Structural Characterization of Au/TiO_2@SBA-15 Nanocomposite Catalysts

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Ordered mesoporous silica materials are one of the most important scaffolds for constructing advanced nanocomposites on the nanometer scale [1]. For example, proteins or enzymes have been immobilized in mesoporous silicas for biotechnological applications, with the aims to improve the chemical/thermal stability of the biomolecules and to overcome the difficulties associated with their recovery and recycling [2]. Mesoporous SBA-15 silica with hexagonally arranged channel-type (5-30 nm in diameter) mesopores are promising supports to immobilize proteins of small to medium size [2]. In addition to the primary mesochannels, SBA-15 generally possesses microporosity in the silica walls originating from the occlusion of the EO chains of the structure-directing agent (Pluronic P-123, $EO_{20}PO_{70}EO_{20}$) during the synthesis [3]. Aiming to combine the advantages of both types of materials, we have developed the methods of selective functionalization and deposition of metal or metal oxide nanoparticles in the micropores of SBA-15 leaving the hydrophobic mesopores fully open [4,5].

Based on the methods, we further prepared novel Au/TiO_2@SBA-15 nanocomposites with ultra-small Au nanoparticles deposited selectively on top of the titania nanoparticles confined in the micropores. These nanocomposites catalysts showed high conversion of propene epoxidation using molecular oxygen as an oxidant. More interestingly, these catalysts only resulted in the desired propylene oxide and other isomerization products, and cracking or hydrogenation products were found. This unique catalytic behavior is completely different from other reported catalysts. To elucidate the interesting catalytic behavior, we applied X-ray absorption spectroscopy (XAS) measurements at both the Au L_{III}-edge and the Ti K-edge for these nanocomposites Au loading: 0.1 wt%, TiO_2 loading 1-10 wt%).

Figure 1 compares the Fourier transforms of Au L_{III}-edge K^3-weighted EXAFS data of the three samples and a reference Au foil. The fitted results are also shown. It was found that despite the high tendency to sintering, the Au nanoparticles in the nanocomposites were very small in size and were about 1.5-1.8 nm. No Au-Ti or Au-O peaks were observed, however. On the other hand, Fig. 2 shows the the normalized the Ti K-edge X-ray absorption near-edge structure (XANES) spectra of the three Au/TiO_2@SBA-15 nanocomposites. The pre-edge peaks exhibit different intensities, suggesting that the fraction of tetrahedrally corridinated Ti species in the nanocomposites were different. In addition, the amount of these Ti species seems to correlate to the catalytic activities of the nanocomposites, suggesting that the tetrahedrally-corrdinated Ti-species might be on or near the exposed surface and might interact with propene molecules to initiate the reaction. Further catalytic studies and in-situ measurements are in progress.

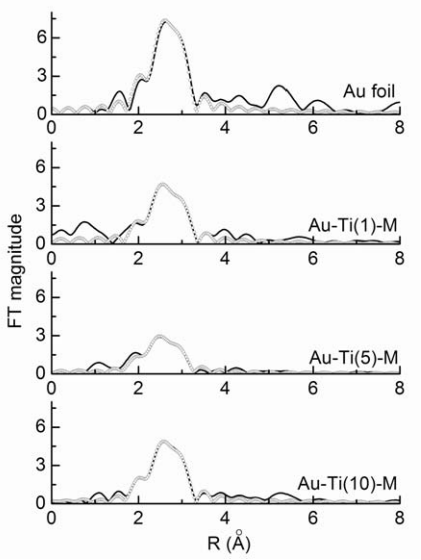
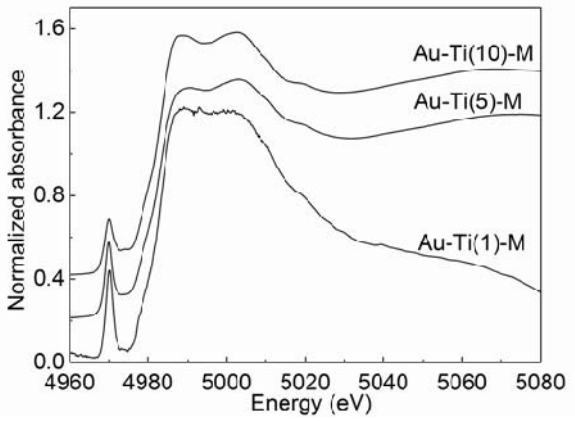


Fig. 1: Fourier transforms of Au L_{III}-edge K^3-weighted EXAFS data of Au/TiO_2@SBA-15 nanocomposites and a reference Au foil. The fitted results are also shown.

Fig. 2: Normalized Ti K-edge XANES spectra of Au/TiO_2@SBA-15 nanocomposites.



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