

Structural Determination of Nano-particles and Functional Groups in Porous Oxides with X-ray Absorption Spectroscopy

Shih-Yuan Chen (陳仕元)¹, Din-Goa Liu (劉定國)²,
Jyh-Fu Lee (李志甫)², and Soofin Cheng (鄭淑芬)¹

¹Department of Chemistry, Taiwan University, Taipei, Taiwan

²Research Division, National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Our laboratory has recently developed an one-step aqueous sol-gel and hydrothermal process to efficiently synthesize large mesoporous silica materials with crystallized SnO₂ nanorods embedded in the mesochannels when the Sn/Si molar ratios in the gel were in the range of 0.05 – 0.1. The phase transformation from 2D hexagonal *P6mm* to 3D hexagonal *P6₃mmc* pore structure was observed by using *ex-situ* and *in-situ* XRD techniques. The size of crystallized SnO₂ nanorods with tetragonal phase was 5 – 10 nm in diameter and 10 – 30 nm in length based on TEM photographs. The domain size of SnO₂ nanorods were examined by Sn *K*-edge X-ray absorption spectroscopy and EXAFS analysis.

The Sn *K*-edge X-ray absorption spectra of calcined Sn-MSM are shown in Figure 1. The as-made materials showed similar spectra with that of calcined materials. They displayed similar features in the absorption edge, i. e. the XANES spectra, with that of commercial SnO₂ material. It indicated that the structural symmetry and oxidation number of tin oxides incorporated into the mesoporous silica materials was probably similar to that of bulk SnO₂ material.

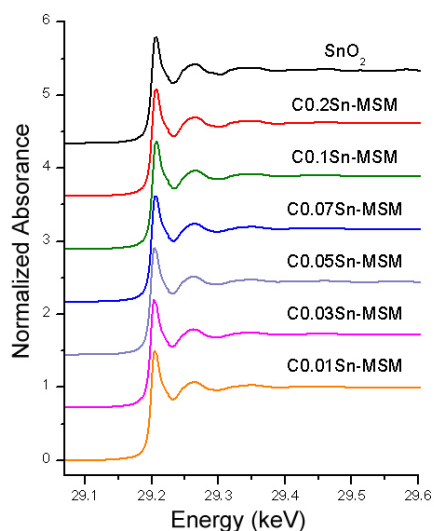


Figure 1. The Sn *K*-edge X-ray absorption spectra of (a) as-made and (b) calcined Sn-MSM synthesized with varied Sn/Si ratio in the gel.

Similar to the observation in XANES spectra, the Fourier transform spectra of $\chi(k)*k^3$ weighted in *k* space of as-made and calcined Sn-MSM with varied Sn loading were similar to that of bulk SnO₂ but their amplitude in the Fourier transform spectra displayed in *k*-space was increased by increasing the Sn loading in

the xSn-MSM samples (not shown here). The Fourier transform spectra of $\chi(k)*k^3$ weighted in *R* space of calcined xSn-MSM in *R* spaces are shown in Figure 2. Equally, the intensities of three peaks found in the Fourier transform spectra in *R*-space were increased by increasing the Sn loading in the sample independent of the thermal and hydrothermal treatment since the spectra of as-made (not shown here) and calcined showed similar features. The three peaks were the contribution of Sn-O1, Sn-Sn1 and Sn-O2 from the amorphous SnO₂ layer and nano SnO₂ crystalline concentric on the silica framework. It also revealed that the domain size of incorporated tin oxide was small in the Sn-MSM with low Sn loading and it was increased by increasing the Sn loading in the materials.

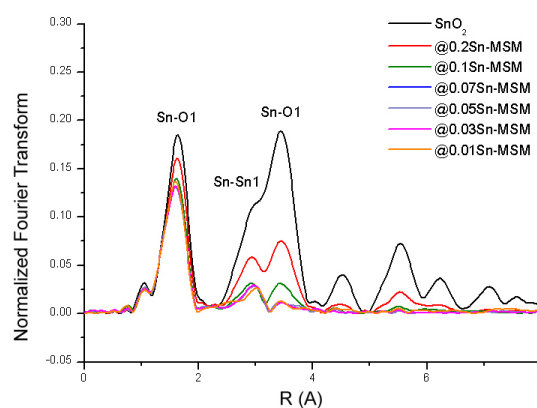


Figure 2. The Fourier transform spectra of $\chi(k)*k^3$ weighted in *R* space of calcined Sn-MSM synthesized with varied Sn/Si ratio in the gel.