

Structural Analysis of Cyanide Treated Au Catalysts Under Partial Oxidation Conditions

Kyoko K. BANDO*¹, Jason GAUDET², Zhaoxia SONG¹, Yuichiro KOIKE³, S. Ted OYAMA*^{2,4}

¹AIST, Tsukuba, Ibaraki 305-8565, Japan

²Virginia Polytechnic Institute & State University, Blacksburg, VA 24061, U.S.A

³KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

⁴The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan

Introduction

Supported Au catalysts show unique catalytic properties when the size of Au clusters is controlled within several nanometers. It is reported that the Au clusters of 2 – 4 nm in size are appropriate for direct production of propylene oxide (PO) from propylene (PE) with hydrogen and oxygen under gas phase reaction conditions [1]. In order to learn more about the catalytic properties of Au metallic clusters, the structure, electronic state, and catalytic activity of samples which do not contain metallic clusters were compared with samples that contain Au metallic clusters. For that purpose, a treatment of the catalyst with a cyanide solution was employed. It is reported that cyanide treatment can suppress the formation of metallic Au particles in a catalyst [2]. We applied this method to Au/TS-1 catalysts and prepared catalysts with different extents of cyanide treatment. In situ XAFS observation of the catalysts under reaction conditions was carried out. Preliminary results indicate that the Au species in cyanide treated catalysts retained an oxidized electronic state even under reaction conditions [3]. In this work, further analysis was performed of the in situ XAFS data and the results are discussed in connection with the catalytic reactivity.

Experimental

Preparation of Au/TS-1 was carried out as explained elsewhere [3]. One sample was treated with an aqueous solution of 2.00M NaCN pH-adjusted with NaOH to 12.5, and a second sample was treated with NaOH at the same pH but without NaCN. (They are identified as 2.00CN and 0.00CN, respectively). Each sample was washed thoroughly with water and dried under vacuum at room temperature. In situ Au L_{III}-edge XAFS measurements were carried out at beamline NW10A. XAFS spectra under propylene partial oxidation conditions (C₃H₆/H₂/O₂/He = 1/1/1/7, 443 K, 0.1 MPa) were obtained every 10 min in a step-scanning mode using the same pretreatment and reaction conditions as those used in the catalytic testing reactor, but with He as the inert gas. All spectra were obtained in fluorescence mode using an SSD detector. The cell was designed for in situ fluorescence measurements provided with a flow delivery system[4]. XAFS data were analyzed with REX2000 (Rigaku Co.) and IFEFFIT 1.2.8.

Results and discussion

Figure 1 shows Fourier transforms of Au L_{III}-edge EXAFS spectra taken before and during the reaction. The 0.00CN sample before reaction shows a strong peak at 0.16 nm, which is assigned to Au-O of Au oxide species (Fig.1(a) solid line). Under reaction conditions, the peak of Au-O disappeared and a new peak appeared at 2.5 nm, which is assigned to Au-Au of Au metal clusters (Fig.1(a) broken line). These results correspond well to the XANES analysis [3]. On the other hand, for the 2.00CN catalyst, two strong peaks were observed for the sample before the reaction (Fig.1(b) solid line). Under the reaction conditions, these two peaks became weaker but are clearly observed at the same position (Fig.1 (b) broken line). According to the literature, KAu(CN)₂ gives a similar spectrum [5]. The first peak at 0.16 nm is fitted well with Au-C bonds and gives a coordination number of 4.6 before reaction, and 2.2 during the reaction, which indicates that the oxidation state of Au changed from +3 to +1. The 0.00CN catalyst showed activity for PO production, whereas, the 2.00CN catalyst produced only propane. It is suggested that Au+I has a high capacity for hydrogenation.

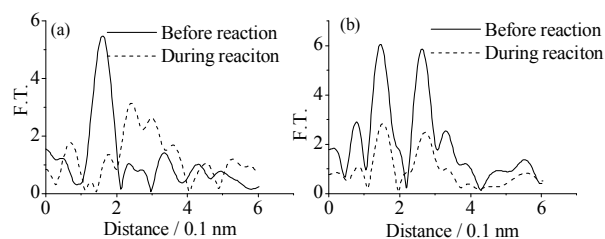


Fig. 1 Fourier transform of Au L_{III}-edge EXAFS ($k^3\chi(k)$) of 0.00CN (a) and 2.00CN (b) before and during the PE partial oxidation reaction.

References

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* kk.bando@aist.go.jp , oyama@vt.edu