

Size Dependent Redox Property of Supported Co Catalyst

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Abstract

The chemical state conversion of the Co catalysts supported on silica prepared by the impregnation method was investigated by means of the *in-situ* XAFS technique. The particle size of the Co species was controlled by the addition of citric acid into the precursor solution. The average particle diameter was 4 nm, and it was smaller than that of the Co species prepared without citric acid. The reduction temperature of the small CoO particle was shifted to higher, whereas the oxidation temperature of the small Co⁰ particle was shifted to lower. The specific redox property for the small particle is caused by the interaction with supporting SiO₂. The redox temperature between Co₃O₄ and CoO was independent on the particle size difference.

1. Introduction

Cobalt catalysts supported on metal oxide supporting material such as SiO_2 and Al_2O_3 are known to have catalytic activity and selectivity for the Fischer–Tropsch reaction (FT), the ethanol steam reforming reaction, and the CO oxidation reaction, which are important processes to resolve the energy and environmental issues for the modern society [1-3]. The particle size of the active species for supported metal catalysts is one of the factors to improve the catalytic performance. It is expected that high catalytic active is exhibited by increasing the number of active sites on the particle surface. The particle size reduction of active metal species is the most straightforward approach to increase the surface active sites.

There are various studies about the preparation method to support the small active metal species, such as the hydrothermal synthesis, the sol-gel method, the liquid phase reduction method, and the impregnation method with organic additives [4-6]. It has been reported that the Co particle size affects to the catalytic performance for the CO oxidation and the FT reaction [3,7]. Analyzing of chemical states for small Co species under the reaction atmosphere will give important knowledge to develop the cobalt catalysts with high performance. We have previously reported the redox property of the small Ni particles supported on SiO_2 [8]. The reduction temperature of the small NiO particles was shifted to higher, whereas the oxidation of metallic Ni(0) proceeded at lower temperature for the small particles [9]. The temperature shifts influence to the preparation and treatment conditions before the utilization, and also they are very important to understand the actual active species under the reaction conditions.

In this study, the particle size dependence for the redox reactions of the supported Co species have been investigated by mean of the *in-situ* XAFS technique. The small Co particles supported on SiO_2 were prepared by the impregnation method with citric acid (ImpCit). The results are compared with the Co catalyst prepared by the conventional impregnation method (Imp).

2. Experimental

The supported Co catalysts were prepared by the impregnation method using SiO_2 powder distributed by the Catalysis Society of Japan (JRC-SIO-10). The stoichiometric amount of citric acid was added into an aqueous solution of cobalt nitrate to control the Co particle size for the ImpCit method. The solution was stirred for 1 h at room temperature and

dried at 80 °C for 48 h. The obtained powder was calcined at 700 °C in air for 2 h. In the case of the Imp method, the similar procedure was carried out without the addition of citric acid. The Co loading was set to be 10 wt.% for both preparation methods.

The *in-situ* XAFS measurements were carried out at BL-3 of the SR Center (Ritsumeikan University) and BL-9C of the Photon Factory (KEK) at the Co K edge in the transmission mode. The prepared samples were heated to 900 °C at 10 °C /min under the diluted H₂ (10 vol.% balanced by He, 200 cm³/min) gas flow. The XAFS measurements were performed at the temperature-programmed reduction (TPR) process. The sample was then cooled to room temperature by keeping the H₂ gas flow, and the flow gas was switched to diluted O₂ (10 vol.% balanced by He, 200 cm³/min) at room temperature. The samples were reheated to 700 °C at 10 °C /min, and the XAFS measurements were carried out during the temperature-programmed oxidation (TPO) process. The XAFS scans for 1 min were repeated with the time interval of 2 min.

3. Results and Discussion

The particle size of the supported Co species for the reduced sample was measured by the transmission electron microscopy (TEM). The distribution histograms of the particle size are shown in Figure 1 together with typical TEM images for the sample prepared by the Imp and the ImpCit methods. It was found that the diameter of the Co particle distributed in the range for 6 to 35 nm with the average value of 18 nm for the Imp sample. On the other hand,

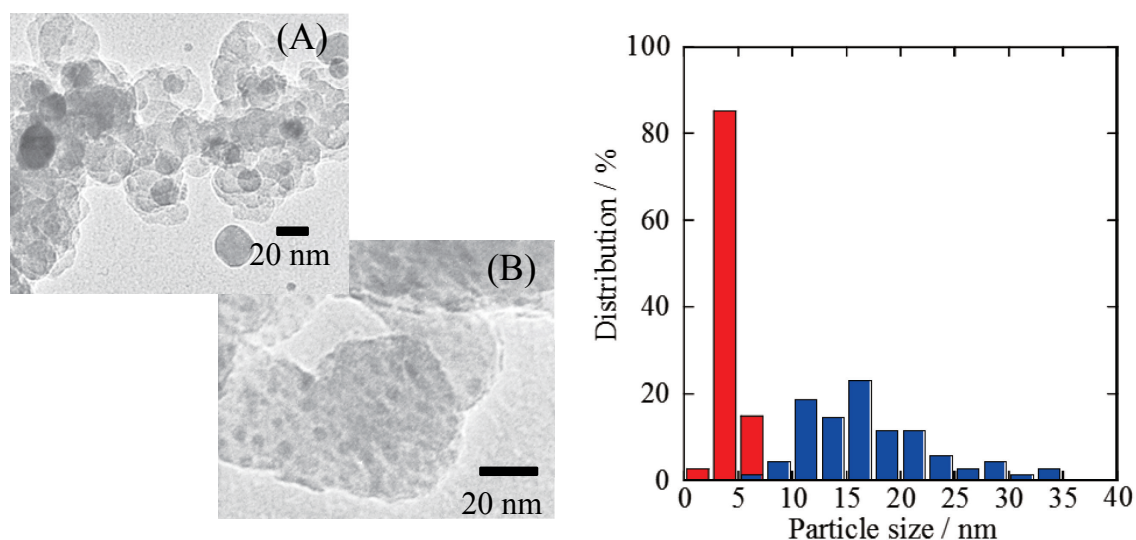


Figure 1. TEM images and particle size distribution for the reduced Co catalysts prepared by Imp (A and blue bars) and ImpCit (B and red bars).

the Co particle size prepared by ImpCit was homogeneous, and the average value of the particle size was 4 nm.

The XANES spectral change during the TPR and TPO processes are shown in Figure 2. The initial XANES spectrum before the TPR process was in agreement with that of Co_3O_4 for both Co catalysts. The absorption edge was shifted to the lower energy with increasing temperature, and the XANES spectrum was changed to that of CoO . The spectrum was further changed for both samples, but the final spectrum at the end of the TPR process was not consistent with each other. The final XANES spectrum of the Imp sample was almost identical to that of Co^0 , whereas that of the ImpCit sample indicated the mixture between CoO and Co^0 . The spectral change during the TPO process was almost the reverse of the TPR process with the edge shift to the higher energy and the enhancement of the white line peak intensity. The XANES spectrum was finally returned to that of Co_3O_4 .

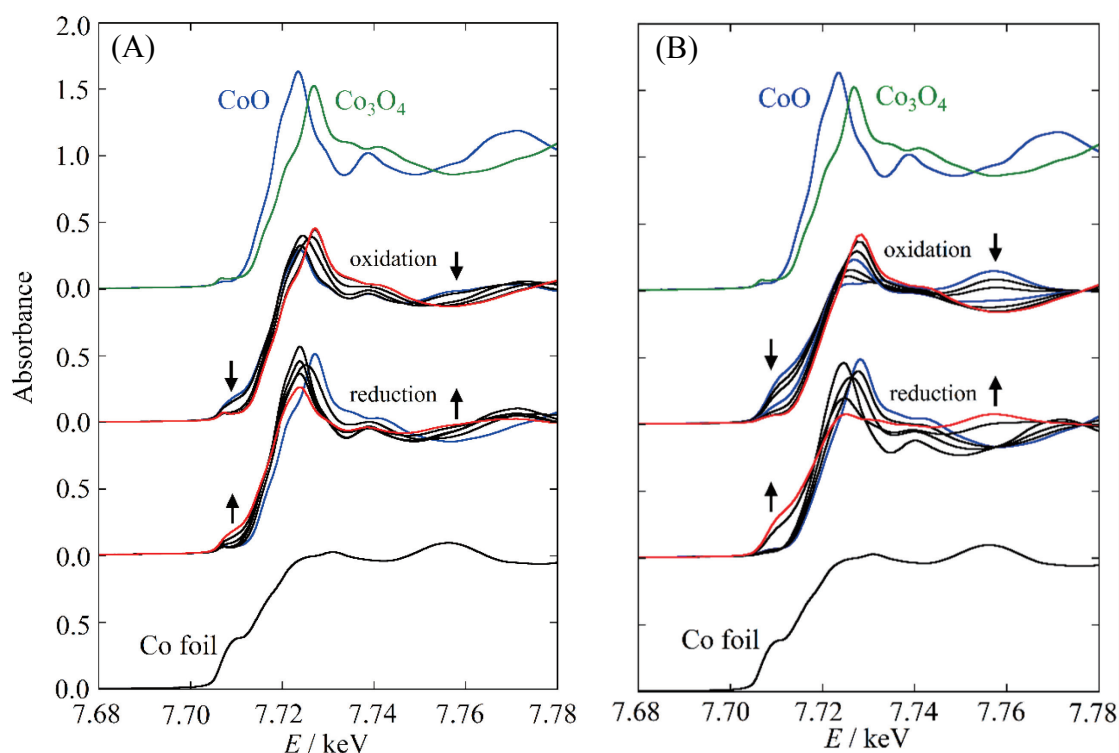


Figure 2. XANES spectral change during the TPR and TPO processes for the Co catalysts prepared by the ImpCit (A) and Imp (B) method.

The sample composition was analyzed by the linear combination fitting of the XANES spectrum based on those of reference samples of Co_3O_4 , CoO , and Co^0 . The determined values of mole fractions are plotted as a function of temperature in Figure 3. As suggested in the XANES spectral changes, the two-step reduction processes, that is, from Co_3O_4 to CoO

and from CoO to Co^0 , was observed for both the Co catalysts during the TPR process. The temperature at which the first reduction from Co_3O_4 to CoO occurred at around 450°C was in agreement within the experimental uncertainty for both catalysts with different particle size. In contrast, the reduction from CoO to Co^0 for the Imp sample with the larger particle size proceeded at much lower temperature than the ImpCit sample with the smaller particle size. The higher temperature shift of the latter reduction suggests that the CoO species is stabilized on silica because of the similar O atom arrangement at the particle surface. Because both the reactant and the product are oxide for the first reduction process, the reduction temperature is independent on the particle size. For the TPO process, the smaller Co^0 particles (ImpCit) were oxidized at lower temperature by about 100°C than the larger particles (Imp). This shift is also explained by the relative stability of the CoO species on silica rather than the Co^0 species. Similar to the TPR process, the conversion temperature between the CoO and Co_3O_4 species was independent on the particle size. As clearly suggested in Figure 3, the CoO species is not quantitatively formed at any temperature range regardless of the particle size. It suggests the relative stability of Co_3O_4 than CoO under the oxidizing atmosphere.

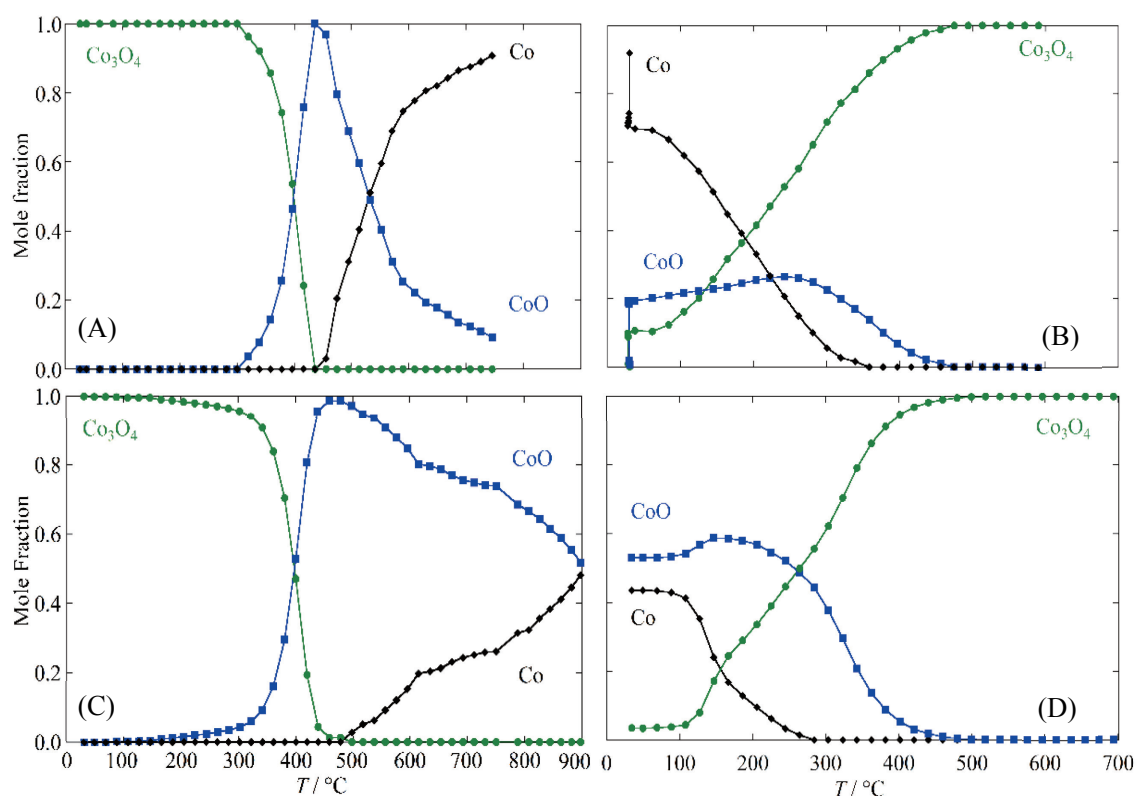


Figure 3. Mole fraction of the Co species in the Co catalysts prepared by the Imp (A and B) and ImpCit (C and D) method during the TPR (A and C) and TPO (B and D) process.

4. Conclusion

The higher reduction temperature of small CoO particles and the lower oxidation temperature of small Co⁰ particles were demonstrated by means of the *in-situ* XAFS technique for the TPR and TPO processes of the Co catalysts supported on silica. The strong interaction of the CoO species with supporting SiO₂ may contribute to the relative stability of the small CoO particles. On the other hand, the redox temperatures between Co₃O₄ and CoO are independent on the particle size. It suggests that the interaction of Co₃O₄ with SiO₂ is similar to that of CoO.

Acknowledgment

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References

- [1] S. Sun and N. Tsubaki, *Appl. Catal. A*, **202**, 121 (2000).
- [2] A. F. Lucrecio, J. D. A. Bellido, A. Zawadzki and E. M. Assaf, *Fuel*, **90**, 1424 (2011).
- [3] V. Iablokov, R. Barbosa, G. Pollefeyt, I. V. Driessche, S. Chenakin and N. Kruse, *ACS Catal.*, **5**, 5714 (2015).
- [4] L. Shi, K. Tao, T. Kawabata, T. Shimamura, X. J. Zhang and N. Tsubaki, *ACS Catal.*, **1**, 1225 (2011).
- [5] L. Shia, C. Zengb, Q. Linb, P. Lub, W. Niub and N. Tsubaki, *Catal. Today*, **228**, 206 (2014).
- [6] E. Lester, G. Aksomaityte, J. Li, S. Gomez, J. G. Gonzalez and M. Poliakoff, *Prog. Cryst. Growth Chem.*, **58**, 3 (2012).
- [7] G. L. Bezemer, J. H. Bitter, H. P. C. E. Kuipers, H. Oosterbeek, J. E. Holewijn, X. Xu, F. Kapteijn, A. J. V. Dillen and K. P. D. Jong, *J. Am. Chem. Soc.*, **128**, 3956 (2006).
- [8] S. Yamashita, Y. Yamamoto, M. Katayama, Y. Inada, *Bull. Chem. Soc. Jpn.*, **88**, 1629 (2015).
- [9] Y. Yamamoto, S. Yamashita, M. Katayama, and Y. Inada, *Memoirs of the SR Center*, **17**, 115 (2015).