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XAFS Characterization of Au Nanoparticles Supported on Sm-CeO_2

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Introduction

In the southern and eastern Asian countries, efficient utilization of abundant biomass resources could be a key technology for not only sustainable development but also mitigation of CO_2 emission. Selective oxidation of alcohols is one of the important techniques for conversion of biomass to useful chemical substances. In addition to that, if molecular oxygen can be utilized as an oxidant material, that would make an environmentally friendly and highly economical chemical process. It is well known that supported Au catalysts show unique reactivity toward selective oxidation reactions with molecular oxygen, and it is also reported that they show high performance in alcohol oxidation. Therefore, we applied the supported Au catalysts to selective oxidation reactions of benzyl alcohol with molecular oxygen, and found that Sm promoted CeO_2 supported Au catalysts show high activity in them. In this work, we conducted XAFS analysis of Au/Sm-CeO_2 to elucidate the structure of active Au sites.

Experimental

The catalyst support material was prepared by a non-hydrothermal sol-gel method with $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ as precursors[1]. The content of Sm in the support was 4 mol%. Deposition of Au was conducted by a DP method with $HAuCl_4 \cdot 3H_2O$ as a Au source[2]. After the deposition treatment, the catalyst was calcined at 573 K for 4 hours.

A catalytic test was conducted with a reaction mixture composed of 4 ml toluene, 4mmmol benzyl alcohol, and 0.1 ml dodecane as an internal standard. Suspension of 0.1 g of catalyst in the reaction mixture was kept at 363 K for 3 h under a bubbling of oxygen at 50 ml/min.

The XAFS experiment was conducted at BL7C and 9C in a transmittance mode and a fluorescence mode. The as-prepared catalysts were pressed into pellets, kept in plastic bags and used as-is for the measurements.

Results and discussion

Catalytic performances were compared among CeO_2, Sm-CeO_2, Au/CeO_2 and Au/Sm-CeO_2. The Au/Sm-CeO_2 catalyst showed the highest conversion of benzyl alcohol (27.4%) with a selectivity of 99% to benzaldehyde. Figure 1 depicts Au L_{III}-edge XANES spectra observed for Au foil and the catalyst. The XANES spectrum of the catalyst has almost the same profile as that of Au foil, indicating that the Au species in the catalyst were in a metallic state. Figure 2 shows Fourier transformed EXAFS spectrum observed for Au/Sm-CeO_2. Curve-fitting analysis of the main peak from 0.17 – 0.34 nm gives a coordination number of 10.1 and a distance 0.285 nm for Au-Au scattering. This result also confirms the presence of metallic Au nanopartcles on Au/Sm-CeO_2.

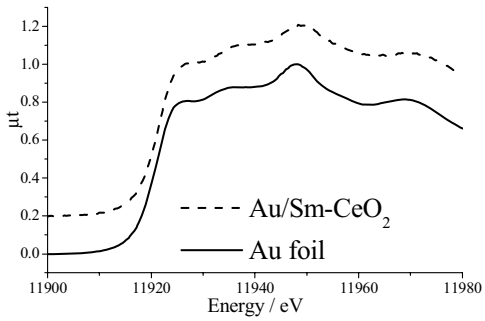

Figure 1. Au L_{III}-edge XANES

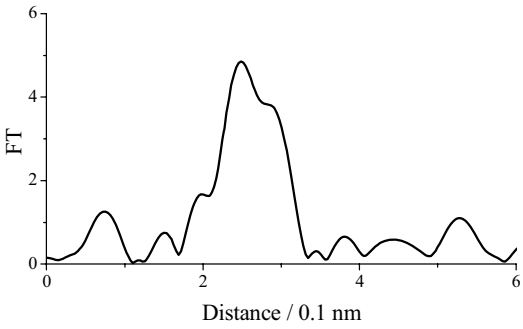

Figure 2. Fourier transform of Au L_{III}-edge EXAFS ($k^3\chi(k)$)

References

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