

In situ XAFS Analysis of Au/TS-1 Catalysts - Effect of Cyanide Treatment on Structure and Reactivity -

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Introduction

Supported Au catalysts are known to have high ability for propylene oxide (PO) production directly from propylene (PE) with hydrogen and oxygen under gas phase reaction conditions[1]. Although much has been investigated regarding the active structure of Au, particle size, oxidation state, and local structure around active Au sites are still matters of issue. In this work, we prepared cyanide treated Au/TS-1 catalysts. Cyanide treatment can suppress the formation of metallic Au particles in a catalyst[2], and that makes it possible to see the role of metallic particles in catalysis by comparison among catalysts with different extents of cyanide treatment. In situ XAFS observation of the catalysts under reaction conditions was carried out and the results are discussed in connection with their catalytic reactivity.

Experimental

The support (TS-1) was prepared according to the literature[3], and Au was supported on TS-1 by deposition precipitation method[4]. 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 L₃-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[5]. XAFS data were analyzed with REX2000 (Rigaku Co.).

Results and discussion

Figure 1 shows Au L₃-edge XANES spectra observed before and during the reaction. Both catalysts show strong white lines before reaction ((a), (c)), which means that Au species in the as-prepared catalysts were in a Au³⁺ state for both catalysts. Under the reaction conditions, for

the catalyst without cyanide treatment (b), the white line disappeared and a XANES spectrum characteristic of metallic Au was observed. On the other hand, for the cyanide treated catalyst, a strong white line still remained under the reaction conditions(d), indicating that the Au atoms remained in a Au³⁺ state. The white line had a shoulder peak at 11928 eV before the reaction, but it disappeared under the reaction conditions, suggesting some structural change around Au³⁺ during preparation. The catalytic test shows that the 0.00CN catalyst produced PO, propane, and CO₂ (selectivity was 56 %, 40 %, and 3.5 %, respectively), whereas, the 2.00CN catalyst produced only propane. These results show that the oxidized Au species catalyzed only hydrogenation of PE, and the catalyst containing Au metallic particles had an activity for PO production, which agrees well with the result reported in the literature[1].

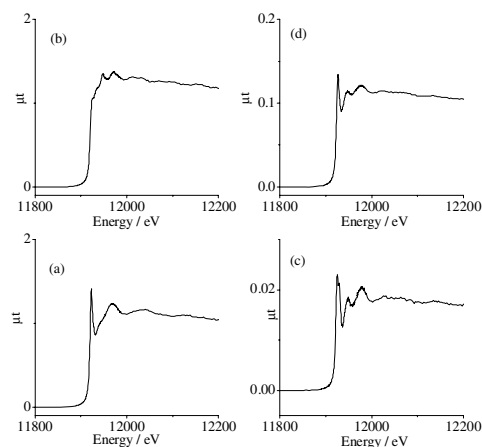


Fig.1 In situ Au L_{III}-edge XANES spectra observed for 0.00CN ((a):before reaction , (b):during reaction) and 2.00CN((c):before reaction, (d): during reaction) .

References

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