

Time-resolved study on dynamic chemical state conversion of SiO₂-supported Co species by means of dispersive XAFS technique

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Abstract. The chemical state conversion of the Co species supported on SiO₂ was investigated using the *in-situ* and the time-resolved XAFS techniques. The supported Co₃O₄ species was finally reduced to metallic Co with the stable intermediate state of CoO for both the temperature-programmed and time-course processes. The oxidation of Co⁰ traced the reverse route to Co₃O₄, whereas the relative stability of the Co₃O₄ species to the CoO intermediate under the oxidative environment diminished the composition of CoO. The time-resolved measurement for the oxidation reaction showed an additional intermediate at the early stage of the CoO intermediate formation suggesting the Co⁰ particle dispersion.

1. Introduction

The supported Co catalysts are well known to have the high activity in various catalytic reactions such as Fischer–Tropsch synthesis, hydrogenation, desulfurization, and ethanol steam reforming [1]. The chemical state conversion of the active Co species causes the degradation of the catalytic performance. Therefore, the direct characterization and its structure determination of such active species under the reaction gas conditions are imperative for the stable utilization of the catalysis process. Besides the applicability of the XAFS spectroscopy to *in-situ* observations of metal species under a real reaction condition, *in-situ* quick XAFS provides quantitative information on supported phases formed during the cobalt catalyst activation, in terms of the structural, as well as temperature and rate of formation and decomposition [2]. The time-resolved XAFS technique is powerful to clarify the reaction mechanism of chemical conversions for catalytically active materials, the time-resolved dispersive XAFS (DXAFS) technique was applied to measure the dynamic process of the chemical state conversion for the supported metal catalysts [3,4]. In this study, the chemical state conversions on a supported Co catalyst have been investigated by means of the *in-situ* XAFS and the time-resolved DXAFS techniques, and the redox reactions of the Co species supported on SiO₂ will be discussed.

2. Experimental

The Co catalyst was prepared by the impregnation method using SiO₂ (192 m²/g) from the Catalysis Society of Japan. The Co(NO₃)₂•6H₂O was dissolved in deionized water and the SiO₂ powder was suspended in the solution. The mixture was stirred for 1 h and was dried for 24 h at 80 °C. The obtained catalyst precursor was subjected to a calcination treatment at 600 °C for 2 h in air. The Co loading was set to be 10 wt.%.



The *in-situ* XAFS measurements were performed at the BL-12C station of PF (KEK, Japan) using a Si(111) double-crystal monochromator. The sample powder was first exposed to dilute H₂ flow (10 vol.% balanced by He, 200 cm³/min) in an *in-situ* observation cell and was heated to 750 °C at 10 °C/min (temperature-programmed reduction: TPR). Once cooling to room temperature by keeping the H₂ gas flow, the gas was changed to dilute O₂ (10 vol.% balanced by He, 200 cm³/min), and the sample was heated to 600 °C at 10 °C/min (temperature-programmed oxidation: TPO). The XAFS spectra were repeatedly recorded with the interval time of 2 min during both processes.

The dynamic changeover of the chemical state was studied by the time-resolved DXAFS technique at the NW2A station of PF-AR (KEK, Japan) using a Si(111) bent crystal as the polychromator with the bending radius of 2.0 m. The Co catalyst was set in a batch-type DXAFS cell [5], and the sample was heated to 600 °C at 20 °C/min. The reaction gas (pure H₂ at 6.5 kPa for reduction of Co oxides and pure O₂ at 1.8 kPa for oxidation of metallic Co) was rapidly injected to start the reaction into the cell after the evacuation. The time-resolved spectra were recorded with the time resolution of 10 ms.

3. Results and discussion

The XANES spectral changes for the TPR and TPO processes are shown in figure 1. The initial spectrum of TPR was identical to that of Co₃O₄, and the XANES spectrum was finally changed to metallic Co. During the conversion from Co₃O₄ to Co⁰, the transient spectrum was almost consistent with that of CoO with the white line peak at 7725 eV. The XANES spectral change for the TPO process showed that the Co⁰ species was reversibly oxidized to Co₃O₄. The composition analysis based on the XANES spectrum was thus carried out by the linear combination of three reference species, Co⁰, CoO, and Co₃O₄, and the calculated values of mole fraction are plotted in figure 2(a) as a function of temperature. Figure 2(a) clarifies that the divalent CoO species quantitatively exists at *ca.* 450 °C under the dilute H₂ gas flow. The spectral reproducibility is given in figure 2(b) for a stable CoO intermediate formed during TPR at 436 °C. In contrast, the composition of CoO is diminished to *ca.* 20 % under the oxidative atmosphere during the TPO process. It is evaluated that the CoO species are readily converted to the final product of Co₃O₄ (see figure 2(a)) because of the relative stability of Co₃O₄ to CoO under the oxidative atmosphere. The *in-situ* XAFS measurements reveal that the reversible redox reactions between Co₃O₄ and Co⁰ take place on supporting SiO₂ via the intermediate state of CoO and that the stability of CoO is significantly affected by the gas environment. At room temperature, an obvious composition change was observed when the flow gas was switched from H₂ to O₂. The composition analysis revealed that the Co⁰ species was partially oxidized to CoO (20 %) and Co₃O₄ (10 %) by the exposure to O₂ at room temperature.

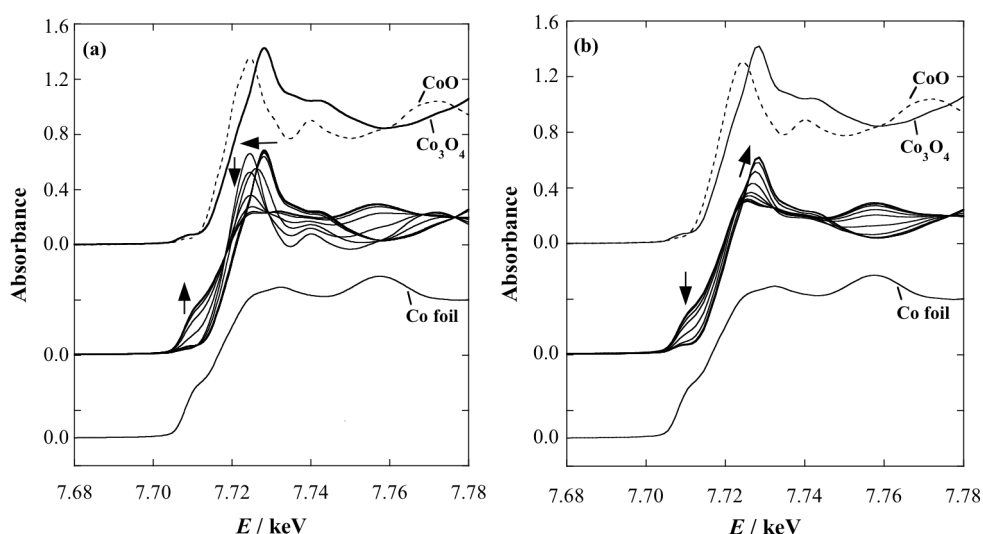


Figure 1. XANES spectral change during the TPR (a) and TPO (b) process of Co/SiO₂.

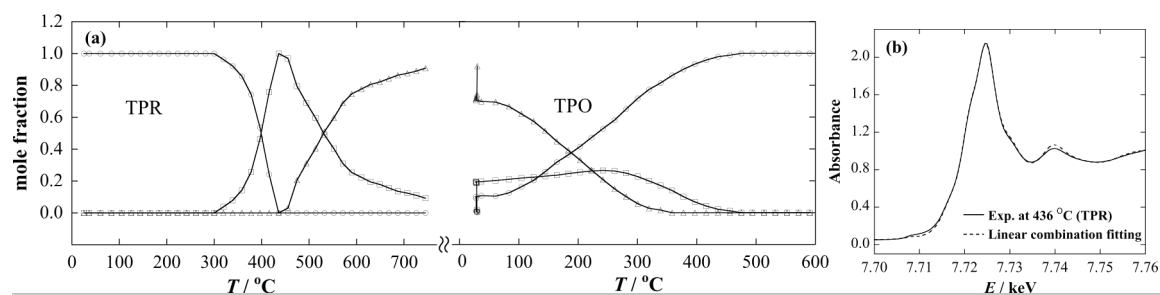


Figure 2. The temperature variation of components species, Co^0 (triangles), CoO (squares) and Co_3O_4 (circles), during the TPR and TPO process (a) and a comparison between the calculated and observed spectra at 436 °C during TPR for a stable CoO intermediate (b).

The time-resolved XANES spectral change is presented in figure 3 for the redox reactions between Co_3O_4 and Co^0 measured by the DXAFS instrument. For both reactions, the observed spectral changes are quite similar to those for the TPR and TPO processes shown in figure 1. In the case of the reduction of Co_3O_4 by H_2 (figure 3(a)), the two-phase change is clearly observed and the intermediate spectrum with the white line peak at 7725 eV is in agreement with that of CoO . Thus, it is concluded that the first step corresponds to the reduction from Co_3O_4 to CoO , which is followed by the succeeding reduction from CoO to Co^0 . The stepwise conversions are observed in the dynamic process similar to the TPR process. The intermediate CoO species have the lifetime of a few seconds under the present experimental conditions.

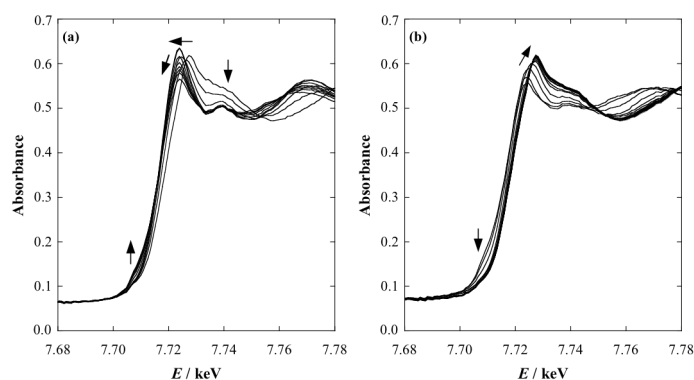


Figure 3. XANES spectral change measured at 600 °C after a rapid exposure of H_2 (6.5 kPa) to $\text{Co}_3\text{O}_4/\text{SiO}_2$ (a) and of O_2 (1.8 kPa) to Co^0/SiO_2 (b).

The similar XANES change during the oxidation reaction (figure 3(b)) to that for the TPO process (figure 1(b)) suggests that the reaction proceeds with the unstable intermediate of CoO . The detailed analysis shown in figure 4 for the observed absorbance change at 7721 eV, corresponding to the isosbestic point of the second step, clearly indicates that the oxidation process is composed of three steps. As shown in figure 4(a), a slight enhancement of the absorbance at 7723 eV without the energy shift was observed within 0.5 s after the injection of O_2 gas. The energy shift of the white line peak to 7725 eV was observed at the second step from 0.5 s to 1.7 s, as shown in figure 4(b), and it was identical to the difference between metallic cobalt and CoO . The second step is thus assigned to the conversion to CoO , and an additional intermediate species is suggested to form at the first step within 0.5 s. The white line peak was further shifted to the higher energy side after the second step and was finally matched to that of Co_3O_4 at 5.0 s as shown in figure 4(c). Only the enhancement of the absorbance without the energy shift at the first step may suggest the Co^0 particle dispersion promoted

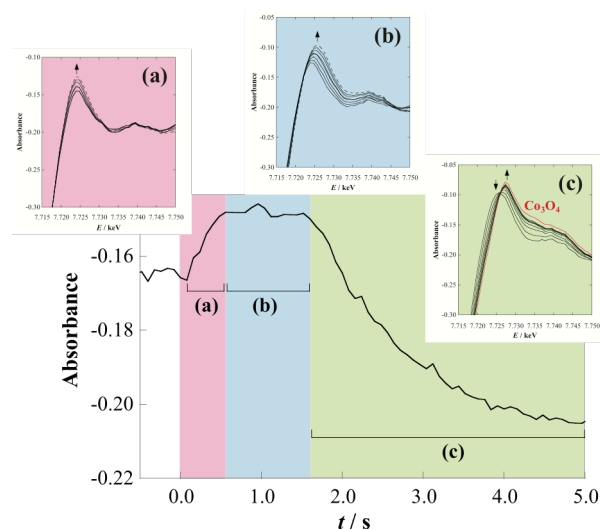


Figure 4. The X-ray absorbance change at 7721 eV as a function of time measured at 600 °C under 1.8 kPa of O₂. XANES spectral change for the time region after the exposure to O₂ from 0 to 0.5 s (a), from 0.5 to 1.7 s (b), and from 1.7 to 5 s (c). In (c), the spectrum of Co₃O₄ is shown for comparison.

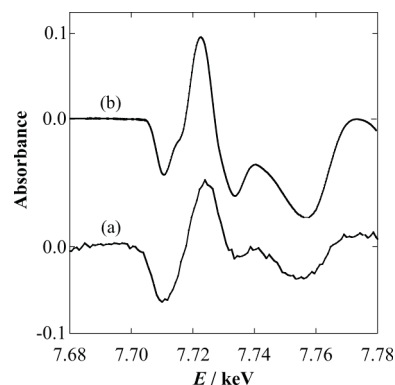


Figure 5. The spectral difference at the first step of the oxidation between 0 and 0.5 s (a) and that between Co foil and supported metallic Co⁰ species measured at 0 s.

by the O₂ gas exposure. Figure 5 indicates that the spectral difference observed at the first step between 0 and 0.5 s is consistent with the difference spectrum between Co foil and the supported Co⁰ particle. This consistency suggests that the first step of the oxidation process (figure 4(a)) corresponds to the dispersion of the supported Co⁰ particle. It is considered that the additional intermediate state, the dispersed Co⁰ species, is generated by the adsorption of oxygen at the surface defect of the Co⁰ particle. The dispersed Co⁰ species is then oxidized to Co₃O₄ via CoO at the succeeding two steps.

4. Conclusions

The temperature-programmed and time-resolved XAFS measurements for the redox reactions of the supported Co species on SiO₂ revealed that the chemical state conversion between Co₃O₄ and Co⁰ proceeded reversibly with the intermediate state of CoO. The transient composition of CoO during the reduction process reached almost 100 %, whereas the diminished composition under the oxidative atmosphere indicated the relative stability of Co₃O₄ to CoO. The detail analysis for the oxidation reaction showed an additional intermediate at the early stage suggesting the Co⁰ particle dispersion.

Acknowledgement

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References

- [1] de la Osa A R, de Lucas A, Romero A, Valverde J L and Sanchez P 2011 *Fuel*. **90** 1935
- [2] Hong J, Marceau E, Khodakov A Y, Griboval-Constant A, Fontaine C L and Briois V 2012 *Chem. Eur. J.* **18** 2802
- [3] Katayama M, Niwa Y, Doi K, Yamashita S and Inada Y 2013 *J. Phys.: Conf. Series* **430** 012053
- [4] Yamashita S, Katayama M and Inada Y 2013 *J. Phys.: Conf. Series* **430** 012051
- [5] Uemura Y, Inada Y, Bando K K, Sasaki T, Kamiuchi N, Eguchi K, Yagishita A, Nomura M, Tada M, and Iwasawa Y 2011 *Phys. Chem. Chem. Phys.* **13** 15833