

Synthesis of Mesoporous Vanadium Silicate Molecular Sieves

Kondam Madhusudan Reddy, Igor Moudrakovski and Abdelhamid Sayari*

Department of Chemical Engineering and CERPIC Université Laval, Ste-Foy, Québec, Canada G1K 7P4

Substitution of vanadium into the framework of mesoporous MCM-41 molecular sieves has been achieved; these materials were found to be very efficient catalysts for the selective oxidation of large organic molecules using hydrogen peroxide.

Vanadium silicate molecular sieves are a new class of catalysts with remarkable catalytic properties in the selective oxidation of various organic molecules.¹ All vanadium-modified molecular sieves reported previously are microporous solids with severe restrictions to oxidise large organic molecules.¹

Recently, Kresge *et al.*² discovered a new family of mesoporous molecular sieves designated as M41S. MCM-41, one of the members of this extensive family of materials, possesses a hexagonal array of uniform mesopores.^{2,3} MCM-41 has been synthesized with uniform channels varying from approximately 15 Å to more than 100 Å in size. The pore size was found to be dependent on the chain length of the organic template (surfactant) used in the hydrothermal synthesis. In this communication, for the first time, we report the preparation and characterization of mesoporous vanadium silicate molecular sieve, V-MCM-41. The activity of V-MCM-41 in the oxidation of 1-naphthol and cyclododecane is also reported.

The hydrothermal synthesis of V-MCM-41 was carried out using gels with the following molar composition: $\text{SiO}_2 \cdot x \cdot \text{VO}_2 \cdot 0.17\text{Na}_2\text{O} \cdot 0.5\text{RBr} \cdot 30\text{H}_2\text{O}$, where $x \leq 0.02$ and RBr designates the organic template.

In a typical synthesis, fumed silica (Cab-O-Sil M5) was dissolved in a NaOH solution and stirred for 30 min. Then an aqueous solution of vanadyl sulfate was added to the mixture which was stirred for an additional 3 h before adding the organic template, dodecyltrimethylammonium bromide. After one more hour of stirring, the resulting mixture was poured into a 100 ml Teflon lined stainless-steel autoclave which was tumbled at 25 rpm at 373 K in an oven for 6 d. After crystallization, the product was filtered, washed with deionised water, dried at 373 K and calcined in air at 823 K for 6 h. The product yield was about 90%. The pure-silica polymorph of MCM-41 was synthesized using the same procedure, except that no vanadium was added.

The X-ray diffraction pattern of V-MCM-41 (Fig. 1) matches well that of the vanadium-free silica polymorph MCM-41 and also the patterns reported by Kresge *et al.*² One major peak along with three small peaks were observed. Beck *et al.*³ indexed these peaks for a hexagonal unit cell the parameter of which was calculated using $a_0 = 2d_{100}/\sqrt{3}$. It was also observed that the d_{100} d -spacing, which indicates approximate pore size, increases with the chain length of the organic template. Table 1 shows the d -spacing and unit cell parameter of V-MCM-41 and its silica polymorph. The increase in the unit cell parameter of V-MCM-41 compared to its pure silica analogue (Table 1) confirms the presence of vanadium in the silicate framework. Insertion of metal ions larger than silicon brings about an increase in the unit cell parameters because of the longer M–O bond distance. Similar findings were reported for all microporous vanadium silicates. In these reports, the expansion of the unit cell was considered as an indication of the presence of vanadium in the molecular sieve framework.¹ Note however that in our case, the increase in the unit cell parameter is somewhat too high because of the large uncertainties on low diffraction angle values.

The N_2 adsorption isotherms of V-MCM-41 and its silica polymorph are characteristic of mesoporous materials with uniform pore size.^{2–4} These isotherms show an inflection characteristic of capillary condensation within the pores. The relative pressure at which this inflection occurs increases with the diameter of the pores.³ In our case, it occurred at p/p^0

between 0.15 and 0.20. The average pore diameter for both samples as calculated using the BJH model⁵ are given in Table 1. BET surface areas were about 950 $\text{m}^2 \text{g}^{-1}$.

The strongest indication that vanadium belongs to the molecular sieve framework was provided by ^{51}V NMR spectroscopy. Fig. 2 shows the ^{51}V NMR spectra of calcined V-MCM-41 recorded under both static and magic angle spinning (3300 Hz) conditions. In both cases two signals were observed; a major signal at $\delta -527$ with a shoulder at $\delta -506$ which is better resolved in MAS spectrum. The relative intensities of these two peaks were 65 and 35% respectively. Isotropic chemical shifts of *ca.* $\delta -500$ are typical of tetrahedral vanadium(v).¹⁶ The occurrence of two peaks may be indicative of two tetrahedral vanadium species with different local environments.^{6d} The observed linewidths at half height were *ca.* 20 and 12 ppm for static and MAS conditions, respectively; much narrower than for supported vanadium oxide catalysts. This kind of narrow signal without anisotropy have been observed in monomeric orthovanadates with isolated tetrahedrally coordinated vanadium ions.⁶ Finally the absence of a NMR peak with a chemical shift of about $\delta -300$ indicates that our V-MCM-41 material is free of

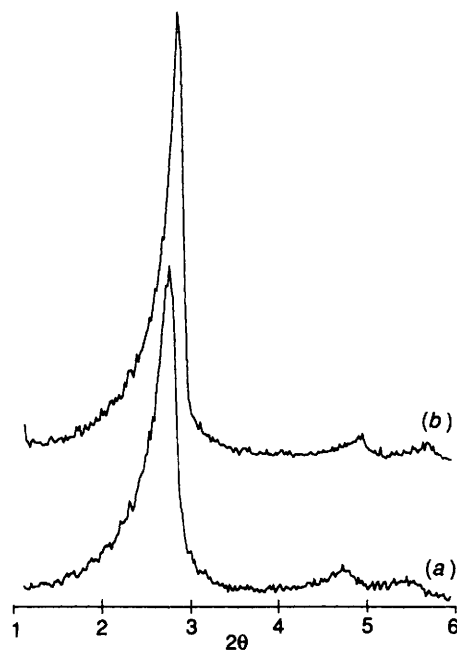


Fig. 1 X-Ray powder diffraction patterns of V-MCM-41 (a) and its silica polymorph (Si-MCM-41) (b)

Table 1 Properties of MCM-41 molecular sieves

Sample	Si/V in gel	Si/V in product	XRD d_{100} d -spacing/Å	Unit cell parameter a_0 /Å	Average pore diameter/Å
V-MCM-41	50	60	32.2	37.18	25.8
MCM-41 silica polymorph	—	—	31.3	36.14	25.2

V_2O_5 .⁶ This conclusion was also confirmed by Raman spectroscopy.

The catalytic activity of V-MCM-41 was tested in the oxidation of two large organic molecules, cyclododecane and 1-naphthol by diluted hydrogen peroxide (30 wt%). The oxidation of 1-naphthol was carried out batchwise in a round bottom flask, whereas the oxidation of cyclododecane was carried out in a 300 ml Parr autoclave. The reaction conditions for cyclododecane oxidation were as follows: 0.1 g catalyst, 25 ml solvent (acetonitrile), 2 g reactant, 3 mole ratio of H_2O_2 to reactant, 373 K reaction temperature and 24 h of reaction time. The oxidation of 1-naphthol was carried out at 353 K for 6 h using 0.2 g catalyst, 10 ml solvent (acetonitrile), 2 g reactant and 3 mole ratio of reactant to H_2O_2 . The products were analysed by gas chromatography (HP 5890A) using a capillary column (HP-1). In the oxidation of cyclododecane, the products were mainly cyclododecanone (67%) and cyclo-

dodecanol (27%) with 34.2% conversion and 21% H_2O_2 selectivity. Oxidation of 1-naphthol led mainly to 1,4-naphthoquinone (84 wt%) and 1,4 dihydroxynaphthalene (11 wt%), 1,2 naphthoquinone (5 wt%) with a very high hydrogen peroxide efficiency of 64% at about 11.3% conversion. These results clearly show that V-MCM-41 is highly active and selective for the partial oxidation of cyclododecane and 1-naphthol.

In conclusion, for the first time a mesoporous vanadium containing molecular sieve V-MCM-41 has been synthesised. V-MCM-41 has a great potential as catalyst for the synthesis of fine chemicals.

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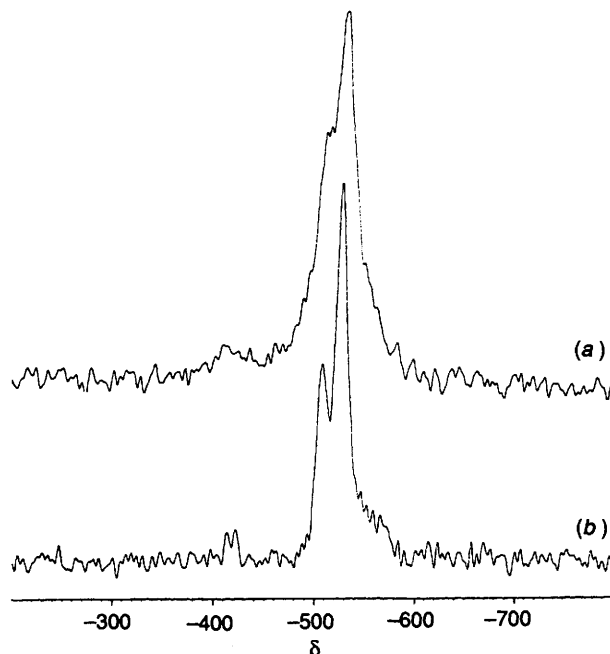


Fig. 2 ^{51}V NMR spectra of calcined V-MCM-41, (a) static and (b) MAS (3300 Hz). The spectra were recorded on a Bruker AMX-300 spectrometer at a frequency of 78.9 MHz (magnetic field 7T); the number of accumulations was 8000. Chemical shifts were measured using $VOCl_3$ as a reference.

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