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EXAFS study of the adsorption of ethylene and water on the Cu/SiO_2 catalysts

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Introduction

The epoxides are very important intermediates for many chemical materials, although those formations can hardly control. The utilization of photocatalysts for selective oxidation has been demonstrated. The investigation of photocatalytic oxidation is significant for explaining the reaction mechanism, because the photocatalytic reaction is easily to observe the interaction intermediate of products with catalysts [1]. We have demonstrated the photooxidation of alkene on silica photocatalyst [2]. The process using a photocatalyst offers a unique route to the oxidation, but overoxidation is accompanied with the high oxidation potential of the photocatalysts such as TiO_2.

In this study, we have investigated the selective photooxidation of ethylene using water as an oxidant without molecular oxygen over copper oxide supported on silica. The XAFS study has clarified the structure of the active species and the interaction with the reactants.

Experimental Section

Copper oxide supported on silica (Fuji Silicia, Cariact G-10; BET surface area, 176 $m^2 \cdot g^{-1}$; mean pore diameter, 13.7 nm) was prepared by impregnation with an aqueous solution of $Cu(NO_3)_3$ (Wako Pure Chemical Industries). The solvent was removed by evacuation at ca. 330 K. The resulting wet solid was freeze-dried, then calcined in air for 5 h at 673 K. The sample will be designated as 0.5 wt% CuO_x/SiO_2.

Profiles of X-ray absorption near-edge structure (XANES) for the samples were taken at room temperature in Transmission mode for K-edges of Cu at beam-line BL01B1 of SPring-8. After introduction of water and/or ethylene, the sample also was sealed with polyethylene films in nitrogen atmosphere.

Results and Discussion

Ethylene is adsorbed on copper oxide supported on silica while it is the key process of the ethylene photooxidation over the solid. The adsorption and the effect of water to the adsorption have been investigated by the XAFS measurement. In the profile of the Fourier transform of Cu K-edge EXAFS for the sample containing 0.1wt% of copper, a major peak is present at around 1.7 Å with a minor peak at around 2.7 Å (see Figure 1-a). The former peak can be attributed to the coordination to the neighboring oxygen atoms (Cu-O) and the latter to the neighboring copper atoms (Cu-O-Cu). Introduction of ethylene to this sample at room temperature results in the appearance of another strong peak at around 1.5 Å (see Figure 1-b). Since this peak can be attributed to the coordination to carbon atoms (Cu-C), the ethylene certainly adsorbs on the copper ions. When a water vapor is introduced to the sample adsorbing ethylene, the peak at 1.5 Å disappears, showing that water inhibits the adsorption of ethylene on the copper ions (see Figure 1-c). Therefore it means that the interaction between ethylene and copper is weaker than that between water and copper.

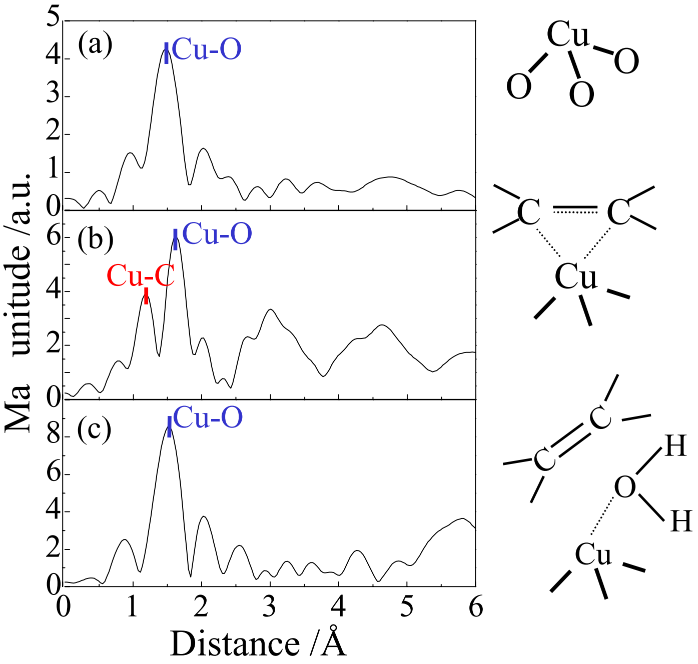

Figure 1. Fourier transform of EXAFS for 0.5 wt% Cu/SiO_2 catalyst evacuated at 700 ℃ (a), and catalyst adsorbed C_2H_4 (b) and C_2H_4/H_2O (c).

References

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