h. A white, porous material was obtained.

V–MCM-41 synthesis

We prepared 25 ml of a solution of 8.323 g CTAB with 3.838×10^{-4} mol V(V) (as $NaVO_3 \cdot 4H_2O$) and 5.454×10^{-4} mol AR in water. Six V–MCM-41 samples were prepared with different V contents. The samples were prepared by dissolving 5.59 g CTAB in V_1 ml water plus V_2 ml V–AR solution ($V_1 + V_2 = 16.75$ ml). The expected V content ranged from 4.875 to 1.250 mgg^{-1}. The other steps of the synthesis were the same. The water obtained, when the gel was washed, was titrated to determine the amount of V which was not retained in the mesoporous material. The as-synthesised material was red, whereas it was white after calcination.

Characterisation

The V content of the mesoporous material was measured by X-ray fluorescence with a Phillips PW 1400 X-ray fluorescence spectrometer with a rhodium anode operated at 60 kV and 40 mA, with a LiF 200 crystal under vacuum.

The nonretained V in the water obtained when the gel was washed was analysed by the 3,3′-dimethylnaphtyline method [21].

Mercury porosimetry was performed using a Carlo Erba porosimeter 2000.

Wide-angle X-ray diffractograms were made with a Phillips PW 1710 diffractometer, a copper anode and a curved graphite monochromator.

Transmission electron microscopy was performed with a JEOL 100 CX II transmission electron microscope, operated at 100 kV with a magnification of 100,000 × . Observations were made at bright field. Powdered samples were placed on copper supports of 2,000 mesh.

The nitrogen adsorption isotherms at 77.6 K were measured with a Micrometrics model Accusorb 2100 E instrument. Each sample was degassed at 373 K for 720 min at a pressure of 10^{-4} Pa.

Results

The V content of the samples is shown in Table 1.

The wide-angle X-ray diffractograms showed a broad band centred at about 0.44 nm of amorphous silica. No significant differences were seen between samples.

The mercury porosimetry results are shown in Fig. 1 for three samples. $dV/d\log R$ versus pore radius curves, which are interpreted as pore size distributions, are shown in Fig. 2. There are no significant differences between all the pore size distributions at a significance level of $\alpha = 0.05$ (significance only occurs at $\alpha = 0.49$). In consequence, an average value of $R = 2{,}596 \pm 66$ nm was taken. This value was computed by the minimum variance unbiased linear estimation method [22].

The adsorption–desorption isotherm and the mesopore size distribution of pure MCM-41 and two V–MCM-41 samples are presented in Figs. 3, 4 and 5. The isotherms are of type IV, typical of mesoporous solids; however, the adsorption isotherm shape at $p/p_0 > 0.95$

Table 1 V (V) content of the different samples

Sample	Expected value (mgg^{-1})	Determined by X-ray fluorescence (mgg^{-1})	Determined by titration of the nonretained V (mgg^{-1})	Percent retention
A	4.875	2.264	1.65	46.4
B	4.100	1.434	1.77	35.0
C	3.900	1.622	1.22	41.6
D	2.49	0.825	0.779	33.1
E	1.90	0.383	–	54.3
F	1.25	0.679	–	20.2

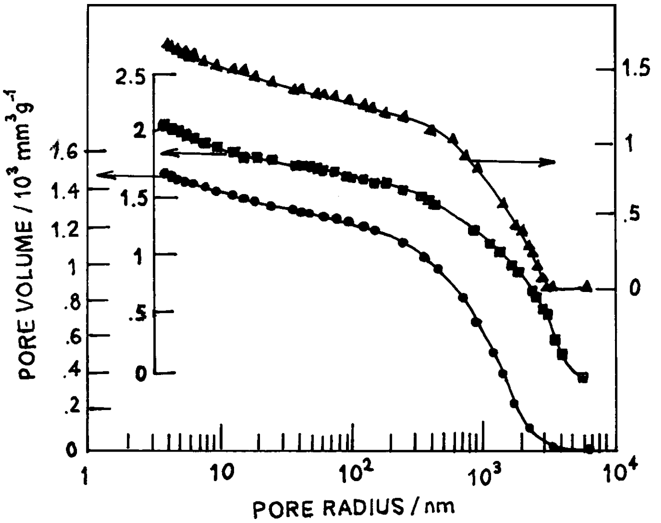

Fig. 1 Pore volume versus pore radius by mercury porosimetry. Pure silica MCM-41 (*circles*); V–MCM-41E (*squares*); V–MCM-41 B (*triangles*)

suggested that the intercrystallite macropores were filled and that multilayer deposition occurred. The inflection in the adsorption isotherm indicates the mesopore filling. The coordinate of the inflection point depends on the pore size. Hysteresis loops of type H2 may be seen in the figures and are associated with capillary condensation taking place in mesopores [23] with both ends open [24]. According to de Boer [25] these types of hysteresis loops appear when the capillaries are regular or irregular cylinders or prisms open at both ends. Furthermore, the desorption hysteresis at low p/p_0 values indicates micropore filling. According to Cohan [26] no pores of actual radii less than about a molecular diameter could be effective in causing hysteresis (actually, the critical radius was taken to be two molecular diameters), and Cohan showed that for a number of systems the desorption branch rejoined the adsorption one at p/p_0 values corresponding to pore radii close to twice the estimated size of the adsorbate molecules. The plot of the derivative of the pore volume per unit weight with respect to the pore radius (dV/dR) is shown in part b of each figure. Some micropores (whose radius is about 1 nm) are present in some samples. The sharp pore size distribution of pure silica MCM-41 confirms that their mesopores are uniform; however, some samples with V have a broader pore size distribution, which are bimodal. In general, there are two sharp bands (Fig. 5), but in some cases they may be superimposed (Fig. 4). The Brunauer–Emmett–Teller surface area is shown in Table 2 together with the average pore sizes.

The uniform mesopore structure of all the samples is evident in the transmission electron microscope lattice image shown in Fig. 6. Transmission electron microscopy of the calcined samples shows the regular hexagonal array of uniform channels that is characteristic of MCM-41. When viewed in the direction perpendicular to their axis, the pores were seen to be arranged in patches composed of regular rows. The hexagonal structure with each pore surrounded by six neighbours was present in all the samples.

Discussion

Only 38 ± 11% of the original V was retained in the mesoporous samples. The V which was not retained in the siliceous matrix may be recovered from the washing water and recycled.

MCM-41 prepared with CTAB as a template by hydrothermal synthesis typically has a pore radius of about 1.5–1.8 nm and a surface area of about 1,000–1,240 m^{2}g^{-1} [27, 28]. The MCM-41 prepared with the method described earlier has a similar pore radius (2.1 ± 0.4 nm) but a smaller specific area (990 m^{2}g^{-1}). The addition of V via the complex adsorbed on the micellar surface did not affect the specific area, but the pore radius distribution was shifted towards the smaller pore radius. In addition, the pore radius distribution

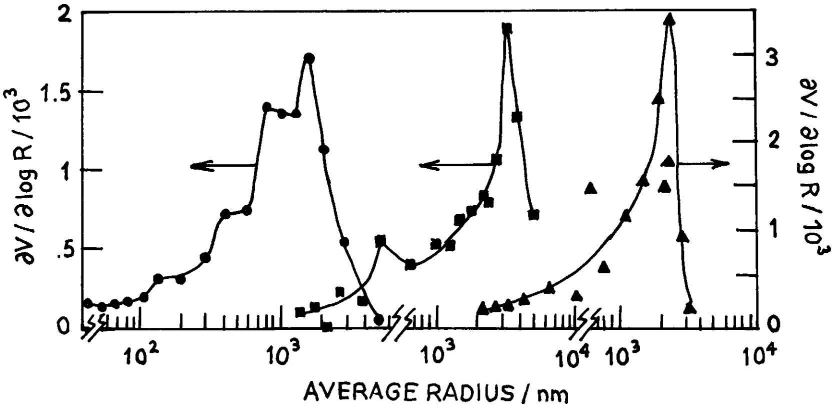

Fig. 2 $dV/d\log R$ versus pore radius by mercury porosimetry. Pure silica MCM-41 (Poisson macropore average value, μ, of 2,670 ± 190 nm, Poisson standard deviation, λ, of 2,080 nm) (*circles*); V–MCM-41 E ($\mu = 2{,}380 \pm 100$ nm, $\lambda = 1150$ nm) (*squares*); V–MCM-41 B ($\mu = 2{,}790 \pm 100$ nm, $\lambda = 1{,}390$ nm) (*triangles*)

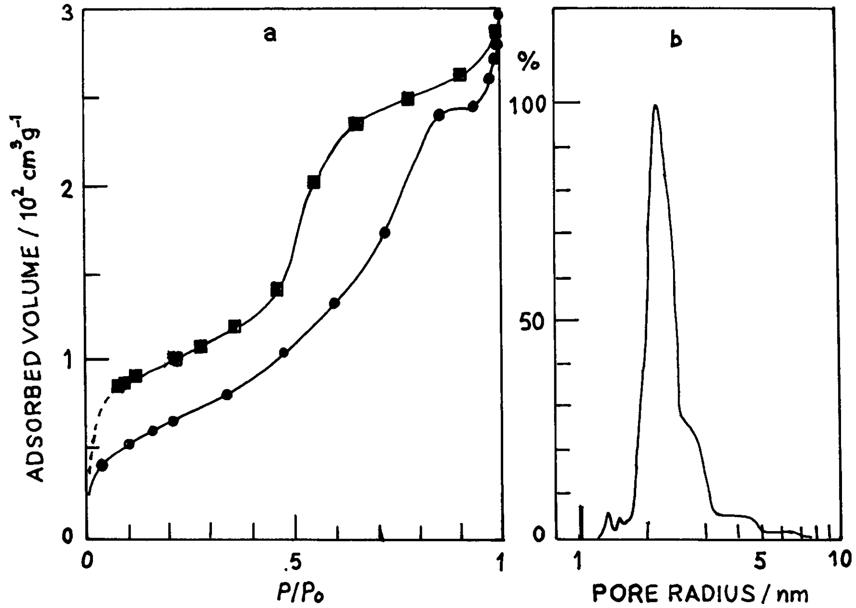

Fig. 3 **a** Adsorption (*circles*)–desorption (*squares*) of nitrogen on pure silica MCM-41. **b** d*V*/d*R* versus pore radius

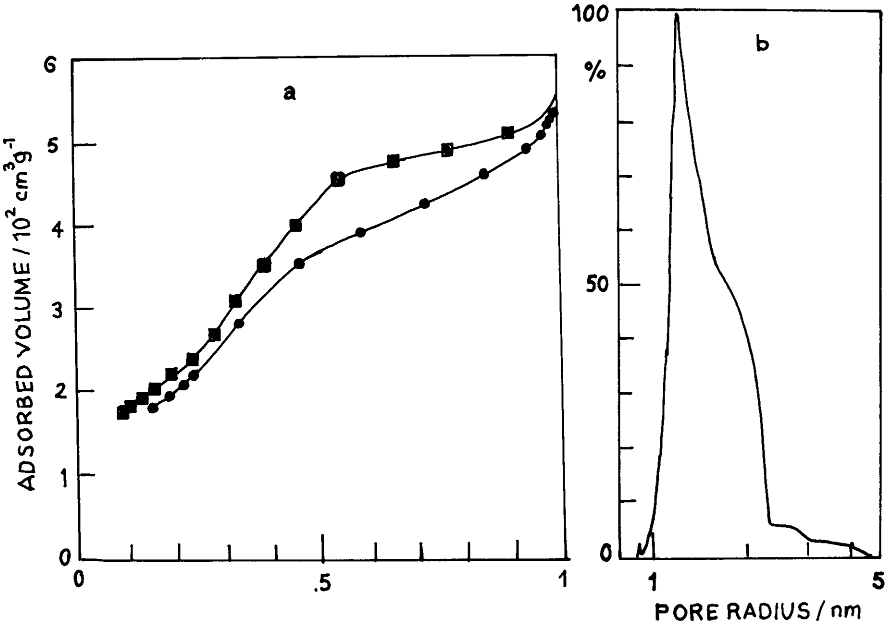

Fig. 4 **a** Adsorption (*circles*)–desorption (*squares*) of nitrogen on V–MCM-41E. **b** d*V*/d*R* versus pore radius

became bimodal (in one sample, it was trimodal). Similar changes were observed in other modified mesoporous materials. A small expansion of pore diameters was detected in cubic MCM-48 mesoporous silica when zirconium was included in the synthesis gel and coprecipitated with silica, whereas a small contraction was detected when zirconium was incorporated after the synthesis of the pure silica MCM-48 [29]. Bimodal mesoporous siliceous MCM-41 was also prepared by Rathousky et al. [30] and normal mesopores and larger pores with sizes ranging from 15 to 25 nm were obtained. The total surface area of that bimodal silica was about 750 m^2g^{-1}. The total mesopore volume was about 2 cm^3g^{-1}. The difference between small and large mesopores was larger in the materials of Rathousky et al. than in our own mesoporous materials.

Sonwane et al. [28] pointed out that mesoporous MCM-41 materials comprise several levels of structure (mesopores, crystallites, grains and particles), each having its characteristic length scale spanning over 4 decades of resolution. By mercury intrusion porosimetry, they found that MCM-41 materials have a

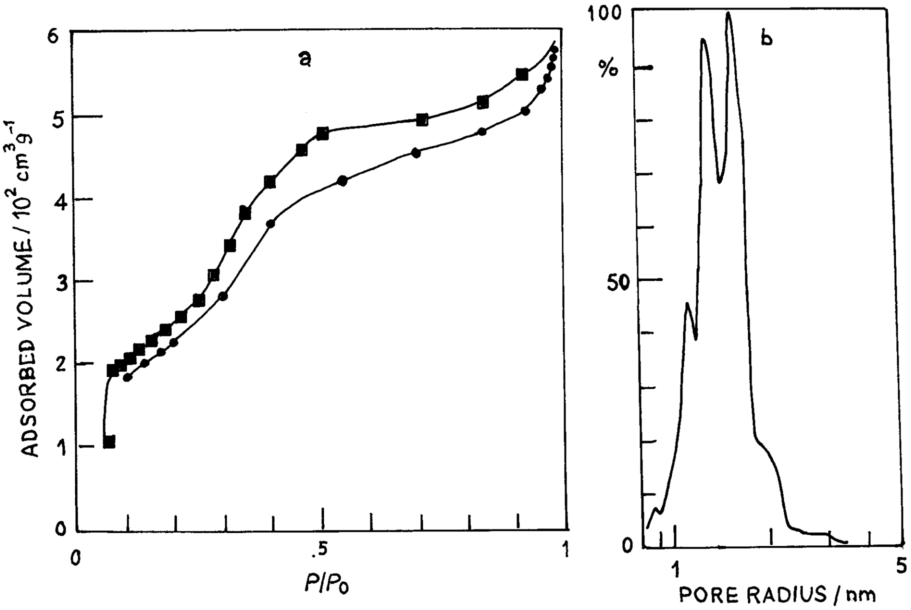

Fig. 5 **a** Adsorption (*circles*)–desorption (*squares*) of nitrogen on V–MCM-41B. **b** d*V*/dR versus pore radius

Table 2 Properties of the different samples of mesoporous material

Sample	Surface area (m^2g^{-1})	Average mesopore radius (nm)	Pore surface (m^2g^{-1})[a]
Pure MCM-41	990	2.1	1,002 ± 25
A	964	1.5–1.9	1,050 ± 15
B	1,243	1.5–1.7	1,147 ± 14
C	954.1	1.1–1.7	1,159 ± 11
D	1,242.6	1.1–1.6–1.8	1,569.1 ± 1.0
E	986.5	1.4–2.0	1,021 ± 21
F	973.2	1.1–1.5	1,187 ± 13

[a] Average between adsorption and desorption values

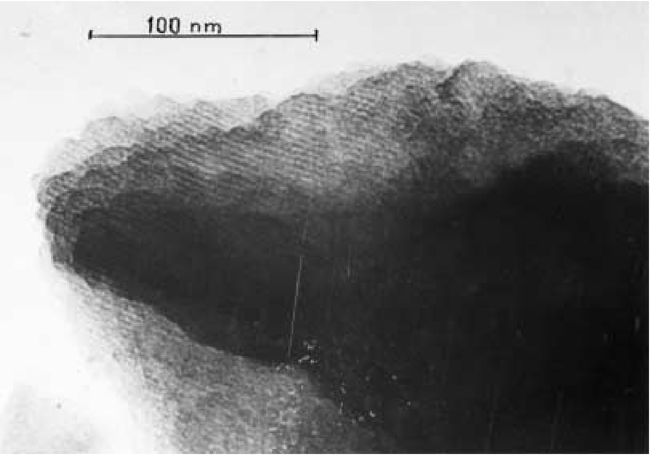

Fig. 6 Electron microphotography of V–MCM-41B, showing patches composed of regular rows viewed in the direction perpendicular to the mesopore axis

macroporous fractal dimension of 2.7–3, and the dimensions of the grains range from 0.1 to 0.4 μm. The fractal dimension of the mesopores was 2 and they are therefore very smooth. The walls of the mesopores may collapse at higher pressures of mercury, whereas at very low pressures mercury intruded into the interparticle space. This corresponds to a macropore size of 0.35 μm or greater (pressure lower than 2 MPa). The crystallite size was about 8–25 nm. We found an average macropore radius of 2.596 ± 0.066 μm, with no significant difference among the samples. This means that the crystallite structure did not seem to be affected by the inclusion of V in the mesoporous material.

Concluding remarks

- The inclusion of V(V) on the inner surface of the mesoporous MCM-41 via the adsorption of the V(V)–AR–CTAB complex on the template aggregates' surface prior to silica gelation gave a V-doped material.
- About 38% of the initial V was retained by the siliceous matrix, and the remaining V may be recuperated from the washing water and recycled.

- The amount of V affected the pore size distribution of the MCM-41 obtained. V–MCM-41 had a bimodal pore size distribution.

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