XANES Study of Local Structures of Ti Species in the CuO/TiO_2

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Phosphine (PH_3) is one of commonly used dopant gases in semiconductor industries. PH_3 is highly toxic and causes human death immediately at 300 ppm or after exposure at 0.3 ppm for 8 hours a day for one week. Therefore, development of promising adsorbents to effectively remove PH_3 attracts large attention.

In this study, we incorporated Cu^{2+} into TiO_2 matrix using sol-gel method and found high removal capacities for PH_3. The capture of PH_3 by CuO/TiO_2 is proposed to involve with transformation of PH_3 to phosphate according FTIR analysis. Dissociative chemisorption of PH_3 on the copper accompanied with rearrangement of surface hydroxyl groups and dehydrogenation firstly results in Cu-P=O species. Then, the Cu-P=O species gradually transforms to H_3PO_4 by sequential reaction with water in conjunction with dehydrogenation. The X-ray absorption spectroscopy (XAS) using synchrotron radiation is a powerful technique to investigate the structural and electronic properties of the X-ray absorbing atom and about its local environment. In this report, the effects of chemisorption of PH_3 on CuO and transformation to phosphate species with hydroxyl groups on TiO_2 surface have been studied by X-ray absorption near edge structure (XANES) technique. The Ti *K*-edge X-ray absorption spectroscopy (XAS) spectra were carried out at beam-line 16A1.

Figure 1 shows the pre-edge of Ti *K*-edge XANES spectra of anatase and rutile TiO_2 standard and the Cu/TiO_2 obtained as-prepared and after base treatment. The pre-edge structure of TiO_2 contained three characteristic absorptions, which were named as A1, A2, and A3. A1 reprented as an exciton band absorption, while A2 and A3 were assigned to the electron transition from 1*s* to t_{2g} and e_g 3*d* degenerate states, respectively. The As-Cu/TiO_2 exhibited higher intensity in the A2 peak relative to the sample after base treatment, indicating that the As-Cu/TiO_2 materials had more distorted octahedral TiO_6 unit.

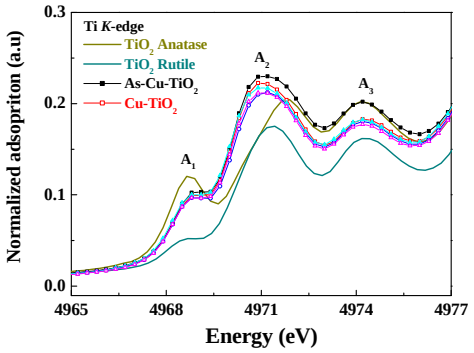

Fig. 1: Pre-edge of As-Cu/TiO_2, Cu/TiO_2, anatase and rutile TiO_2.

Figure 2 shows the pre-edge of Ti *K*-edge XANES spectra of the Cu/TiO_2 after adsorption of PH_3 in the N_2 and in the humic air. No matter the adsorption underwent in the inert or humic conditions, similar absorption features were observed in the Cu/TiO_2 samples. Comapred to *K*-edge XANES spectrum of the fresh Cu/TiO_2, the A2 absorption slightly decreased after adsorpotion of PH_3. Since the Cu^{2+} was reduced to Cu^{+} after binding with PH_3, the electron density around Ti^{4+} centers increased. This led electron transition from 1*s* to 3*d* states more difficult. The changes in the electronic structures of Ti^{4+} ions clearly proved that the PH_3 was chemisorbed on the Cu^{2+} centers in the beginning and then converted into phosphate species after exposure of H_2O.

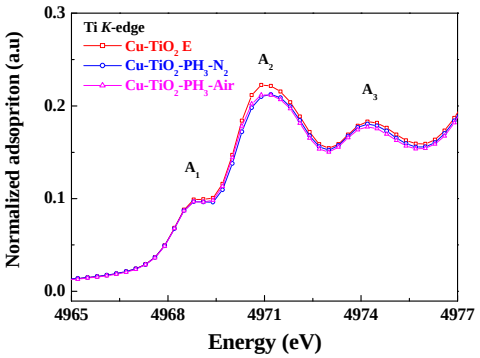

Fig. 2: Pre-edge of the Cu/TiO_2 after adsorption of PH_3 in N_2 and in the humic air.