

In situ XAFS analysis system for high-pressure catalytic reactions and its application to CO₂ hydrogenation over a Rh/Y-zeolite catalyst

Kyoko K. Bando,^{a*} Takeru Saito,^{a#} Koichi Sato,^a Tomoaki Tanaka,^a Franck Dumeignil,^a Motoyasu Imamura,^a Nobuyuki Matsubayashi,^a and Hiromichi Shimada^a

^aNational Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan

[#]Present address: Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan
Email: bando@nimc.go.jp

An *in-situ* XAFS cell was developed and used for the structural analysis of a Rh ion-exchanged zeolite catalyst during high-pressure hydrogenation of carbon dioxide. The *in-situ* cell enabled analyses of the catalyst structures that changed with the reaction atmosphere and elapsed time; the peak assigned to Rh-O scattering changed to that assigned to Rh-Rh scattering at 404 K during the pretreatment by hydrogen. After 30 min. of the carbon dioxide hydrogenation reaction, the peak intensity assigned to Rh-Rh scattering increased corresponding to the increase in the catalytic activity

Keywords: *in-situ* XAFS, Rh/zeolite catalyst, CO₂ hydrogenation

1. Introduction

The structures of catalysts are greatly dependent on the reaction atmosphere due to direct chemical interaction with the reactants (Clausen, 1998). Thus, information on the structure of active catalytic sites under reaction conditions is essential for designing better catalysts. XAFS is one of the most promising tools for the *in-situ* analysis of catalysts, because chemical reactants are in general transparent for x-rays at the K-shell absorption edges of catalyst species. In addition, most of the active catalytic sites do not have long-range ordered structures and thus cannot be analyzed by diffraction techniques.

In the present paper, we designed and assembled an *in-situ* XAFS cell that could be used under high pressure and high temperature. The cell was then applied to the structural analysis of a Rh ion-exchanged zeolite catalyst (RhY, Rh loading of 5 wt%) that showed higher activity and selectivity to methane in the hydrogenation of CO₂ than conventional Rh catalysts (Bando et al., 1998). The catalyst structure and reaction products were continuously analyzed during the catalyst pre-reduction and the following reaction.

2. Experimental

The schematic of the *in-situ* transmission XAFS cell designed for high-pressure catalytic reactions is shown in Fig. 1. The cell had two acrylic resin windows with a thickness of 3 mm that can be used up to 6 MPa. The absorption (μ) of x-rays at Rh K-edge (23.2 keV) by the windows were calculated at 0.3 that was sufficiently smaller than the absorption by the sample (ca.2).

The pressure, temperature and flow rate of gases were monitored and controlled outside of the hatch attached to the beam line so that a series of the experiments could be done without closing the x-ray

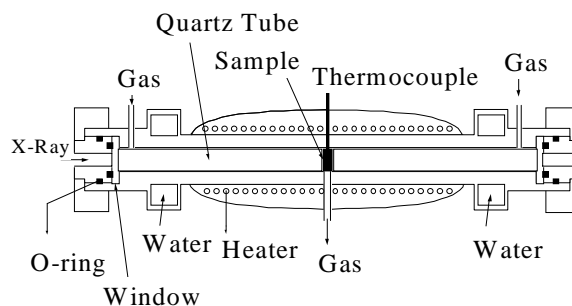


Figure 1
Schematic of a high pressure *in-situ* XAFS cell.

shutter. The exhaust gas was completely converted into CO₂ and H₂O with a complementary supply of H₂ and air, followed by venting to a duct.

The XAFS measurements were carried out at BL10B of the Photon Factory of the Institute of Materials Structure Science, Higher Energy Accelerator Research Organization (KEK-IMSS-PF), using a Si(311) channel-cut monochromator. All the spectra were obtained in the transmission mode by using two ion-chambers filled with Ar for I₀ and Kr for I. The XAFS spectrum was obtained by step scanning of the monochromator with an accumulation time of 0.5 sec. per each point.

A five wt.% Rh ion-exchanged Y-type zeolite catalyst (RhY) was prepared by ion-exchange using RhCl₃·3H₂O (Wako) and NaY zeolite (Nishio SK-40), followed by calcination in air at 673 K for 6 h. For XAFS analysis, 0.3 g of RhY was pressed into a disk and set in the cell. Prior to the reaction, the catalyst in the cell was reduced at 723 K for 1 h with a flow of 100 cm³/min of 20% H₂/Ar, when the heating rate was 7 K/min. The CO₂ hydrogenation reaction was carried out at 523 K with a flow of 100 cm³/min. of 25% CO₂/H₂. The total pressure during the reaction was kept at 3 MPa.

The collected data were analyzed according to the procedure described elsewhere (Bando et al., 2000.). Curve-fitting analysis was conducted on $k^3\chi(k)$ in k -space (k range = 3 – 17 Å⁻¹) using REX (Rigaku Co.), where k indicates a wave number of a scattered photoelectron and χ represents a normalized EXAFS oscillation. The phase shift and the back scattering amplitude for the analysis were extracted from EXAFS spectra for Rh foil. The measurements of Rh foil were carried out at various temperatures from 323 K to 723 K under a flow of Ar to analyze the spectra of the catalysts taken at different reaction temperatures.

3. Results and discussion

3.1 Reduction Process

Figures 2 and 3 show the change in the EXAFS oscillations ($k^3\chi(k)$) and Fourier transform of EXAFS during hydrogenation pretreatment before CO₂ hydrogenation. The EXAFS spectra display successive changes corresponding to the changes in the local structure around Rh with rising temperature (Fig. 2 (a)→(b)→(c)). The structural change is more clearly shown in Fourier transformed spectra as shown in Fig. 3. A peak at 0.17 nm in Fig. 3 (a) taken at room temperature is assigned to Rh-O scattering, indicating the formation of Rh oxide species. As the temperature increased, the peak due to Rh-O scattering decreased, whereas a new peak assigned

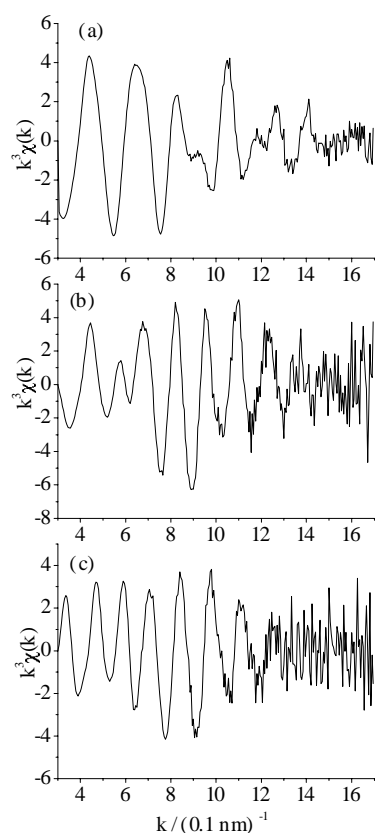


Figure 2

In-situ EXAFS oscillation ($k^3\chi(k)$) observed during H_2 hydrogenation of RhY. (a) r.t. in N_2 , (b) at 404 K in 20% H_2/Ar and (c) at 707K in 20% H_2/Ar .

to Rh-Rh scattering of metal clusters emerged at 0.24 nm. The spectrum taken at the end of the pre-treatment (at 707 K, Fig.3 (i)) shows only the peak assigned to Rh-Rh scattering. Thus, the Rh species changed from oxide to metal most rapidly between 338 K and 404 K. The decrease in the intensity of Rh-Rh scattering above 540 K is ascribed to the deviation of Rh-Rh interatomic distance due to thermal oscillation. Note that the above observations demonstrate a typical advantage of *in-situ* XAFS analysis that minimizes the extrinsic deviation of the spectra, for instance the deviation of the sample thickness, because all the XAFS spectra were obtained on a fixed cross-section of the sample.

3.2 High pressure CO_2 hydrogenation

Figure 4 shows the changes in the peak intensities assigned to Rh-Rh scattering in the Fourier transformed EXAFS oscillation as well as the yield of CH_4 during the hydrogenation of CO_2 . During the whole reaction the peak intensities of Rh-Rh scattering were between 9 and 11, which corresponded to Rh-Rh coordination numbers of 7-8 by curve-fitting analysis. This indicates that most of the Rh metal in the Rh/Y catalyst formed clusters with diameters smaller than 1.3 nm of the supercage of Y-type zeolite. Namely, the catalytically active Rh clusters were located inside the zeolite cage during the whole reaction period.

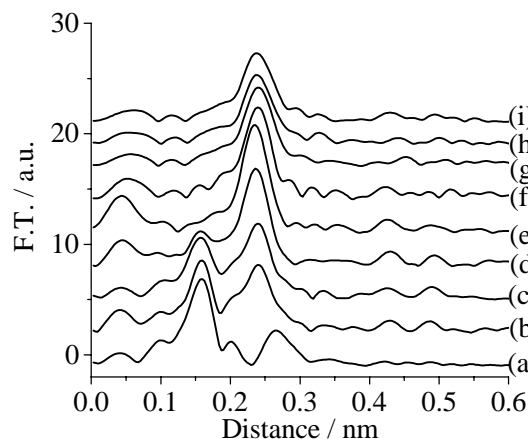


Figure 3

Fourier transform of *in-situ* EXAFS oscillations ($k^3\chi(k)$) observed during H_2 hydrogenation of RhY. (a) r.t. in N_2 , (b)-(i) were observed in 20% H_2/Ar at (b) 297 K, (c) 338 K, (d) 404 K, (e) 472 K, (f) 540 K, (g) 612 K, (h) 679 K, and (i) 707 K.

The peak intensity due to Rh-Rh scattering increased between 20 min. and 30 min. of the reaction time elapsed. This was likely resulted from the change in the structure of Rh clusters and probably related to the increase in the yield of CH_4 observed after 20 min. of the reaction. An increase in the peak height is not necessarily ascribed to the growth of clusters because of the asymmetry of pair distribution functions at high temperatures. Nevertheless, the simultaneous increases in the peak height and catalytic activity suggest the genesis of an optimal structure that gives the highest performance after the 20 min. of reaction elapsed. The following decrease in the CH_4 yield was probably due to the active site poisoning that could not be detected by the present XAFS measurement. Detailed analysis of the XAFS spectra is now under progress for the precise structural change of active catalytic sites. It should be noted again that the above changes could be detected by the use of the *in-situ* measurement system that suppressed extrinsic deviations of XAFS data.

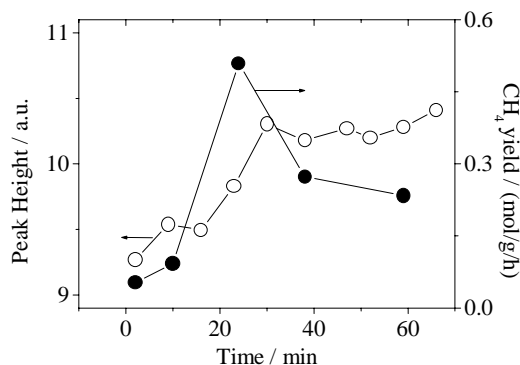


Figure 4

Change in the peak height of Rh-Rh scattering in Fourier transformed EXAFS oscillation ($k^3\chi(k)$) (open circles), together with CH_4 yield (closed circles).

4. Conclusion

In the present study, an *in-situ* XAFS cell for high-pressure catalytic reactions was designed and developed. The cell was then applied to the analysis of a Rh ion-exchanged Y-type zeolite catalyst during hydrogenation pre-treatment and CO₂ hydrogenation. The result revealed that Rh oxide in the RhY catalyst was reduced to Rh metal clusters at 404 K during the pre-treatment. During the hydrogenation of CO₂, EXAFS spectra exhibited a structural change of Rh species that corresponded to an increase in the catalytic activity. These results evidenced an advantage of *in-situ* XAFS analysis on the catalyst structures.

References

- Bando, K. K., Soga, K., Kunimori, K., Ichikuni, N., Okabe, K., Kusama, H., Sayama, K., & Arakawa, H. (1998) Appl. Catal. A: General 173, 47-60
Bando, K. K., Ichikuni, N., Soga, K., Kunimori, K., Arakawa, H., & Asakura K. (2000) J. Catal., 194, 91-104
Clausen, B. S. (1998). Catal. Today 39, 293-300