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Synthesis of Mesoporous V–Mg–O Nanofibers

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ABSTRACT

A mesostructured V–Mg–O was synthesized for catalytic purposes using vanadium(V) oxide and magnesium chloride as sources and various surfactants or surfactant mixtures as templates. Among the surfactants employed, it was found that cetyltrimethylammonium bromide (CTAB) and the mixture of CTAB and hexadecylamine (HDA) templated fibrous lamellar-like mesostructures. The mixture of CTAB + HDA was more efficient in templating the fibrous mesoporous V–Mg–O than the individual surfactants.

Introduction. Because of their promising characteristics, such as large and tailorable pore sizes, narrow pore size distributions, long-range ordering of the pore packing, high specific surface areas, variable framework compositions and, in most cases, high thermal stability, the mesoporous materials have been utilized or could be potentially used for selective adsorption[1−3] and catalysis[4−7] and as functional materials.[8−12] So far, the synthesis of mesoporous materials was focused on (i) the enlargement of the pores and the stabilization of the mesostructure; (ii) the modification of the mesoporous silicate by incorporating heteroatoms and the preparation of mesoporous materials from other elements; and (iii) the morphology control. The emphasis was, however, mostly on the first two features. Generally, the mesoporous materials were obtained as aggregates and loose agglomerates of small particles. However, for numerous applications in catalysis, chemical sensors, or as optical devices, specific morphologies may be required. In the present letter, we report about the synthesis of nanofibrous mesoporous V−Mg−O, whose formation we noted during the preparation of a catalyst for the oxidation of alkanes.

Experimental Section. *Syntheses*. All reagents were purchased from Aldrich and used without further purification. A certain amount of vanadium(V) oxide was first dissolved in a 0.1 M dilute sodium hydroxide solution with stirring and heating at the boiling temperature of the solution. Then, an aqueous solution containing magnesium chloride and a surfactant (dodecylbenzenesulfonic sodium salt (SDBS), cetyltrimethylammonium bromide (CTAB), hexadecylamine (HDA), or triblock copolymer poly(ethylene oxide)-poly-(propylene oxide)-poly (ethylene oxide) (PEO−PPO−PEO)) was added with intense stirring to the vanadium-containing solution. The pH had to be adjusted to a value in the range 3∼4, using a dilute hydrogen chloride solution. The final mixture had the molar composition of $V_2O_5/MgCl_2/0.25$

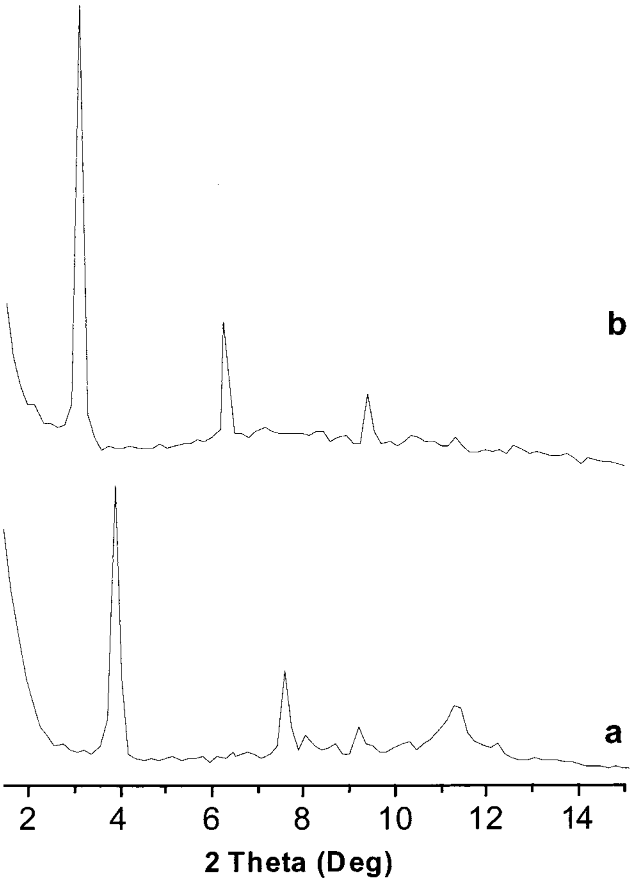

Figure 1. XRD spectra of mesostructured V−Mg−O synthesized with (a) CTAB and (b) CTAB + HDA as surfactant.

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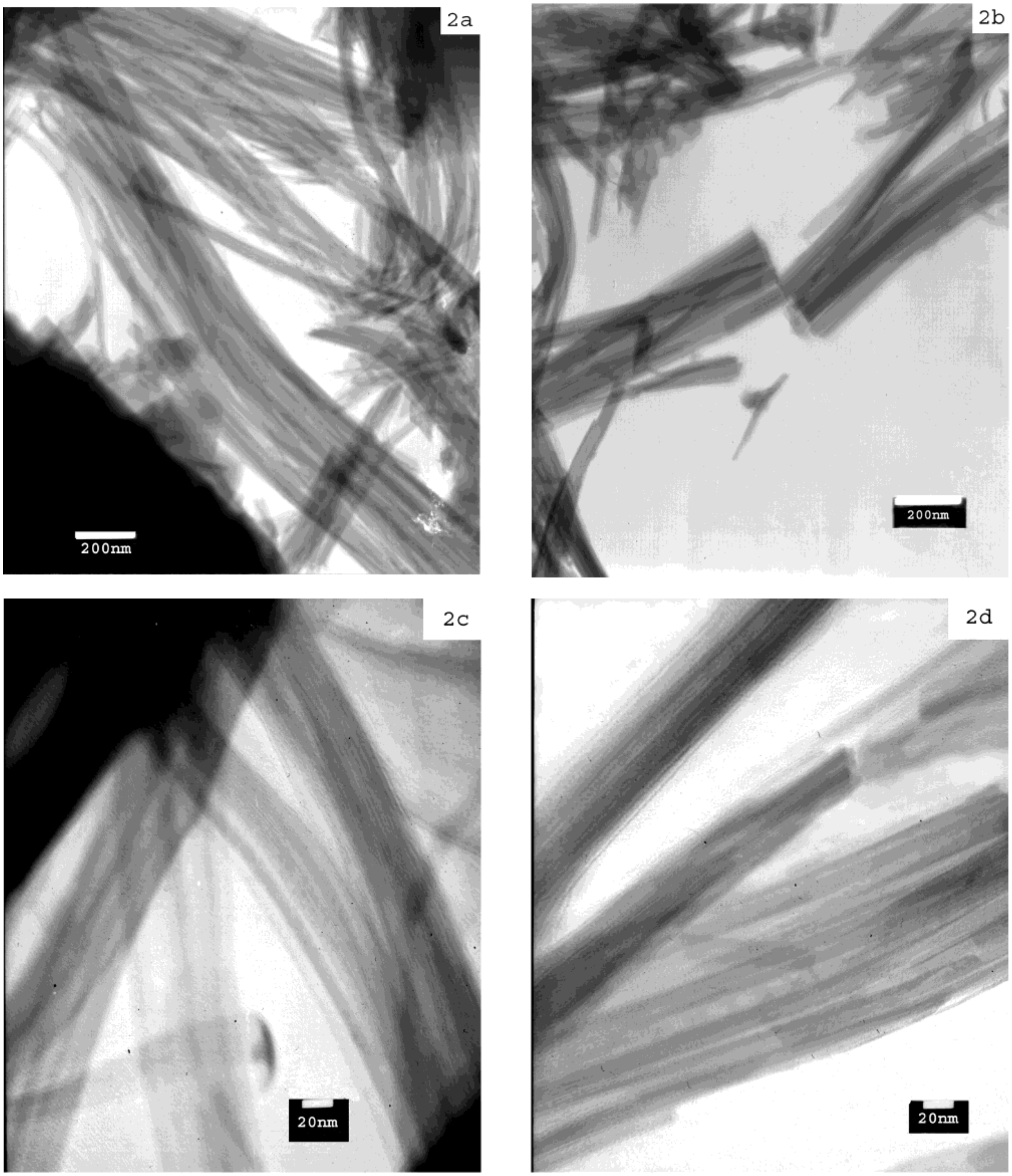

Figure 2. TEM micrographs of mesostructured V−Mg−O synthesized with (a) and (c) CTAB; and (b) and (d) CTAB + HDA as surfactant. ((a) and (b) are with lower and (c) and (d) with higher resolutions.)

surfactant/295 H_2O. The gel obtained was stirred at room temperature for about 24 h and then kept for aging for 2 days. The solid product was recovered by filtration, washed with distilled water, dried at 373 K for 12 h, and further used for the X-ray diffraction and transmission electron microscopy characterization.

Characterization. X-ray diffraction (XRD) spectra were obtained on a Siemens D500 diffractometer using Cu Kα radiation of wavelength 1.5406 Å. The diffraction data were recorded for 2 θ angles between 1 and 15°, with a resolution of 0.02°.

Transmission electron microscopy (TEM) was carried out on a JEM-2010 electron microscope equipped with a tungsten gun operating at an accelerating voltage of 200 kV. The samples were ground in methanol and supported on a holey carbon film located on a Cu grid.

Nitrogen adsorption−desorption isotherms were determined at 77 K with a Micromeritics ASAP 2010 gas sorption and porosimetry apparatus. Before the measurements, the synthesized samples were pretreated in a flow of nitrogen from room temperature to 623 K at a heating rate of 10 K/min and kept at 623 K for 8 h to remove the surfactant template. Then, the sample was transferred to an ASAP 2010 apparatus and outgassed at 623 K for 4 h under a vacuum of 1×10^{-3} Torr. The specific surface area was determined by using the BET method and the pore volumes were estimated at a relative pressure $P/P_0 > 0.99$, assuming full surface saturation with nitrogen. The pore size distribution was obtained from the N_2 desorption branch by using the BJH (Barrett−Joyner−Halenda) method.

The energy dispersive spectroscopy (EDS) investigation was carried out with specimens treated as for the N_2 adsorption experiments, using a Hitachi S-4000 field emission SEM, operating at 20 KeV. The spectra were obtained using a PGT IMIX X-ray microanalysis equipment and were collected for 100 seconds at a 44.9° takeoff angle.

Results and Discussion. In the preparation of the mesoporous V−Mg−O, various surfactants, which are popular in the synthesis of the mesoporous silicate, such as SDBS, CTAB, HDA, or PEO−PPO−PEO, have been tested. It was found that SDBS, HDA, and PEO−PPO−PEO were inactive in templating a mesoporous V−Mg−O phase, as evidenced by the XRD spectra, which exhibited no diffraction peaks for $2\theta < 15°$. However, a mesoporous structure could be obtained when the cationic surfactant CTAB was employed. We have also examined the following equimolar mixtures of surfactants, SDBS + HDA, SDBS + CTAB, and CTAB + HDA, and found that only the mixture CTAB + HDA was effective in the formation of a mesoporous V−Mg−O phase. Figure 1 presents the XRD spectra of two of the synthesized samples. One can see that for the sample prepared with CTAB, there are three main peaks at $2\theta = 3.848°$, 7.548°, and 11.299° (Figure 1 a), corresponding to d spacings of 2.294 (d_{001}), 1.170 (d_{002}), and 0.782 (d_{003}) nm, respectively. Similarly, three main peaks can be observed at $2\theta = 3.082$, 6.180, and 9.281 (Figure 1 b) for the sample prepared with the mixture CTAB + HDA, corresponding to d spacings of 2.864 (d_{001}), 1.429 (d_{002}), and 0.952 (d_{003}) nm, respectively. Both samples have a lamellar-like mesostructure, due to the equidistance of the three peaks in Figures 1a and 1b. There are also some weak peaks, for instance the weak peak at $2\theta = 9.156°$ in Figure 1a, which is probably caused by a nonindexed compound between V, Mg, and O. The intensities of the main peaks in Figure 1b are much stronger than those in Figure 1a. The above results indicate that the sample prepared with CTAB + HDA has a more regular structure than that prepared with CTAB alone.

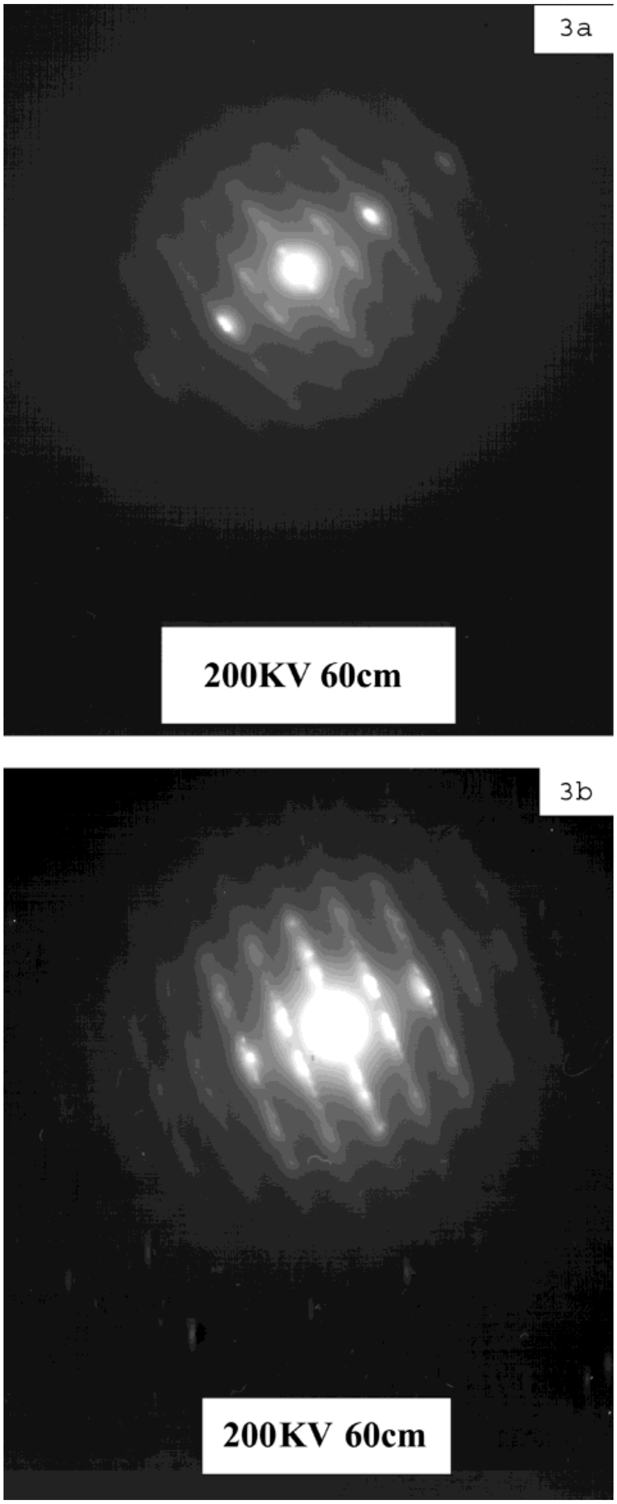

Figure 3. Electron diffraction patterns of mesostructured V−Mg−O synthesized with (a) CTAB and (b) CTAB + HDA as surfactant.

The structure and morphology of the samples were also examined by TEM and electron diffraction, and the micrographs and the diffraction patterns are presented in Figures 2 and 3, respectively. One can see from the TEM micrographs that the samples prepared with CTAB (Figure 2a) and with CTAB + HDA (Figure 2b) have the morphology of fibers with an average diameter of about 50 nm and an average length longer than 1 μm. These fibers have a lamellar-like structure, being composed of numerous fine fibers with average diameters of about 0.6 nm and separation distances of 1.7 and 2.2 nm for the samples prepared with CTAB (Figure 2c) and CTAB + HDA (Figure 2d), respectively. The selected area electron diffraction patterns (Figure 3a and 3b) exhibit sharp reflections with layered symmetry extended to the fourth order, indicating a long-range order in the fine structure of the mesophase. The arrangement of the diffraction spots is more ordered for the sample prepared with CTAB + HDA (Figure 3b) than that prepared with CTAB alone (Figure 3a), indicating a more ordered structure in the former case. There are two sets of diffraction spots in both cases, with one set normal to the other one. One can calculate that the d spacings corresponding to these diffraction spots are about 0.675 and 0.185 nm, respectively.

The samples heat-treated as mentioned above were also examined via nitrogen adsorption−desorption. The isotherms of both samples prepared with CTAB and CTAB + HDA were of type IV, according to the IUPAC classification, and exhibited the characteristic hysteresis loop of mesoporous materials. The specific surface areas, pore volumes, and the average pore sizes are, respectively, 237.67 m^2/g, 0.45 cm^3/g, and 7.56 nm for the sample prepared with CTAB + HDA and 177.96 m^2/g, 0.30 cm^3/g, and 6.74 nm for those prepared with CTAB alone. The pore size distribution was much narrower for the sample prepared with CTAB than with CTAB + HDA.

The surface V/Mg mole ratios of the samples, which were heat-treated as for the nitrogen adsorption−desorption experiments, were determined by EDS. The results show that there is an enrichment in vanadium on the surfaces of the samples. The vanadium/magnesium ratio is somewhat larger on the surface of the sample prepared with CTAB (V/Mg = 1: 0.15) than with CTAB + HDA (V/Mg = 1: 0.22). The enrichment in vanadium is caused by the much lower surface free energy of V_2O_5 than MgO (V_2O_5 has a surface free energy of 90 ergs/cm^2 at 963 K and MgO a surface free energy of 1000 ergs/cm^2 at $T = 298$ K[13]).

Conclusion. Mesostructured V−Mg−O samples were prepared using V_2O_5 and $MgCl_2$ as sources and CTAB or the mixture CTAB + HDA as templates. The synthesized samples exhibited a fibrous morphology (50 nm in diameter) consisting of numerous fine fibers (separated by an average distance of about 2 nm). The mixture of surfactant CTAB + HDA templated a mesoporous V−Mg−O with a larger pore size and higher regularity than CTAB alone.

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