The Applications of X-ray Absorption Spectroscopy in the Study of Copper Nanocatalysts for Selective Oxidation of Propylene with Dioxygen

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Abstract

Supported nanocatalysts containing highly dispersed metals generally exhibit high activity in heterogeneous catalysis, mainly owing to their high surface area with an abundance of low-coordination surface sites. The preparation of metal catalysts on high-surface-area supports remains challenging because nanosized metals tend to agglomerate or sinter during catalyst preparation and/or under catalytic reactions. This is especially true for the preparation of copper catalysts, which have been widely applied in important industrial processes and are promising for selective oxidation and other reactions. We have devoted to the studies of selective oxidation of propylene with dioxygen catalyzed by supported copper and gold nanoparticles[1-3]. In these studies, X-ray absorption spectroscopy (XAS) plays a crucial role in probing the electronic structure and size of the metal species during the catalyst preparation as well as under catalytic reaction conditions. In this contribution, strategies of preparing nanocomposites of mesoporous silica and copper nanoparticles are introduced. Emphasis is placed in the newly developed one-pot synthetic route to prepare copper nanocatalysts featuring high surface area, high degree of silica condensation, and high dispersion of copper species. The as-prepared and hydrogen-reduced catalysts were characterized by XAS and other techniques to reveal the nanosized and highly dispersed copper species on meso(nano)porous silica. Moreover, results of in-situ XAS, together with in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and other techniques, suggested that the metallic copper transformed and mainly stayed in the 1+ oxidation state under catalytic reaction conditions. It was concluded that factors including the small size of copper and the presence of silanol groups on the silica support were crucial for the catalytic performance of the catalysts. The one-pot synthetic route was extended to prepare copper nanocatalysts containing additional components. As an example, catalysts containing copper and zinc were prepared and optimum amount of zinc loading was found. The structure-activity relationship of the copper/zinc nanocatalysts was studied by (in-situ) XAS and related techniques.

Keywords – Copper catalyst; Heterogeneous catalysis; Selective oxidation of propylene; X-ray absorption spectroscopy.

References

[1] C.-H. Liu, Y. Guan, E. J. M. Hensen, J.-F. Lee, and C.-M. Yang, "Au/TiO_2@SBA-15 nanocomposites as catalysts for direct propylene epoxidation with O_2 and H_2 mixtures" *J. Catal.*, vol. *282*, pp. 94-102, 2011.

[2] C.-H. Liu, N.-C. Lai, J.-F. Lee, C.-S. Chen, and C.-M. Yang, "SBA-15-Supported highly dispersed copper catalysts: Vacuum-thermal preparation and catalytic studies in propylene partial oxidation to acrolein" *J. Catal.*, vol. *316*, pp. 231-239, 2014.

[3] N.-C. Lai, M.-C. Tsai, C.-H. Liu, C.-S. Chen, C.-M. Yang, "Efficient selective oxidation of propylene by dioxygen on mesoporous-silica-nanoparticle-supported nanosized copper" *J. Catal.*, vol. *365*, pp. 411-419, 2018.