

XAFS Analysis for Redox Reactions of Cobalt Catalysts Supported on Silica

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1. Introduction

Supported cobalt catalysts are known to show high activity for various chemical reactions, such as Fischer–Tropsch conversion, hydrogenation of carbon monoxide, desulfurization, ethanol steam reforming, and so on [1]. The structure and the chemical state of the Co species supported on oxide supports are imperative to understand the reaction mechanisms of the catalysis reactions. X-Ray absorption fine structure (XAFS) technique can determine the electronic state and the local structure of metal species at the atomic level, and thus it is a powerful research tool to clarify the redox property of supported metal catalysts because of the applicability at high temperature under reaction atmosphere.

In this study, the chemical states of the Co species have been analyzed by *in-situ* quick XAFS technique (QXAFS) for the prepared cobalt catalysts supported on silica under oxidative and reductive atmosphere at elevated temperature.

2. Experimental

The supported Co catalysts were prepared by the impregnation method using silica (JRC-SIO-10) distributed from the Catalysis Society of Japan. The Co loading was set to be 5 and 10 wt%. The powder of silica was suspended in an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako). The solution was stirred for 1 h at 60 °C, and was dried at 80 °C for 24 h. The obtained powder was calcined at 600 °C in air for 2 h.

In-situ QXAFS measurements at the Co K edge were carried out in the transmission mode at BL-3 of SR Center (Ritsumeikan University) and BL-12C of Photon Factory (High Energy Accelerator Research Organization). Sample powder was first exposed by the diluted hydrogen (10 vol% balanced by He, 200 cm³/min) and was heated to 750 °C at 10 °C/min. The XAFS spectra were repeatedly measured with the time interval of 2 min during the reduction process (temperature-programmed reduction, TPR). The flow gas was then changed to the diluted oxygen (10 vol%), and the sample was heated to 600 °C at 10 °C/min. The XAFS measurements were performed during the oxidation process (temperature-programmed oxidation, TPO).

3. Results and discussion

The XANES spectral change for the TPR process is shown in Fig. 1. The initial XANES spectrum is perfectly in agreement with that of Co_3O_4 , and the edge energy is shifted to the lower side with increasing temperature. The XANES spectrum is finally changed to that of metallic Co^0 . During the conversion from Co_3O_4 to Co^0 , the transient spectrum is almost consistent with that of CoO with the white line peak at 7725 eV. The results of the component analysis based on the XANES pattern fitting are given in Fig. 2. It is found that two reduction processes, *i.e.*, Co_3O_4 to CoO and CoO to Co , proceed at lower temperature for the catalyst with the lower Co loading, suggesting that the thermodynamic stability of the Co species relates to the particle size supported on silica. The larger particle tends to resist to the reduction reactions.

The XANES spectral change for the TPO process is shown Fig. 3, and it is confirmed that Co^0 particles are finally oxidized to Co_3O_4 . The redox processes proceed reversibly between Co_3O_4 and Co^0 on supporting silica. The transient XANES spectrum is apparently different from that of CoO , and the divalent Co oxide is unstable relative to Co_3O_4 under the oxidative atmosphere. Thus the formed CoO is considered to be oxidized immediately to Co_3O_4 .

The oxidation state of the supported Co species is variously changed in response to the gas atmosphere and temperature. The obtained information is very important to assign the real active species for many catalysis reactions of the supported Co catalysts.

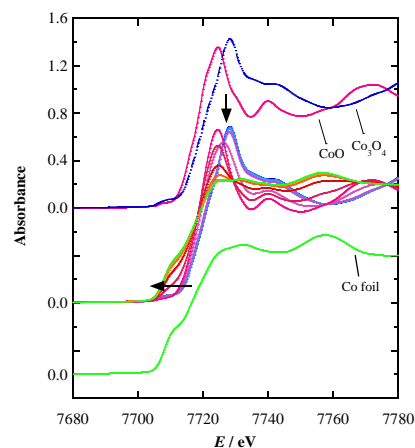


Fig.1. XANES spectral change during the TPR process for Co/SiO_2 (10 wt%).

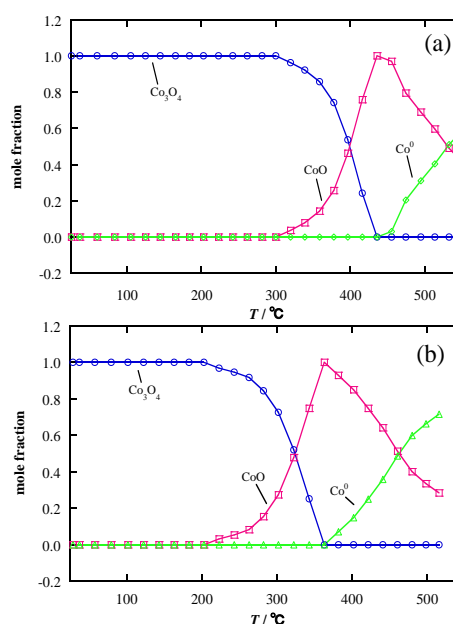


Fig.2. Temperature variation of components during the TPR process for Co/SiO_2 with the loading of 10 wt% (a) and 5 wt% (b).

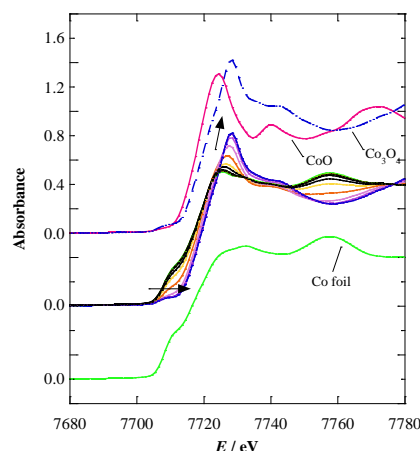


Fig.3. XANES spectral change during the TPO process for Co/SiO_2 (10 wt%).

References

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- [2] A. F. Lucrecio, J. D. A. Bellido, A. Zawadzki, and E. M. Assaf, *Fuel*, **90** (2011) 1424.