X-ray Absorption Spectra of Titanium-Containing Mesoporous SBA-15 Applied to CO_2 Photoreduction

Chin-Jung Lin (林進榮)[1], Yi-Jhen Feng (馮怡蓁)[1,2], Wen-Yueh Yu (游文岳)[1], and Shu-Hua Chien (簡淑華)[1,3]

[1]**Institute of Chemistry, Academia Sinica, Taipei, Taiwan**
[2]**Department of Chemistry, National Central University, Chungli, Taiwan**
[3]**Department of Chemistry, National Taiwan University, Taipei, Taiwan**

Photocatalytic reduction of CO_2 into high energy products has been extensively studied as a major alternative to address the greenhouse effect caused by excess CO_2 in the atmosphere, which also provides a non-fossil fuel. In this artificial photosynthesis process, TiO_2 is the mostly common used photocatalyst in aqueous and gasous media due to its chemical stability, non-toxicity, and reasonably low cost. Hwang et al [1] have demonstrated the utilization of mesoporous molecular sieves (MCM-41, MCM-48 and SBA-15) to highly disperse TiO_2 exhibits much higher photocatalytic reactivity for the reduction of CO_2 with H_2O as compared to bulk TiO_2, in which SBA-15 shows superior enhancement of photocatalytic reactivity. Thus, TiO_2 highly dispersed within mesoposros molecular sieves would facilitate the development of a process that could be designed for highly efficient photocatalytic systems.

In this work, titanium-containing mesoporous SBA-15 (Ti-*vc*-SBA (Ti/Si=0.01 (w/w))) was synthesized through a modified preparation process of SBA-15 by ternary surfactant system (C_{16}TMAB, SDS and P123), sodium silicate as Si source and $(NH_4)_2TiF_6$ as Ti source, under weak acidic conditions (pH=5), followed by grafting TiO_2 onto Ti-*vc*-SBA using TBOT/hexane solution in a cooling reflux system Meanwhile, Ti-SBA synthesized via hydrothermal method using P123 alone as template was modified by TiO_2 (TiO_2/Ti-SBA) for comparison. Initially, the prepared materials were characterized by XRD, HRTEM, AAS, nitrogen sorption isotherm, UV-vis and XPS. X-ray absorption Near edge structure (XANES) data were collected using synchrotron radiations at NSRRC BL17C1 beam lines.

The dimensions of Ti-SBA are in the micrometer size range, whereas Ti-*vc*-SBA are quite thin (thickness< 100 nm). Most Ti-SBA have channels lying parallel to the surface, although some with perpendicular channels were observed. In contrast, the face-up nanochannels of Ti-*vc*-SBA were the only structures we saw.The XRD patterns of Ti-*vp*-SBA and Ti-SBA exhibit a peek of (1 0 0), which are the characteristic of a highly ordered hexagonal structure. UV-Vis spectra of TiO_2/Ti-*vc*-SBA and TiO_2/Ti-SBA show that the band edge of 360 nm is observed. The AAS and XPS data show the more amount of TiO_2 were added onto Ti-*vc*-SBA as compared to that of Ti-SBA.

A feature of the pre-edge spectrum at the Ti K-edge is sensitive to the symmetry of the surrounding atoms, being dipole forbidden, as indicated that the octahedral symmetry of Ti(Ⅳ) has a low intensity, whereas tetrahedral symmetry is allowed and intensive[2]. This effect has led to the extensive use of pre-edge spectra for establishing the coordination of titanium in oxide coumpounds. As shown in Fig. 1 (a) and (b), both Ti-*vc*-SBA and Ti-SBA exhibit an intense single pre-edge peak, indicating the titanium oxide species in both *vc*-SBA-15 and SBA-15 have tetrahedral symmetry of the titanium site. Highly dispersed titanium oxide species in the frameworks of SBA-15 were obtaind. The presence of small, broad, additional peaks were detected as in Fig. (c) and (d), existing an aggregated octahedrally coordinated titanium oxide species as well as the tetrahedrally coordinated titanium oxide species. This implies extraframework titanium oxide species were formed after refluxing Ti-*vc*-SBA and Ti-SBA with TBOT/hexane solution. A correlation of the titanium content in the samples with XANES results relates the increase of the Ti/Si ratio with an increase of the highly coordinated titanium oxide species and a decrease of the pre-edge peak intensity. TiO_2/Ti-*vc*-SBA exhibited higher photocatlytic reactivity in CO_2 photoreduction than TiO_2/Ti-SBA, resulting from higher amount of highly dispersed titanium oxide species incorporated and higher accessible to reactants.

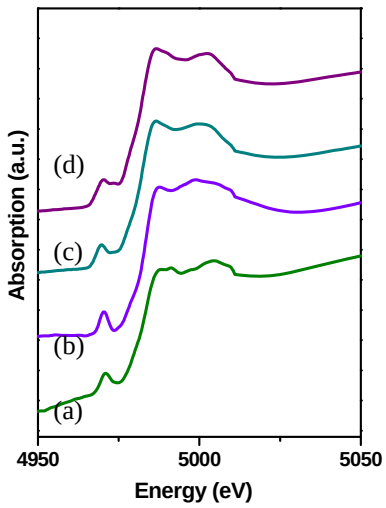

Figure 1. The XANES spectra of Ti-SBA (a), Ti-*vc*-SBA (b), TiO_2/Ti-SBA (c) and TiO_2/Ti-*vc*-SBA (d).

References:
[1] J.Hwang, J. Chang, S. Park, K. Ikeue, and M. Anpo, Top. Catalysis **35**, 311 (2005).
[2] G. N. Vayssilov, Catal. Rev. Sci. Eng. **39**, 209 (1997).