XAFS studies on local structure of Ag or Au doped catalysts

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The gold catalysts have a high activity of propylene oxidation to propylene oxide for the thermal reaction at room temperature. In this case, the particle size of gold is one of the most important factors of propylene oxidation activity. Hydrogen formation is observed in the photoreaction of propylene with H_2O on the Au/TiO_2 catalyst. However the activity of hydrogen formation immediately decreases with the passing of reaction time. It may be due to the accumulation of products to the active site or the aggregation of gold particles. In this study, we investigated the alteration of particle size for the photoreaction.

Au/TiO_2 catalysts (P-25, Au:1wt%) was prepared by Deposition-Precipitation method. The catalysts were calcined at 400℃ for 4h in air. Prior to the reaction, the sample was usually heated in oxygen at 250℃ for 30min. The photoreaction was carried out for 6h at 5℃ and 80℃under UV light irradiation by using fix-bed flow reactor. The reaction gas of 10vol% C_3H_6 in Ar including 6000ppm H_2O was fed, and the effluent gas was analyzed by two type gas chromatographs equipped with TCD and FID detectors, respectively. The XAFS spectra were measured at BL01B1 facility. The Au L_{III} -edge absorption spectra were recorded in the fluorescence mode at 295 K. Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3-15 $Å^{-1}$.

Figure shows the Fourier transform of Au L_{III}-edge EXAFS for the unused Au/TiO_2. The strong peak at around 2.8Å is assigned to the neighboring Au atoms (Au-Au). While the Fourier transform of Au L_{III}-edge EXAFS for the Au/TiO_2 after reaction at 5℃ and 80℃ were also shown in this figure. The intensities of Au-Au peak in the both reaction conditions are almost same, although the photoreaction activity at 5℃ is much higher than that of 80℃. On the other hand, the peak intensity of unused catalyst at around 2.8Å is a little smaller than those of the used catalysts. However the initial activity of the hydrogen formation at 5℃ was 17 times as high as the final activity. Therefore we consider that the aggregation of gold particles is not responsible for inactivation. The accumulation of hydrocarbon products to the catalyst surface may take place the inactivation of hydrogen formation. In fact, the formation of hydrocarbon products in gas phase was scarcely observed by GC. EXAFS measurement is indicated that the photoirradiation does not cause the aggregation of gold particles.

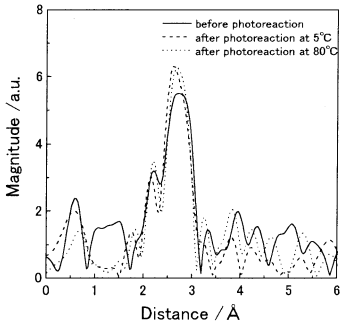

Figure 1. Fourier transform of EXAFS for used and unused Au/TiO_2 catalysts.

XAFS Study of Barium Compound in NOx Storage-Reduction Catalyst

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Introduction

Recently, NOx storage and reduction (NSR) catalysts for an automobile lean-burn engine have been developed [1]. The NSR catalyst consists of precious metals (mainly Pt), alkaline and alkaline earth metals as NOx storage compound, and supports such as alumina. NOx is trapped in the NSR catalyst under lean conditions, and then the trapped NOx is reduced to nitrogen during rich or stoichiometric operations. We have been investigating the state of Pt species and barium compounds by XAFS method. As a result of the previous analysis (proposal No. 2000B 0118-NX-np), there weren't clear differences in barium compounds on various fresh NSR catalysts. This study focuses on the states of barium compounds after sulfur poisoning.

Experimental

Catalysts were prepared by impregnating various supports listed in Fig. 1 with an aqueous solutions of $Pt(NO_2)_2(NH_3)_2$ and $(CH_3COO)_2Ba$. They were calcined at 773 K in air for 1 h with pretreatment under the reductive condition, followed by heating at 673 K in air for 0.5 h. Sulfur poisoning tests were performed in a stream of a simulated exhaust gas containing sulfur dioxide at 873K. Ba L_I-edge XAFS spectra for the catalysts were measured at room temperature in the transmission mode at BL01B1 station.

Results

To investigate the supports effect on NSR catalysts for sulfur poisoning, the states of barium were observed by XAFS method. Figs. 1 and 2 show Ba L_I-edge XANES spectra of the catalysts and standard samples, respectively. Compared to the spectra of the standard samples, Ba XANES spectra of the catalysts were all almost similar to that of $BaSO_4$. It is considered that the barium compounds in the various sulfur poisoning catalysts consists of mainly $BaSO_4$. However, Ba XANES spectra for the NSR catalysts were slightly different from each other. For example, the intensity of absorption peaks at 6000 eV of the $Pt/Ba/ZrO_2$, $Pt/Ba/TiO_2$ and $Pt/Ba/SiO_2$ catalysts was smaller than that of the $Pt/Ba/Al_2O_3$ catalyst.

We are planning to investigate the catalytic performance after sulfur poisoning to reveal the relationship with this analysis.

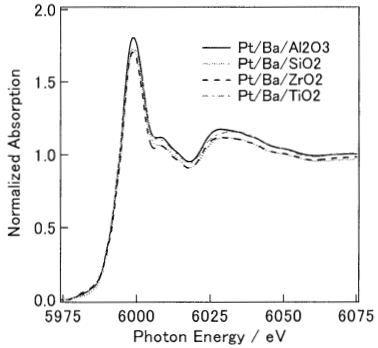

Fig.1. Ba L_I-edge XANES spectra of sulfur poisoning catalysts.

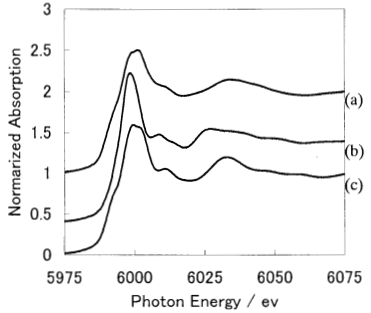

Fig. 2. Ba L_I-edge XANES spectra of the standard samples: (a)$BaCO_3$, (b)$BaSO_4$, (c)BaO

Reference

[1]N.Takahashi et al., Catal. Today **27** (1996) 63