In-situ XAFS analysis of Rh ion-exchanged Y-type Zeolite catalysts
2. Under reaction conditions

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Introduction

Rh ion-exchanged Y-type zeolite catalysts (RhY) are highly active for methane formation from CO_2 and H_2, compared with other Rh catalysts supported on conventional amorphous oxides. To elucidate correlation between the surface structure and catalytic activity, a new XAFS analysis system with an ***in-situ*** cell for high-pressure and high-temperature was developed. The structures of Rh nanoparticles under catalytic CO_2 hydrogenation reaction conditions were investigated

Experimental

A five wt% RhY catalyst was prepared by the ion-exchange method as explained elsewhere [1].

The catalyst (0.3 g) was pressed into a disk with a diameter of 10 mm, and set in an in-situ EXAFS cell (Fig.1 [2]). It can be used up to 723 K under ambient pressure and to 523 K under 3 MPa. Prior to the catalytic CO_2 hydrogenation reaction, the catalyst was reduced under a flow of diluted H_2 (20% H_2 / Ar) at 723 K. The reaction was conducted at 523 K under a total pressure of 3 MPa. The reactant gas was composed of 25 % CO_2 and 75 % H_2. The flow rate was 120 ml/min. The exhausted gases were treated with H_2 and air to completely transform into H_2O and CO_2, which were then transferred to a duct.

All the Rh K-edge XAFS spectra were measured in the transmittance mode at BL-10B. Curve-fitting analysis was carried out by REX (Rigaku Co.). The model parameters for analysis were extracted from an EXAFS spectrum of Rh foil heated at the same temperature as the catalyst.

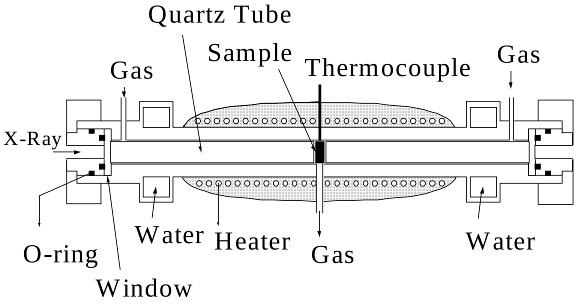

Fig.1 Schematic of an in-situ XAFS cell adapted from ref. 2.

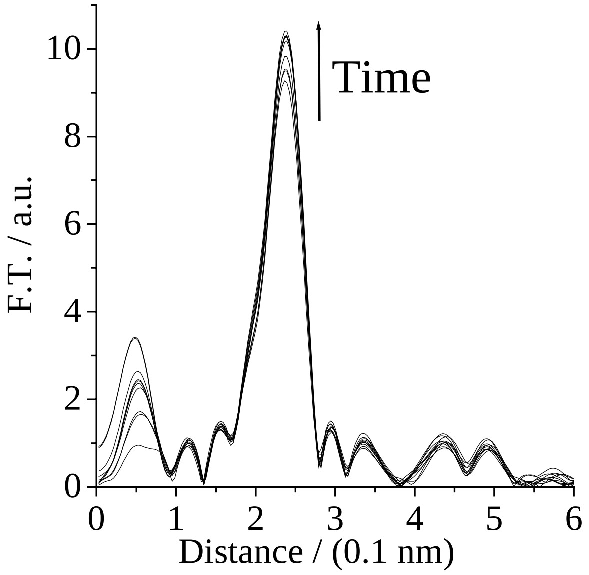

Fig.2 Fourier transforms of Rh K-edge EXAFS spectra ($k^3\chi(k)$) during CO_2 hydrogenation observed every 7 min. from the reaction time of 2 min to 66 min.

Results and Discussion

Figure 2 shows Fourier transforms of EXAFS spectra observed under the reaction conditions. The quality of spectra was good. The meaningful change observed during the reaction was only the increase in the intensity of the main peak at 0.24 nm: the intensity of the main peak increased as the reaction time elapsed. This indicates that some deformation or aggregation of Rh particles occurred during the reaction. However, the above change was not reflected in the curve-fitting analysis result, because intrinsic analytical errors for coordination numbers were about ±1 in the present case. The coordination number for Rh-Rh scattering was 7.3 (after 66 min of the reaction), corresponding to an average particle size of 1.3 nm.

References

[1] K. K. Bando, et al., Appl. Catal. A; General, 173,47 (1998).
[2] K. K. Bando, et al., J. Sync. Rad., 8, 581 (2001).

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