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Catalysis Today 100 (2005) 473–477

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Vanadium incorporated high surface area MCM-41 catalysts

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Abstract

High surface area MCM-41 (1452 m^2/g) and V-MCM-41 materials were synthesized by a direct hydrothermal synthesis method. Characteristic XRD patterns, SEM and AFM photographs indicated no significant change in the morphology of MCM-41 by incorporation of vanadium. XPS and EDS results proved that incorporation of vanadium into the MCM-41 structure was successfully achieved when vanadyl sulfate hydrate was used as the vanadium source. However, use of ammonium vanadate as the vanadium source was not equally successful.

Keywords: MCM-41; Vanadium; V-MCM-41; Hydrothermal synthesis

1. Introduction

Selective oxidation reactions are involved in the development of a number of environmentally benign processes. Vanadium and molybdenum based oxide catalysts are known to have high activity in selective oxidation reactions. Selective oxidation of H_2S to elemental sulfur [1,2], oxidative dehydrogenation of ethane and propane [3–8] and partial oxidation of alcohols to produce hydrogen [9–10] are some of the examples of such selective oxidation reactions where vanadium and/or molybdenum oxide catalysts are successfully used. High surface area of such oxide catalysts is one of the requirements of having high activities.

MCM-41 based catalysts are mesoporous, silicate-structured materials having high surface areas and narrow pore size distributions. These materials, which were originally discovered in 1992 by Mobil researchers, have rather flexible synthesis conditions. Up to date, number of studies have been carried out on the synthesis and characterization of MCM-41 materials [11–16] and it is reported that for most purposes, these materials do not have enough catalytic activity. However, metals or other active compounds can be incorporated into their structure either by direct synthesis or by post-synthesis methods [17].

Vanadium incorporated MCM-41 catalysts (V-MCM-41) may be synthesized by several different methods, including ion-exchange [6], grafting [7], direct synthesis [6–8,18], impregnation [8,19] and chemical vapor deposition [18]. In this study, a direct hydrothermal synthesis method is used which depends upon the gelation of a source of silica with an added metal-surfactant solution. Different sources of vanadium are used in the preparation of V-MCM-41 type catalytic materials with potential applications in partial oxidation reactions.

2. Experimental work

In this work, V-MCM-41 type mesoporous materials, having different metal to silica ratios, were prepared following a direct hydrothermal synthesis procedure. The synthesized materials were then characterized by XRD, SEM, EDS, AFM, XPS, BET, Atomic Absorption Spectroscopy and Helium Pycnometry.

2.1. Chemicals

In the preparation of MCM-41 and V-MCM-41 type materials, an aqueous solution of sodium silicate (27 wt%

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doi:10.1016/j.cattod.2004.10.032

SiO_2, 14 wt% NaOH, Aldrich) was used as the silica source and cetyltrimethylammonium bromide (CTMABr, 99% pure powder, Sigma) was used as the surfactant. Two different vanadium sources, namely, vanadyl sulfate hydrate ($VOSO_4 \cdot xH_2O$, Aldrich) and ammonium vanadate (NH_4VO_3, Merck) were used in the synthesis of V-MCM-41 type materials. Besides these chemicals, sulfuric acid (4N) and sodium hydroxide (1 M, Merck) were used in the synthesis procedure.

2.2. Synthesis of MCM-41

In the hydrothermal synthesis of MCM-41, first of all a solution of surfactant (26.4 g CTMABr in about 150 g deionized water) was prepared and heated up to about 30 °C while mixing, for complete dissolution of CTMABr. This solution was then added to 31.4 g of the sodium silicate solution dropwise by continuos stirring. The formation of a gel was observed at this stage. The pH of this gel was adjusted to 11 by adding sufficient amount of 4N H_2SO_4. The gel thus formed was transferred into a teflon-lined stainless steel autoclave for hydrothermal synthesis in order to facilitate the precipitation of MCM-41 crystals. The hydrothermal synthesis was performed in the autoclave at 120 °C for 96 h. The formed mixture was filtered and washed to recover the solid product. The washing was continued until the pH of the filtrate was about 7. The washed product was dried in vacuum at 40 °C for 24 h. Finally, it was calcined in a tubular furnace in contact with a flow of dry air. In the calcination step, the furnace temperature was increased from room temperature to 550 °C at a heating rate of 1 °C/min and the sample was kept at 550 °C for 6 h. Results of the characterization experiments showed that the calcination procedure was quite important and the flow rate of the dry air passing over the prepared material should be sufficiently high (≥ 1 dm^3/min).

2.3. Synthesis of V-MCM-41

V-MCM-41 materials with V/Si ratios of 0.01, 0.03 and 0.09 (in the solution) were synthesized by following a modified version of the method described in Section 2.2. Silica and surfactant amounts were the same as those in Section 2.2 and the amount of vanadium was varied according to the desired V/Si ratio. Two different vanadium salts were used in order to see the effect of different vanadium sources on the properties of the final product.

2.3.1. Synthesis of V-MCM-41 using vanadyl sulfate hydrate as the vanadium source

Three V-MCM-41 samples with V/Si ratios of 0.01, 0.03 and 0.09 (in the solution) were synthesized by keeping the surfactant and silica amounts the same as those in Section 2.2 and by varying the vanadium added. A solution of surfactant and vanadium was prepared by mixing the surfactant, desired amount of vanadyl sulfate hydrate and deionized water with moderate heating. This solution was added dropwise to the sodium silicate solution by continuous stirring. The pH of the formed gel was adjusted to 11 and the gel was transferred to the autoclave. The hydrothermal synthesis, washing, drying and calcination steps were the same as described in Section 2.2.

2.3.2. Synthesis of V-MCM-41 using ammonium vanadate as the vanadium source

A similar procedure as in Section 2.3.1 was followed, except that the vanadium source used was ammonium vanadate. Sufficient amount of ammonium vanadate was added to the synthesis mixture in order to supply a desired V/Si ratio of 0.09 in the solution.

2.4. Characterization of materials

The XRD patterns of all the synthesized materials were measured using a Philips PW 3040 diffractometer with Cu Kα radiation source (wavelength 0.15406 nm), a step size of 0.02 and a scan speed of 0.025 ($2\theta\ s^{-1}$). The characteristic lattice parameter (the repeating distance "a" between two pore centers) was calculated from the following equation [13,15]:

$$a = 2d_{(1\,0\,0)}\sqrt{3} \tag{1}$$

The BET surface area values and pore size distributions were measured using nitrogen adsorption (Micrometrics/ASAP 2000). Before the measurements, calcined samples were outgassed in vacuum overnight at 110 °C. Pore size distributions and pore diameters were calculated by the BJH method from the adsorption branch of the nitrogen adsorption–desorption isotherms. The pore wall thickness δ was then estimated from the average pore diameter (d_p) and the lattice parameter (a) using the following equation [13]:

$$\delta = a - 0.95 d_p \tag{2}$$

The solid density, the apparent density and the porosity of the synthesized samples were evaluated using the data obtained with a Helium Pycnometer (Micrometrics Pycnometer 1305) and from nitrogen adsorption experiments.

The morphology of the synthesized materials were determined using a Scanning Electron Microscope (SEM, Philips XL 30S FEG) and an Atomic Force Microscope (Digital Instruments MMAFM-2/1700EXL). Near surface compositions of the materials were determined from energy dispersive spectroscopy (EDS) using JSM-6400 SEM (JEOL) equipped with NORAN System 6. The V/Si ratio at the external surface and also the oxidation state of vanadium in the V-MCM-41 structure were evaluated from X-ray photoelectron spectroscopy (XPS). Atomic absorption spectrometry on Philips PU9200X spectrometer was used to determine the V/Si ratio in the solid.

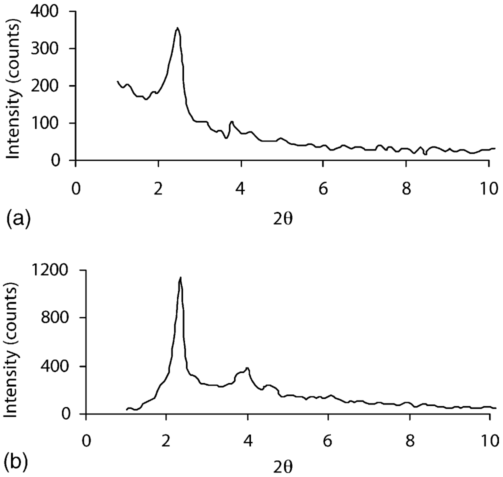

Fig. 1. X-ray diffraction patterns of (a) V9-MCM-41 and (b) V9A-MCM-41.

3. Results and discussion

In the XRD patterns of V-MCM-41 materials prepared using different vanadium sources (Fig. 1), the characteristic sharp Bragg peak corresponding to $d_{(1\,0\,0)}$ and two to four other reflections are detected. For instance, the major peak and the reflections were observed at 2θ values of 2.33, 4.01, 4.49 and 6.05 with the V9A-MCM-41 sample (vanadium source is NH_4VO_3 in this sample, Table 1.). The $d_{(1\,0\,0)}$ spacings and corresponding values of lattice parameter "a" (repeating distance between two pore centers evaluated from Eq. (1)) are reported in Table 1.

The specific surface area values of the synthesized MCM-41 materials were found to be very high (1400 and 1452 m^2/g for the two repeated samples, Table 1). The bulk densities, pore volumes, average pore diameters and porosities of these two MCM-41 materials were also very close to each other showing the reproducibility of the synthesis procedure. A decreasing trend was observed in the BET surface area with an increase of V/Si ratio (in the solution) using $VOSO_4$ as the vanadium source (Table 1). This decrease in specific surface area was accompanied with an increase in bulk density and a decrease in pore volume. The average pore diameters of the MCM-41 and V-MCM-41 materials having V/Si ratios of 0.01 and 0.03 in the solution were around 2.7 nm. A somewhat higher average pore diameter was observed in V9-MCM-41 and V9A-MCM-41 materials. It was interesting to observe that V-MCM-41 catalyst prepared by using NH_4VO_3 as the vanadium source (V/Si = 0.09 in the solution) had a higher BET surface area and a higher pore volume than the corresponding V-MCM-41 catalyst prepared using $VOSO_4$ as the vanadium source.

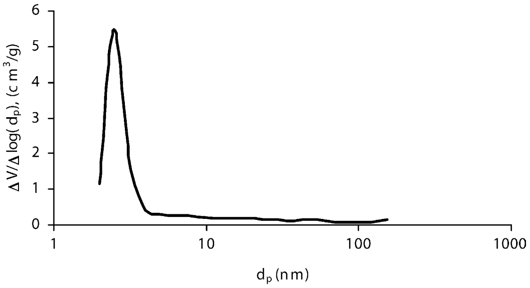

Fig. 2. Pore size distribution of V9A-MCM-41.

The pore wall thickness (δ) of the samples synthesized in this work are estimated from the average pore diameter (d_p) obtained and the lattice parameter "a" using Eq. (2). The δ values (Table 1) for MCM-41 and V-MCM-41 materials (having V/Si ratios of 0.01 and 0.03 in the solution) ranged between 0.92 and 1.06 nm. These values are in good agreement with the published values in the literature [13,15].

Narrow pore size distributions of the materials synthesized in this work are illustrated in Fig. 2. The sponge-like appearance of the V9-MCM-41 and V9A-MCM-41 particles are clearly seen in Fig. 3. In the AFM photograph (Fig. 4), particle shapes and dimensions of MCM-41 (1) are illustrated.

The XPS results showed that the V/Si ratio at the external surface of V9-MCM-41 was about four times higher than the corresponding value for V9A-MCM-41. To clarify this observation, energy dispersive spectroscopic analysis (EDS) of the same samples were also carried out. The EDS results obtained with V9-MCM-41 (sample with a V/Si ratio of 0.09 in the solution using $VOSO_4$ as the vanadium source) gave a V/Si ratio of 0.16. However, the V/Si ratio estimated from the EDS of V9A-MCM-41 (sample with V/Si ratio of 0.09 in the solution, synthesized using NH_4VO_3 as the vanadium source) was only 0.031. These results were also justified by atomic absorption spectroscopy (AAS) analyses of our

Table 1
Physical properties of MCM-41 and V-MCM-41 catalysts

Sample ID	(V/Si) (solution)	BET surface area (m^2/g)	Bulk density (g/cm^3)	Porosity, $\in$	Pore volume (cm^3/g)	Average pore diameter, d_p (nm)	$d_{(1\,0\,0)}$	Lattice parameter, "a" (nm)	Pore wall thickness, δ (nm)
MCM-41 (1)	–	1400	0.66	0.66	1.00	2.69	3.02	3.49	0.94
MCM-41 (2)	–	1452	0.67	0.67	1.01	2.74	3.08	3.56	0.96
V1-MCM-41	0.01	1315	0.71	0.65	0.92	2.71	3.14	3.63	1.06
V3-MCM-41	0.03	813	1.13	0.50	0.44	2.85	3.14	3.63	0.92
V9-MCM-41	0.09	481	1.18	0.62	0.53	3.68	3.60	4.16	0.67
V9A-MCM-41	0.09	1053	0.71	0.76	1.08	3.15	3.79	4.38	1.38

Note: for samples V1-MCM-41, V3-MCM-41 and V9-MCM-41 the vanadium source is $VOSO_4$ and for sample V9A-MCM-41 the vanadium source is NH_4VO_3.

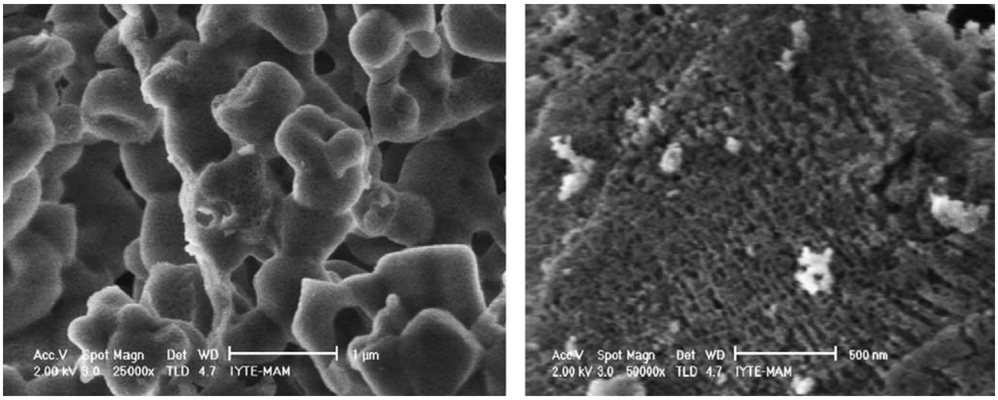

Fig. 3. SEM photographs of (a) V9A-MCM-41 and (b) V9-MCM-41.

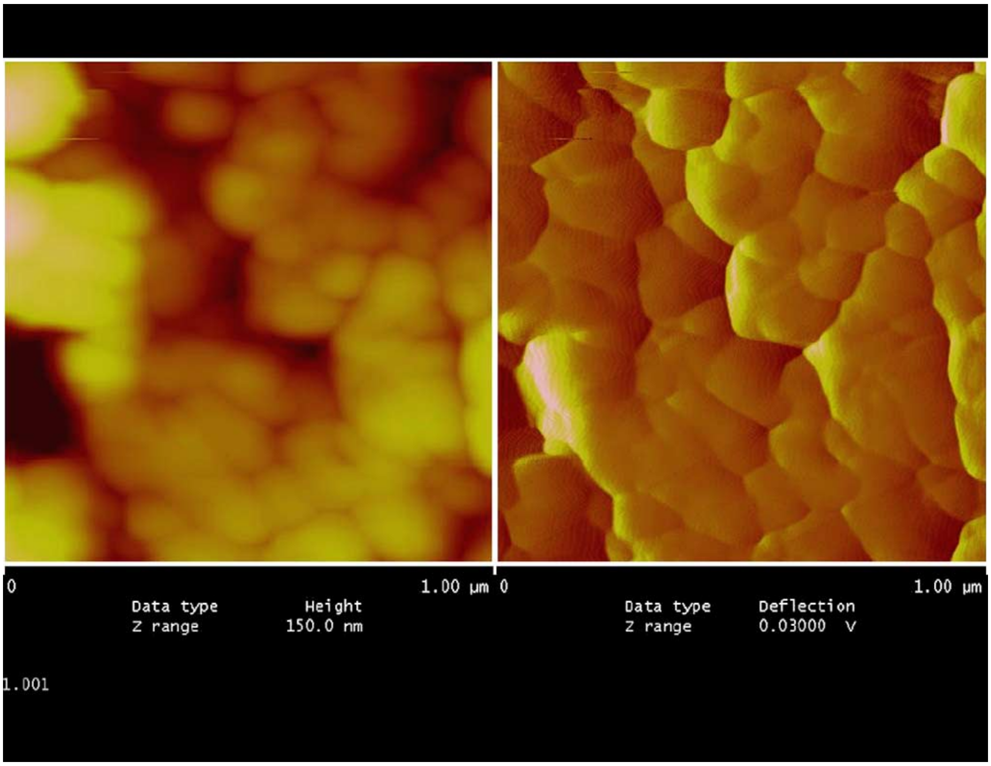

Fig. 4. AFM photograph of MCM-41.

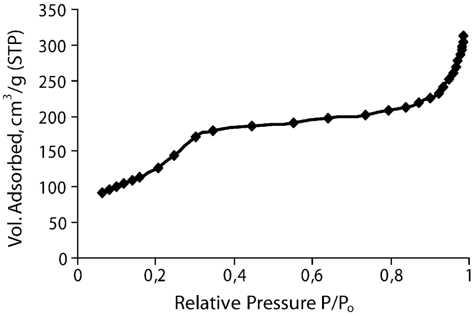

Fig. 5. Nitrogen adsorption isotherm of V9-MCM-41.

samples V9-MCM-41 and V9A-MCM-41. For instance, for V9-MCM-41, the V/Si ratio was obtained as 0.029 from AAS analysis. These results showed that when NH_4VO_3 was used as the vanadium source, most of the vanadium could not be incorporated into the structure of the MCM-41 matrix. However, incorporation of vanadium using $VOSO_4$ as the vanadium source was highly successful. The oxidation state of vanadium in all the V-MCM-41 samples synthesized in this work was found as +5 from XPS peak of V ($2p_{3/2}$) at 517.2 eV.

The nitrogen adsorption isotherms obtained with V9-MCM-41 and V9A-MCM-41 were all found to be Type IV isotherms as described in the IUPAC classification (Fig. 5). Capillary condensation of nitrogen was observed at relative pressures between 0.30 and 0.35. These results were also in agreement with the nitrogen adsorption isotherms reported in the literature for pure MCM-41 [15,16].

4. Concluding remarks

MCM-41 materials prepared in this work had surface area values over 1400 m^2/g. Vanadium was successfully incorporated into the MCM-41 structure following a direct hydrothermal synthesis procedure and using $VOSO_4$ as the vanadium source. Some decrease of surface area was observed with an increase of V/Si ratio. It was shown that if NH_4VO_3 was used as the vanadium source, V/Si ratio in the solid structure was about five times smaller than the corresponding value obtained with $VOSO_4$. Washing and calcination procedures were found to be very critical in the preparation of high surface area MCM-41 type materials.

Acknowledgements

Turkish State Planning Organisation Research Grant DPT-03-04-DPT.2003K120920-05 is gratefully acknowledged. Also we thank to Dr. Sefik Suzer for XPS results and Dr. Halil Kalipcilar for his advice.

References

[1] M.Y. Shin, C.M. Nam, D.W. Park, J.S. Chang, Appl. Catal. A: Gen. 211 (2001) 213.
[2] S. Yasyerli, G. Dogu, I. Ar, T. Dogu, Chem. Eng. Sci., 2003.
[3] G. Karamullaoglu, T. Dogu, Chem. Eng. Commun. 190 (2003) 1427.
[4] N.F. Chen, W. Ueda, Catal. Today 64 (2001) 121.
[5] W. Ueda, K. Oshihara, Appl. Catal. A: Gen. 200 (2000) 135.
[6] Q. Zhang, Y. Wang, Y. Ohishi, T. Shishido, K. Takehira, J. Catal. 202 (2001) 308.
[7] M.L. Pena, A. Dejoz, V. Fornes, F. Rey, M.I. Vazquez, J.M.L. Nieto, Appl. Catal. A: Gen. 209 (2001) 155.
[8] B. Solsona, T. Blasco, J.M.L. Nieto, M.L. Pena, F. Rey, A. Vidal-Moya, J. Catal. 203 (2001) 443.
[9] D. Wei, W.T. Chueh, G.L. Haller, Catal. Today 51 (1999) 501.
[10] S. Lim, G.L. Haller, Appl. Catal. A: Gen. 188 (1999) 277.
[11] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[12] M. Grün, K.K. Unger, A. Matsumoto, K. Tsutsumi, Microporous Mesoporous Mater. 27 (1999) 207.
[13] G. Schulz-Ekloff, J. Rathouský, A. Zukal, Int. J. Inorg. Mater. 1 (1999) 97.
[14] B. Lindlar, A. Kogelbauer, P.J. Kooyman, R. Prins, Microporous Mesoporous Mater. 44–45 (2001) 89.
[15] U. Ciesla, F. Schüth, Microporous Mesoporous Mater. 27 (1999) 131.
[16] M. Jaroniec, M. Kruk, H.J. Shin, R. Ryoo, Y. Sakamoto, O. Terasaki, Microporous Mesoporous Mater. 48 (2001) 127.
[17] G. Oye, J. Sjöblom, M. Stöcker, Adv. Colloids Interface Sci. 89–90 (2001) 439.
[18] G. Grubert, J. Rathouski, G. Schulz-Ekloff, M. Wark, A. Zukal, Microporous Mesoporous Mater. 22 (1998) 225.
[19] N. Lang, P. Delichere, A. Tuel, Microporous Mesoporous Mater. 56 (2002) 203.