

X-ray Absorption Spectroscopy Studied on Au Adsorbed on Thiol-functionalized SBA-15

Shih-Yuan Chen (陳仕元)¹, Soofin Cheng (鄭淑芬)¹
Jyh-Fu Lee (李志甫)², and Ling-Yun Jang (張凌雲)²

¹Department of Chemistry, National Taiwan University, Taipei, Taiwan

²National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Gold in the form of a bulk crystal is chemically inert and stable metal in ambient condition so that bulk gold usually has no activity in catalysis. As the particle size smaller than 10 nm, gold nanoparticles are probably the most active catalysts for CO oxidation in hydrogen-rich environment, which reaction is to produce high purity of hydrogen as a fuel for hydrogen fuel cells. However, gold nanoparticles are easy aggregated into large and inert gold grains at working temperature (even lower than 80 °C) so that its catalytic activity and binding ability are decreased significantly. Mesoporous silica materials of large surface area and high thermal stability are the ideal supports for nanostructured materials. The aggregation and growth of nanostructured materials can be hindered by the silica frameworks. In this annual report, X-ray absorption spectroscopy was used to study the chemical environment of Au adsorbed on thiol-functionalized SBA-15, shortly termed SH-SBA-15, which was prepared in the strong acidic solution [1]. In the adsorption of Au³⁺ ions, SH-SBA-15 (200 mg) was dispersed in 10 mM HAuCl₄ solution (50 mL) for 0.5 h. The solids were recovered by filtering, and vacuum drying at 25 °C for 1 day. The resulting materials were designated as Au@SH-SBA-15-E and Au@SH-SBA-15-W for adsorbing Au³⁺ ions on SH-SBA-15 in ethanol and water, respectively. If the adsorbed Au³⁺ ions were further reduced by NaBH₄, the resulting materials were designated as Au@SH-SBA-15-ER or Au@SH-SBA-15-WR.

Sulfur K-edge X-ray absorption near edge structure (XANES) spectra of SH-SBA-15, and Au adsorbed on SH-SBA-15 are shown in Fig. 1(A). For SH-SBA-15, a strong absorption peak at 2472 eV was observed, indicating that S on SH-SBA-15 is in 0 oxidation state similar to mercaptopropyltrimethoxy silane (SH(CH₂)₃Si(OCH₃)₃) precursor. For Au@SH-SBA-15-W, a strong absorption peak at 2480.2 eV and two split peaks at 2471.6 and 2473 eV were found. The front peak is due to the sulfonic acid species (R-SO₃H), and the later split peaks are due to the disulfite species (R-S-S-R'), based on our previous result [2]. However, for Au@SH-SBA-15-E, two strong absorption peaks at 2471.6, 2473 and one weak peak at 2480 eV were observed. It exhibited that the disulfite species were formed after the Au³⁺ ions were adsorbed on SH-SBA-15 in ethanol. The absorption features of Au@SH-SBA-15-WR and Au@SH-SBA-15-ER samples were similar to that of Au@SH-SBA-15-E, implying that the disulfide species predominately were existed in these samples.

The Au K-edge Fourier transform spectra of $\chi(k) \cdot k^3$ weighted in R space of Au standards and Au adsorbed on SH-SBA-15 are shown in Fig. 2(B). For metallic Au foil, a strong peak was found at 2.68 Å, which is contributed from the nearest Au atoms. For HAuCl₄ (5 mM), the peak

appeared at 1.92 Å is attributed to the nearest Cl atoms. The scattering feature of Au@SH-SBA-15-W was similar that of metallic Au foil, indicating that Au was in the form of a metal. However, the scattering feature of Au@SH-SBA-15-E was similar to that of HAuCl₄ solution, implying that Au absorbed on SH-SBA-15 in ethanol was in the form of a cationic ion. For Au@SH-SBA-15-ER and Au@SH-SBA-15-WR, a strong scattering feature at 1.92 Å and weak scattering features at 2.69 Å were found, probably implying that the Au nanoparticles with metallic Au shell and ionic Au core were formed after NaBH₄ reduction.

In summary, the chemical environments of Au adsorbed on SH-SBA-15 in ethanol and water were studied by X-ray absorption spectroscopy. It was found that S on SH-SBA-15 was easily oxidized to sulfonic acid species, and at the same time the Au³⁺ ions were reduced to metallic Au particles if the absorption of Au was carried out in water. However, if ethanol was used as solvent in adsorption, the Au³⁺ ions were stably adsorbed on SH-SBA-15, and the disulfite species were predominantly formed. When adsorbed Au ions were reduced by NaBH₄, the Au nanoparticles with metallic Au shell and ionic Au core were adsorbed on SH-SBA-15, which contained disulfite species.

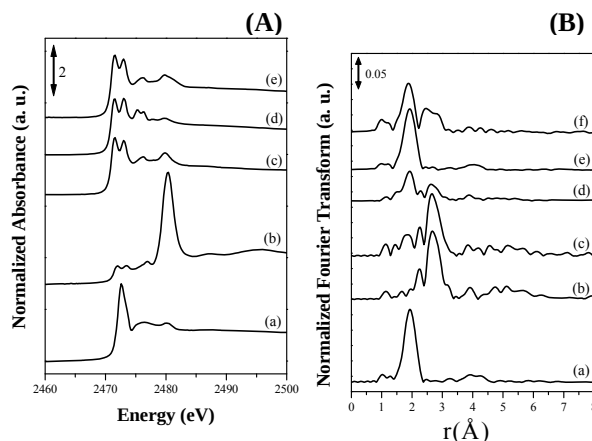


Fig. 1: (A) S K-edge XANES spectra of (a) SH-SBA-15, (b) Au@SH-SBA-15-W, (c) Au@SH-SBA-15-WR, (d) Au@SH-SBA-15-E, and (e) Au@SH-SBA-15-ER materials; (B) Au K-edge Fourier transform spectra of $\chi(k) \cdot k^3$ weighted in R space of (a) HAuCl₄ solution (5 mM), (b) metallic Au foil, (c) Au@SH-SBA-15-W, (d) Au@SH-SBA-15-WR, (e) Au@SH-SBA-15-E, and (f) Au@SH-SBA-15-ER materials.

[1] S.Y. Chen *et al.*, Chem. Mater. **20**, 3906 (2008).

[2] S.Y. Chen *et al.*, J. Phys. Chem. B. **110**, 11761 (2006).