Structural Characterization of Titania Nanotube Catalyst

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Nanoscale materials have attracted great interest because of their novel properties, which are different from those of bulk materials. The materials with nanosized tubular structure include carbon, metal sulfides and metal oxides have been developed. Among the nanostructured oxides, titania has been a focus of extensive research due to its chemical stability, large surface area, non-toxicity, and low production cost. Titania nanotubes have been shown their potentials in many fields such as of photocatalysis, hydrogen sensing and solar cells.

In the present work, titania nanotubes were prepared by hydrothermal method. Briefly, 5 g of TiO_2 powders, obtained from Merck (Art. 808) were dispersed in an aqueous solution of 10 M NaOH (180 ml) and then loaded into a Teflon-lined stainless steel autoclave. The autoclave was statically heated at 110 ^oC for several tens hours. After the hydrothermal treatment, the resultant precipitate was separated by centrifugation and washing with diluted HCl solution, and repeated washing until pH < 7. The sample was then dried in an oven at 110 ^oC. After carefully grinding, titania nanotubes were obtained.

TEM micrographs of the prepared titania nanotubes reveal open ends of the hollow nanotube. The diameter is about 9-10 nm with the inner diameter of around 5-6 nm. The wall of the nanotube consists of 3-5 layers with a layer spacing of about 0.89 nm. According to XRD and Raman spectra, we found that the anatase phase of Merck TiO_2 decreased gradually with the increasing hydrothermal time and finally disappeared after 92 hours. Both XRD pattern and Raman spectrum of the titania nanotubes showed new and weak characteristic peaks attributed to titania nanotubes.

Since there is considerable controversy regarding the structure of titania nanotubes, X-ray absorption spectroscopic experiments were conducted to investigate the structure features of titania nanotubes. The Ti K-edge XANES spectrum of Merck TiO_2 contains three major peaks in the pre-edge region, as shown in Figure 1 (a). These pre-edge features were attributed to the forbidden transitions from the core 1s level to unoccupied 3d states of Ti^{4+} and indicated that Ti atoms in Merck TiO_2 located in a symmetric octahedral coordination. The central pre-edge peak around 4.97 eV increased in intensity with the hydrothermal time. The pre-edge profile of titania nanotubes is similar to that of $Na_2Ti_3O_7$, as can be seen in Figure 2, which indicates that the structure of the titania nanotubes might be close to layered titanate [1]. However, the X-ray absorption fine structures of titania nanotubes and $Na_2Ti_3O_7$ were considerably different, detailed EXAFS analyses on the fine structure of titania nanotubes are in progress.

The thermal stability of titania nanotube was studied with TGA/DTG. The weight loss at around 364 ^oC was due to the phase transformation of titania nanotubes. As evidenced by XRD and Raman spectra, the characteristic peaks of titania nanotubes maintained well at 300 ^oC. The structural evolution of the calcined titania nanotubes is revealed by the progressive formation of anatase phase starting at 400 ^oC. At 700 ^oC the XRD and Raman spectra corresponded to typical anatase TiO_2. Further evidence for structure of the calcined titania nanotubes emerged from X-ray absorption spectroscopy. Ti K-edge XANES spectra showed that the pre-edge features of titania nanotubes sustained well at 300 ^oC. The centered pre-edge peak decreased with higher temperature due to the formation of TiO_2. Titania nanotubes calcined at 700 ^oC was identified as anatase TiO_2. Systematic researches will be continued to study the fine structure of calcined titania nanotubes.

Pt/titania nanotubes catalyst was prepared using titania nanotubes as the supporting material, which showed much higher catalytic activity as compared with Pt/TiO_2 catalyst [2]. Ti K-edge XANES spectrum of Pt/titania nanotubes showed no difference as compared to that of titania nanotubes (Figure 2 (b)), which indicates that the structure of titania nanotubes was not affected after the immobilization of Pt. The influence of titania nanotubes on the oxidation state of Pt particles needs further investigation.

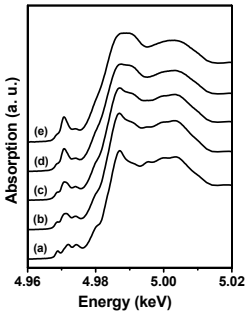

Figure 1. XANES spectra: (a) TiO_2 and titania nanotubes prepared by hydrothermal treatment for (b) 20 h, (c) 44 h, (d) 68 h, and (e) 92 h.

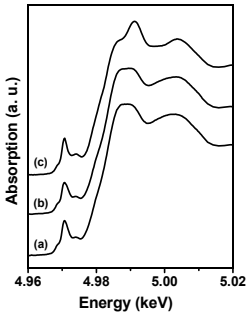

Figure 2. XANES spectra: (a) titania nanotubes and (b) Pt/titania nanotubes, and (c) $Na_2Ti_3O_7$.

References

[1] R. Ma, K. Fukuda, T. Sasaki, M. Osada, and Y. Bando, J. Phys. Chem. B 109 (2005) 6210.
[2] S.-H. Chien, Y.-C. Liou, and M.-C. Kuo, Synthetic Metals 152 (2005) 333.