

Hydrothermal Synthesis of Mesostructured Vanadium Oxide and Application of UV-Ozone Treatment

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Effect on hydrothermal treatment of lamellar vanadium oxides was investigated and the formation of hexagonal and cubic mesophase was found. This lamellar materials were prepared by mixing of cetyltrimethylammonium-bromide and pH-controlled sodium metavanadate solution. Thermal method and UV/O₃ treatment were applied to extract organic template. The structure of resulting product was studied by powder X-ray diffraction and transmission electron microscopy (TEM).

Key Words : Mesoporous, Vanadium oxide, Hydrothermal

Introduction

The attention of mesoporous materials has risen since workers at Mobil Corp. exhibited a new family of mesoporous molecular sieves designated as M-41S in 1992,^{1,2} and a number of their reaction mechanisms and applications have been reported.³ These porous materials have large possibilities for many applications because of their large surface area and pore diameter and, especially, new possibilities in catalysis have led to numerous attempts to synthesize transition metal oxide mesoporous material.⁴⁻⁷ However, the conventional method often used in silica, has taken most of transition metal oxide to lamellar structure rather than mesostructured material.⁴ Therefore, novel synthetic method was required for transition metal oxide mesoporous material such as vanadium oxide. For instant, mesostructured vanadium oxide was synthesized by acid-catalyzed polymerization employing layered vanadium oxide material.^{8,9} Miyayam *et al.* have also reported vanadium mesoporous material was synthesized by calcinations of same layered material at low temperature.¹⁰ Here hydrothermal method with layered vanadium oxide as starting materials was used to synthesize mesostructured vanadium oxide. The reaction temperature and pH were varied and structural transformation of resulting materials was studied by powder X-ray diffraction analyses. UV/O₃ condition was also applied for removing surfactants and the structural changes were studied.

Experimental Section

Synthesis of Vanadium-Surfactant Composite. Cetyltrimethyl ammonium bromide (C₁₆TMABr, Aldrich) and sodium metavanadate (NaVO₃, Aldrich) were used to synthesize the present materials as the synthetic method reported by Luca *et al.*^{8,9} The surfactant solution was

prepared by dissolving C₁₆TMABr in distilled water (2.7 wt%). The vanadate solution of 0.15 M was prepared separately by dissolving 4.57 g NaVO₃ in 250 ML distilled water with stirring, and then the solution was heated at 353 K for 1 hour. After the vanadate solution was cooled to room temperature, pH of the solution was adjusted to 6.8 and 4.8 with HCl solution. Finally, the vanadate composites were isolated by adding excess C₁₆TMABr solution to each vanadate solution of different pH values. The resulting precipitate was filtered, washed thoroughly with distilled water and air-dried for 1 day. These will be denoted C₁₆TMA-V4, and C₁₆TMA-V10 and their XRD patterns are shown in Figure 1.

Synthesis of Mesostructured Vanadium Oxide. 1.5 g of C₁₆TMA-V4 was put into a Teflon vessel with distilled water. The reaction vessel was then placed in an autoclave and held for 32 hours at 463 K. The resulting black powder (sample-a) was filtered, washed with distilled water and dried at room temperature. 1.5 g of C₁₆TMA-V4 was slurred in the distilled ethanol and the pH of suspension was adjusted to pH of 2.2 by adding 0.2 M HCl. After slurring for 1 hour, the resulting brown product was filtered, washed with ethanol and distilled water, and air-dried. The resulting powder was then hydrothermally treated at 453 and 463 K for 24 hours. The dark green powders (sample-b) were obtained, washed thoroughly with water and air-dried. 1.5 g of C₁₆TMA-V10 was slurred in distilled water and then pH was adjusted to about 7.5 with 0.2 M ammonium hydroxide. The pH-controlled suspension solution was then treated hydrothermally at 433 K for 32 hours. The resulting black powder (sample-c) was finally washed with water and air-dried. Initial pH of suspension solution prior to addition of ammonium hydroxide was about 6.0.

Results and Discussion

Preparation of Layered Vanadium Oxide. Figure 1 shows the XRD patterns of each C₁₆TMA-vanadium composite before hydrothermal reaction. The XRD pattern of C₁₆TMA-

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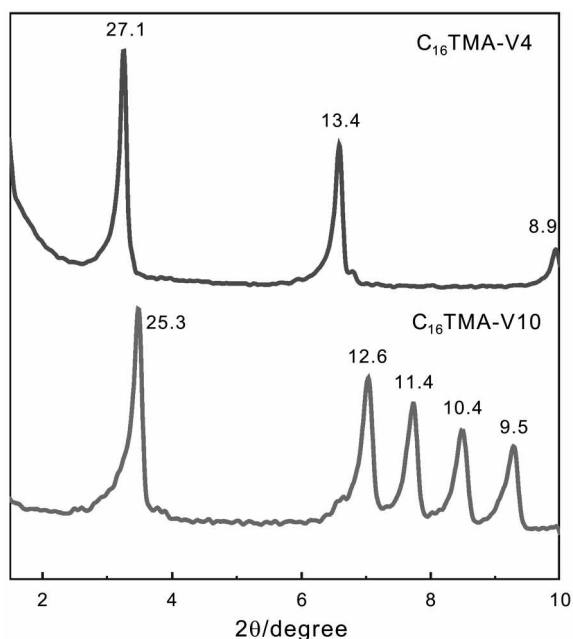


Figure 1. Powder XRD pattern of C_{16} TMA-Vanadate composite.

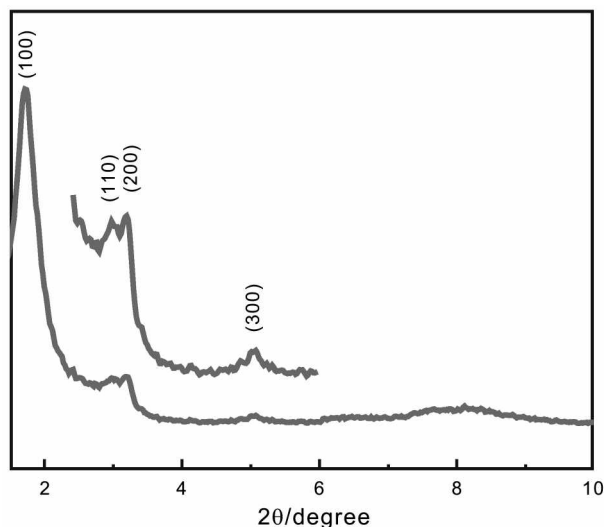


Figure 2. Powder XRD pattern of the sample, synthesized by hydrothermal treatment of C_{16} TMA-V4 at 463 K.

V4 sample contains n , $n+1$ and $n+2$ order reflections (27.1, 13.4 and 8.9 Å) and is similar to that of lamellar structure. The XRD patterns of C_{16} TMA-V10 also show n , $n+1$ order reflection peaks (25.3 and 12.6 Å) but three other peaks (11.4, 10.4 and 9.5 Å) are also given, which are ascribed to decavanadate phase.

Synthesis and Characterization of Mesostructured Vanadium Oxide. XRD powder patterns shown in Figure 2 illustrate structure of C_{16} TMA-V4 sample after hydrothermal reaction at 463 K. The sample may consist of two-dimensional hexagonal $P6mm$ structure and d_{100} spacing of the sample is 51.4 Å. Cubic phase were also obtained after pH control and hydrothermal treatment. The results are shown in Figure 3 and 4. In Figure 3, characteristic peaks for a mesostructure

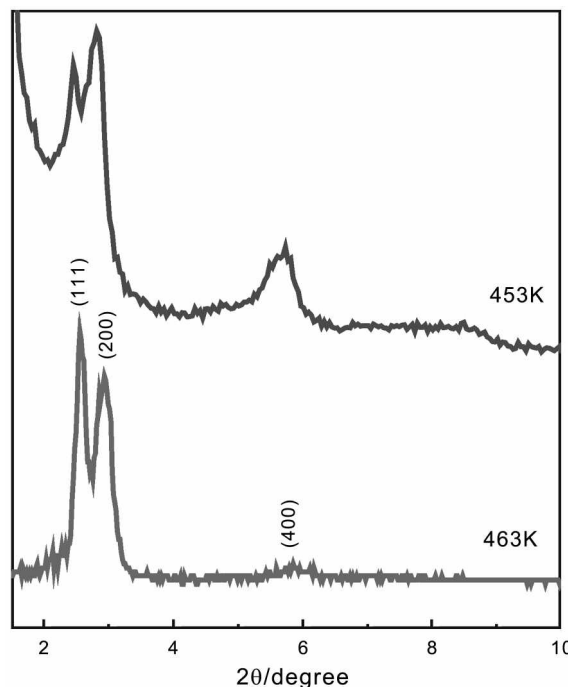


Figure 3. Powder XRD pattern of cubic mesostructured vanadium oxide, obtained from C_{16} TMA-V4.

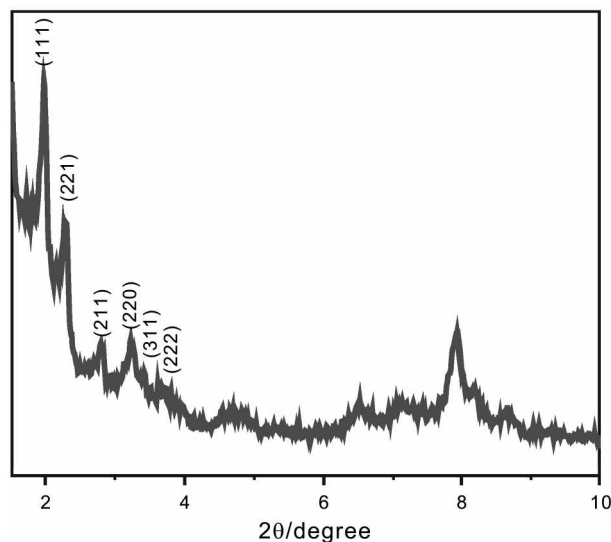


Figure 4. Powder XRD pattern of cubic mesostructured vanadium oxide, obtained from C_{16} TMA-V10.

were observed in sample-b after hydrothermal treated at 453 K. The XRD peaks of sample-b (Figure 3) are indicative of cubic $Fm\bar{3}m$ structure while sample-c involves cubic $Fd\bar{3}m$ structure. The d_{111} value of each cubic sample is 34.5 and 44.6 Å. It is remarkable that hydrothermal treatment of layered vanadate-surfactant composites is efficient for formation of mesostructured vanadium oxide and cubic phase was discovered for the first time in vanadate-surfactant system. It should be noted that all samples exhibit lower thermal stabilities. The structure of the samples was collapsed after calcinations at 603 K but transmission electron micrograph (TEM) of the each uncalcined sample show the

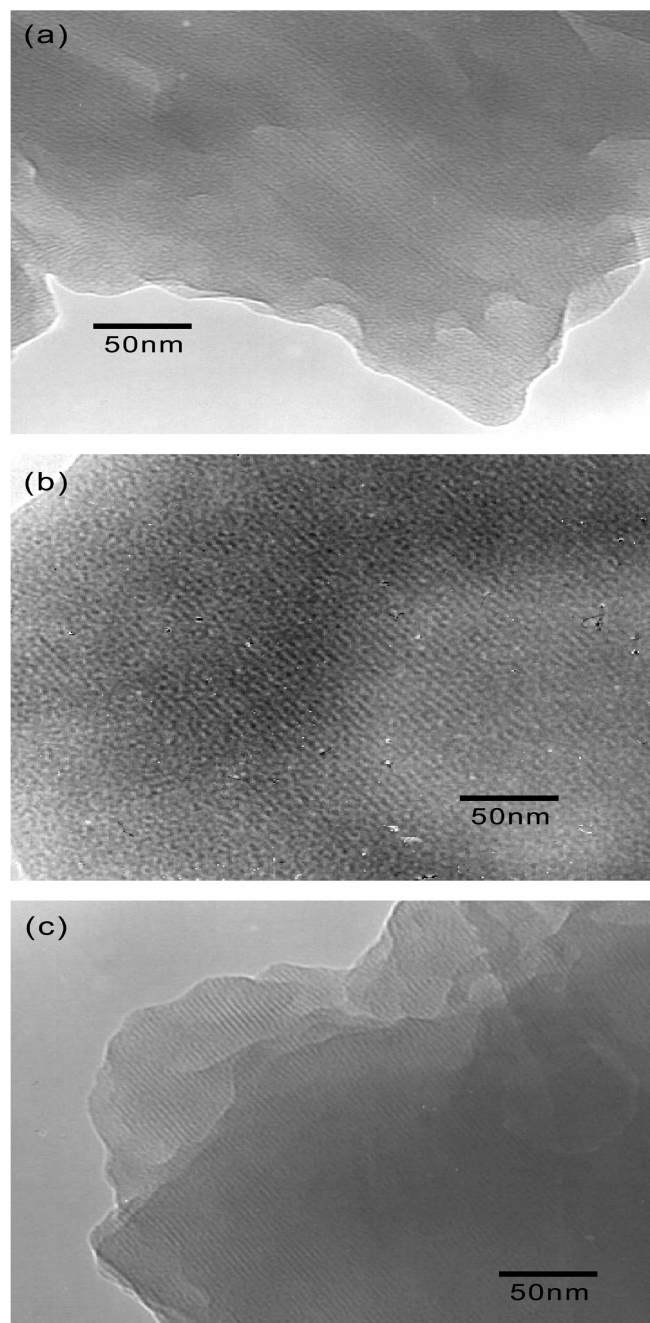


Figure 5. Transmission electron microscope image of (a) hexagonal $P6m$ structure, obtained from C16TMA-V4, (b) cubic $Fm\bar{3}m$ structure from C16TMA-V4 and (c) cubic $Fd\bar{3}m$ structure from C16TMA-V10.

material contains mesostructure rather than layered structure. ED pattern analysis for the samples were unsuccessful.

UV/O₃ Treatment of Mesoporous Vanadium Oxide. In silicate mesoporous system, the UV/O₃ treatment has been applied for removal of surfactants.¹¹⁻¹² Since organic template could not be extracted without structural damage by thermal methods, in the present study UV/O₃ treatment was used to eliminate organic species from the mesoporous material. The XRD patterns in Figure 6 show the transformation sequence of hexagonal mesoporous materials (sample-a) under a UV/O₃ environment for various

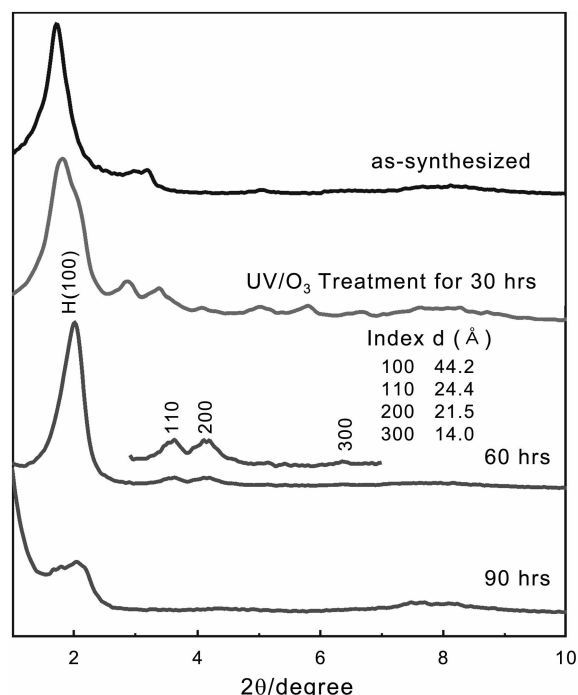


Figure 6. Powder XRD pattern of the samples obtained by UV/O₃ treatment of hexagonal $P6m$ structure at various times.

times. The d_{100} spacing of UV/O₃ treated sample after 60 hours shifts to 44.2 Å from 51.4 Å. One possible explanation is that some oxygen of vanadate reacts with hydrogen in atmosphere to form water and connection of vanadate clusters is formed sharing a oxygen. Removal of surfactants in the present vanadium mesoporous materials was unsuccessful. When the sample-a was treated by UV/O₃ for more than 90 hours, surfactant was extracted more than 50% and structural decomposition occurred. The results about UV/O₃ treatment of the hexagonal structured sample suggest that UV/O₃ treatment could provide an efficient means for the condensation of vanadate clusters but not for removal of surfactant template.

In summary, mesoporous vanadium oxides were after pH control and hydrothermal reaction at various temperatures to form mesophase employing a layered starting material. The poor thermal stability could be resulted from condensation of vanadate, which may be responsible for its fragile structure. Furthermore, this information can possibly provide help on study of transition metal mesoporous materials in inorganic frameworks and surfactant system.

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