

X-ray Absorption Spectroscopic Studies on the Sulfur Environment of Sulfonic Functionalized SBA-15 Materials with Platelet Shape and Short Mesochannels

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Our laboratory has developed a new route to prepare SBA-15 materials with plate-like morphology and short mesochannels. The synthesis route is extended to prepare propylsulfonic acid functionalized SBA-15 materials with plate-like morphology by *in-situ* oxidation of thiol groups on MPTMS which is co-condensed with TEOS during the self-assembly process.

In order to clarify the oxidation states of sulfur species in the materials, samples with various S loadings were examined by using sulfur *K*-edge X-ray absorption near edge structure (XANES) spectroscopy at beam line 16A of National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The sulfur *K*-edge XANES spectra of some sulfur containing standards and propylsulfonic acid functionalized SBA-15 platelets are shown in Figure 1. The sulfur *K*-edge absorption is assigned to the electron transition from the 1s orbital of sulfur to the substantial 3p orbitals and the absorption energy of sulfur species depends on its oxidation state and coordination environment. Generally, the absorption energy and white line intensity increased with the increase in the formal oxidation state, and that allows us to clarify the various sulfur species in the materials. In fresh $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ of antiprism crystal structure, each zirconium is eight-coordinated, with four sulfate groups and four water molecules. The sulfur *K*-edge XANES spectrum of zirconium sulfate sample shows a split absorption peak around 2481.2 and 2481.8 eV, respectively, confirming that the oxidation state of sulfur in the zirconium sulfate is +6. The spectrum of sodium sulfite contains two absorption peaks at 2476.4 and 2480 eV. Because the oxidation state of sulfur in the sulfite ion is +4 which is lower than that in sulfate, the absorption peaks shift to relatively lower energies. As to sodium thiosulfate, a very different feature was seen in its XANES spectrum. Four distinguished peaks with absorption energies around 2470.8, 2474.2, 2478, and 2480 eV are found. According to literature reports, these absorption peaks are the mixed contribution of the excitation of outer sulfur (S^- in the S-S environment of the $\text{S}_2\text{O}_3^{2-}$ ion) and inner sulfur (S^{5+} in the SO_3 environment of the $\text{S}_2\text{O}_3^{2-}$ ion) in the thiosulfate ion.

The sulfur *K*-edge XANES spectrum of MPTMS shows an intense adsorption peak at 2472 eV, indicating that the oxidation state of sulfur on $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$ is -2. The mercaptopropyl functionalized SBA-15 platelet has the sulfur *K*-edge XANES spectrum similar to that of MPTMS, indicating that the oxidation state and chemical environment of sulfurs in the functionalized SBA-15 platelet was not changed during the preparation procedure. In contrast, a

strong absorbance was observed at around 2480 eV in the functionalized SBA-15 platelets prepared with H_2O_2 . It indicates that the mercaptopropyl groups with -2 state are oxidized to propylsulfonic acid groups with sulfur in +4 state by *in-situ* oxidation with H_2O_2 as the oxidant.

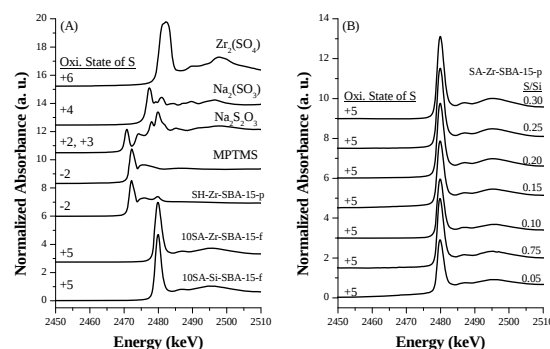


Figure 1. Sulfur *K*-edge XANES spectra of (A) some sulfur containing standards and (B) propylsulfonic acid functionalized SBA-15 platelets with various S loadings.

We have also designed and synthesized covalent anchoring chiral praline derivative on mesoporous SBA-15 by AIBN-mediated radical addition of SH groups to C=C bonds. The S *K*-edge XANES spectra (Fig. 2) show that the peak of SH becomes broader and shifts to higher energy level after immobilization of the chiral ligand. It is attributed to the overlap of peaks of C-S-C (around 2473 eV) and remaining SH. Moreover, two new peaks coresponding to $-\text{SO}_3\text{H}$ and C-SO-C groups at 2482 and 2475.2 eV, respectively, appeared upon lengthening the heating period, which is due to further oxidation of the functional groups.

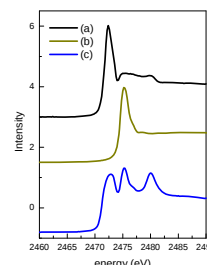


Figure 2. Sulfur *K*-edge XANES spectra of (a) 10%SH-SBA-15, (b) DMSO, and (c) 10%SH-cata.