XANES Study of Chemical States of Cu Species in the TiO_2 Matrix

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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. To evidence the conversion mechanism and investigate the matrix effect on the adsorption capabilities of CuO, we use X-ray absorption near edge structure (XANES) to chacterize the different chemical states of Cu resulted from different adsorption conditions. The Cu *K*-edge X-ray absorption spectroscopy (XAS) spectra were recorded in transmission mode for synthesized powders mounted on a Scotch tape at a wiggler beamline BL01C1 with a double-crystal Si (111) monochromator for energy scanning.

Figure 1a shows the Cu *K*-edge XANES spectra of the Cu species in the Cu_2O and CuO standards and in the Cu/TiO_2 obtained as-prepared and after base treatment. After first differentiation, the absorption peak at 8983 and 8979 eV represents CuO (Cu^{2+}) and Cu_2O (Cu^{+}), repectively. The As-Cu/TiO_2 showed the absorption peak at 8985 eV, indicating $CuCl_2$. After base treatment, the Cu/TiO_2 exhibited a aborption peak at 8983 eV. Since the absorption feature is similar to that of CuO, the Cu^{2+} existed as CuO mainly in the TiO_2 matrix. The imbedded CuO had a pre-edge peak at around 8977 eV, representing the $1s \rightarrow 3d$ transition. Moreover, its characteritic peak of $1s \rightarrow 4p$ transition was more intensive than pure CuO due to the presence of TiO_2 matrix. Because Ti^{4+} contained higher electronegativity than Cu^{2+}, the probability of the transitions into Cu $4p$ states increases. Figure 1(b) shows the Cu *K*-edge XANES spectra of the Cu/TiO_2 after adsorption of PH_3 in N_2 gas and in humic air. Compare to the spectrum of the Cu/TiO_2 before adsorption, the differential peak decreased from 8983 to 8979 eV. The chemical shift to lower energy indicates decreasing valence state of Cu. On the contrary, the Cu exhibited its absorption peak at 8981 eV when the adsorption was proceed in the himic air. This finding evidenced that the Cu^{2+} was reduced after chemisorption of PH_3. However, the adsorbed PH_3 could further react with H_2O to form phosphate species, therby regenerating Cu^{2+} centers.

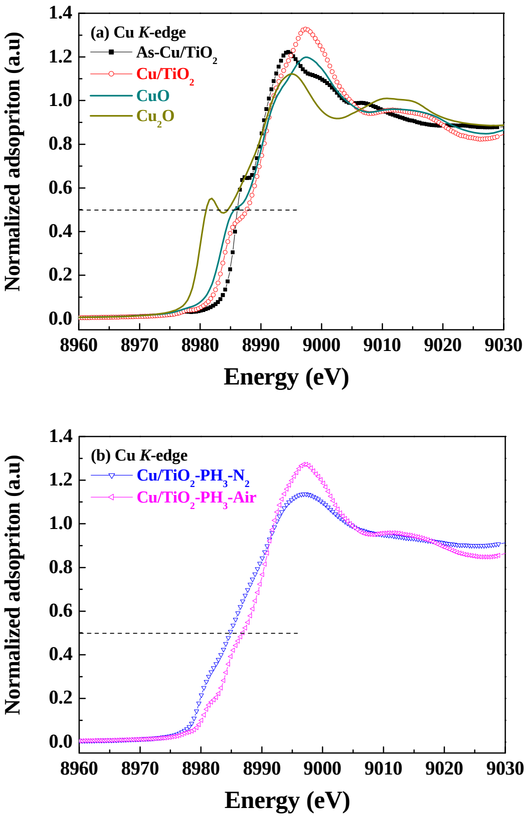

Fig. 1: (a) The Cu *K*-edge XANES spectra of As-Cu/TiO_2, Cu/TiO_2, Cu_2O and CuO. (b) The Cu *K*-edge XANES spectra of the Cu/TiO_2 after adsorption of PH_3 in N_2 and in humic air.