Direct Synthesis of Arenesulfonic Acid with Mercapto-functionalized SBA-15 as a Convenient Catalyst for Bisphenol-A Synthesis

Chin-Chang Chen (陳志昌)[1], Ling-Yun Jang (張凌雲)[2], and Soofin Cheng (鄭淑芬)[1]

[1]Department of Chemistry, Taiwan University, Taipei, Taiwan
[2]Research Division, National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Bifunctionalized catalysts containing arenesulfonic acid groups and a number of promoters of different chemical properties were prepared onto the pore surface of mesoporous solids to investigate the effect of the mixed active sites on the catalytic activities and selectivities in Bisphenol-A synthesis. The resultant organic-inorganic hybrid materials were characterized by powder XRD, nitrogen adsorption-desorption, thermo-gravimetric analysis, elemental analysis, acid capacity titration and X-ray Absorption Near Edge Spectroscopy. These bifunctionalized mesoporous silica materials were tested as catalysts for the condensation reaction of phenol and acetone to from Bisphenol-A. The catalytic results suggested that the arenesulfonic acid groups served as catalytic active sites and other functional groups provided different non-covalent interactions to reactants and thereby controlled the reaction activity and selectivity. The presence of mercapto groups dramatically improved the reaction activity (TON about 100) and selectivity toward *p,p'*-Bisphenol-A (96.2%). A mechanism was proposed where the participation of mercapto groups in a catalytic reaction resulted in the stabilization of the carbonium ion intermediate.

The XANES experiments were performed at beam line 15B at National Synchrotron Radiation Research Center facility at Hsinchu, Taiwan. Standard operating conditions were 1.5 GeV and 120~200 mA. Photon energies were calibrated using the *L*-edge of pure Mo foil.

The sulfur *K*-XANES spectra of the standards and S15-Ar-SO_3H-SH samples are shown in Figure 1. The sulfur *K*-edge XANES studies are very important for the determination of different forms of sulfur from arenesulfonic acid and mercapto functional groups in the samples. The MPTMS spectra are characterized by strong absorption resonances, so-called ‘’white line’’ at 2472.2 eV, indicating the presence of C-S and S-H bonds (in their typical energy position). The sulfur 1s→σ* (S-H) transition has about the same energy as the sulfur 1s→σ* (C-S) transition so that these transitions cannot be distinguished. However, the compounds containing S-H bonds show a typical feature at the high energy side of the white line at about 2475.6 eV corresponding to a Rydberg transition. Moreover, the spectrum obtained from propyl disulfide shows the typical white line structure of C-S-S-C segment. The first peak at the low energy (2471.6 eV) is assigned to the sulfur 1s→σ* (S-S) transition while a second peak ocurring at higher energy (2473 eV) is associated with sulfur 1s→σ* (C-S) transition. The result for S15-Ar-SO_3H (10%) sample indicates that sulfur atom has charge density corresponding to +5 oxidation state, therefore the peak is shifted to higher energy position (2479.6 eV).

The spectra for S15-Ar-SO_3H-SH series show a prominent peak at 2479.6 eV, corresponding to arenesulfonic acid groups. An increase in the amount of MPTMS during co-condensation would increase the intensity of the disulfide (C-S-S-C) peak at 2471.6 eV and 2473 eV. As the concentration of MPTMS was further increased to about 15%, an additional peak appears for S-H bond at 2472 eV, indicating that the S-H groups for MPTMS are easily oxidized to C-S-S-C groups during the co-condensation step. Although the peak is not shown for lower concentration of MPTMS, the existence of –SH groups are most frequent during the preparation.

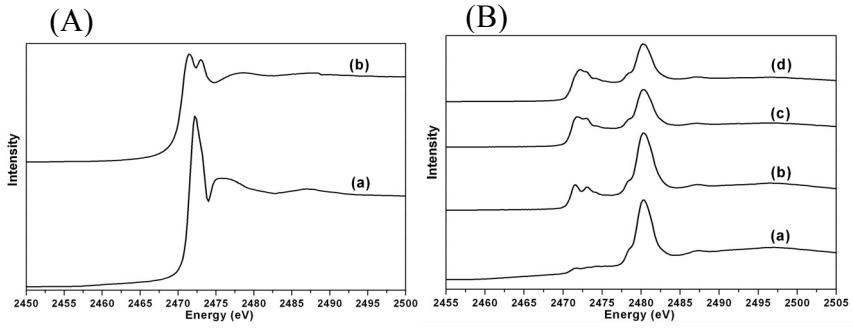

Figure 1. Sulfur *K*-edge XANES spectra of (A) standards: (a) MPTMS and (b) propyl disulfide; (B) mixed arenesulfonic acid with mercapto-functionalized SBA-15: (a) S15-Ar-SO_3H (10%)-SH (2%); (b) S15-Ar-SO_3H (10%)-SH (5%); (c) S15-Ar-SO_3H (10%)-SH (10%) and (d) S15-Ar-SO_3H (10%)-SH (15%).