In situ Quick XAFS studies on the structure of Rh supported on zeolites

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Abstract. Dynamical change of structure of Rh supported on H-USY and Na-USY zeolite was measured by Quick XAFS technique operated under in situ conditions. In the atmosphere of H2, formation of the Rh clusters consist of 13 atoms was observed in H-USY and Na-USY. On the other hand, in the atmosphere of O2, formation of the highly dispersed Rh oxide was observed in H-USY, whereas Rh oxide species did not disperse in Na-USY. In the reduction processes after heating samples in the atmosphere of O2, the highly dispersed metal Rh particles in the H-USY agglomerated with increasing temperature above 553K. Whereas, the generation of stable Rh clusters were observed on the Na-USY. From these finding, it was conclude that the structure and acid sites of USY affected on the dispersion of Rh oxide particles and the generation of metal Rh clusters.

1. Introduction

Metal clusters loaded on zeolite with microporosity exhibit highly characteristic catalytic properties for variety of chemical reactions. As an example of characteristics catalytic properties of metal supported on zeolite, Rh loaded on the zeolite exhibits catalytic activity in the various reactions, such as decomposition of N2O, and hydrodesulfurization of thiophene [1, 2]. Previous study revealed that the structure and the acid sites of zeolite affected the catalytic performance [3-5]. Because the zeolite not only provides acid or base-site and gives shape selectivity but also affects catalytic properties of Rh clusters by interaction of support with metal. To obtain direct information on the metal - support interaction, it is essential to measure the change structure of Rh induced by the acid site of zeolites in reductive or oxidative atmosphere. In this study, we have focused on the influence of acid site in the USY for the Rh species. For this purpose, dynamical change of Rh structure was measured by Quick XAFS technique operated under heating in the reductive or oxidative atmosphere.

2. Experimental

2.1. Preparation of Rh loaded on zeolites

Na-USY zeolite support was obtained in USY (Si/Al2=7.7, Shokubai Kasei Co.) by treating with an aqueous solution of 20M of NaNO3 at room temperature. A Rh loaded on H-USY and Na-USY zeolites by a conventional ion-exchange method using Rh(Cl)3·3H2O (Wako Pure Chemical Industries, Ltd.) aqueous solution. The concentration of Rh was 1 wt%. After ion-exchange, the samples were calcined in the atmosphere at 773K for 1h.
2.2. *In-situ* EXAFS measurement

The Rh K-edge EXAFS measurements were carried out in the transmission mode at BL01B1 of SPring-8. The Si (111) double-crystal monochromator was continuously moved from 4.9 to 4.6° in 60 sec. The energy calibrated using Rh foil as the reference. The Rh supported on zeolite sample was pressed into a self-supporting wafer and placed in an *in-situ* quartz cell. The thickness of 15 mm and diameter of 7 mm of the sample disk were placed in a quartz holder. The sample placed in the cell was heated from room temperature to 773 K with heating rate of 5 K min\(^{-1}\) in 10 % H\(_2\)/He or 10 % O\(_2\)/He of flow rate of 100 ml min\(^{-1}\) at atmospheric pressure. The Rh K-edge XAFS data was recorded every 10 K during H\(_2\) flow and O\(_2\) flow.

Curve-fitting analysis of the collected data was carried out with the commercially available REX2000 (Rigaku Co.) software package. The Fourier transformation of the \(k^3\)-weighted EXAFS oscillation from k space to r space was performed over a range of the 2.60-12.24 Å\(^{-1}\) regions. In the curve-fitting analysis, the parameters for backscattering amplitudes and phase shift functions for nearest-neighbouring Rh-O and Rh-Rh were derived from the EXAFS oscillations obtained for Rh\(_2\)O\(_3\) powder and Rh foil at ambient temperature.

3. Results and Discussion

3.1. Reduction process

The changes in the structure of Rh loaded on H-USY and Na-USY were measured by using Quick-XAFS technique in atmosphere of hydrogen. Figure 1 shows the change in Fourier transforms of \(k^3f(k)\) EXAFS collected after every 10 K. Initially, the signal Rh-O could be seen at 1.7 Å in both spectra, which was assigned to the Rh-O bond characteristics of the Rh oxide species. At the temperature increased, the intensity of these peaks gradually decreased, whereas a new peak attributable to the Rh-Rh bond of metal Rh appeared at 2.4 Å as result of the reduction of the Rh oxide species.

![Figure 1. Dependence of coordination number of Rh-O on the temperature measured in a 10 % O\(_2\) flow; (a) Rh / H-USY, (b) Rh / Na-USY.](image)

The coordination numbers (CN) of the Rh-O and the Rh-Rh bond were determined by curve-fitting analysis, and the data are summarized in figure 2. Initially, steep decreasing the CN of the Rh-O bond started at 423K for H-USY and 363K for Na-USY, suggesting that Rh oxide species in Na-USY were reduced more easily than those in H-USY. At the same time, on both H-USY and Na-USY, the CN of the Rh-Rh became constant as soon as that of the Rh-O disappeared, suggesting that Rh cluster was formed by a simple reduction of the Rh oxide particles. The CN of the Rh-Rh bond kept a constant 5.5 with further increase of temperature. It could be noted that the appearance of the plateau meant the
generation of a stable Rh cluster on both USY. From the CN value, the Rh clusters were estimated consists of 13 atoms. The size of the Rh cluster was estimated to be about 8 Å, which was smaller than the diameter of the supercage of the FAU-type zeolite. Therefore, it is suggested that the Rh cluster was formed inside the supercage of the USY.

Figure 2. Dependence of coordination number of Rh-O (□) and Rh-Rh (●) on the temperature measured in a 10 % H₂ flow; (a) Rh / H-USY, (b) Rh / Na-USY.

3.2. Oxidation treatment before reduction process

Before reduction process, the changes in the structure of the samples were measured with a 10 % O₂ flow. Figure 3 shows the CN of Rh-O bond of Rh oxide plotted as function of temperature. On the H-USY, The CN of Rh-O was kept a constant value 5.3 up to 663 K. However, the CN gradually decreased above 663 K, suggesting that the Rh oxide species highly dispersed inside cage of the USY. In contrast to the H-USY, the CN of Rh-O of the Na-USY was kept a constant value at 5.2 up to 773K. From the results, it was noted that the acid site of USY contribute the dispersion of Rh oxide species in the atmosphere of oxygen.

Figure 3. Dependence of coordination number of Rh-O on the temperature measured in a 10 % O₂ flow; (a) Rh / H-USY, (b) Rh / Na-USY.

3.3. Reduction process after oxidation pre-treatment

After heating of the sample under flowing O₂, the sample was cooled to room temperature and the reduction process was carried out after switching the flowing gas a 10 % H₂ flow. Figure 4 shows the CNs of Rh-O bond of Rh oxide and Rh-Rh bond of metal Rh plotted as function of temperature. On the H-USY, The CN of the Rh-O bond gradually decreased with increasing reduction temperature and
disappeared at 663K. The CN of the Rh-Rh bond was observed at 463K. The CN of the Rh-Rh bond was observed at 463K and kept a constant at value of about 2 up to 553K, suggesting the formation of metal Rh cluster having about 3. Subsequently, the CN of the Rh-Rh bond increased in a linear fashion above 553K. For the last time, the CN value was ~5 at 773 K. This result indicates that the agglomeration of Rh clusters progressed inside cage of the USY with increasing temperature. A pattern of change of structure of metal Rh was different from that in Figure 2. This difference was related to the dispersivity of Rh oxide and the presence of acid site in USY. Therefore, it was speculated that interaction of acid site in USY with highly dispersed Rh oxide enhanced the stability of Rh oxide particles. On the Na-USY, the CN of the Rh-Rh bond appeared at 343K and increased with increasing reduction temperature up to 633K. At the same time, the CN of the Rh-O bond disappeared at 633K, suggesting that the reduction of Rh oxide particles to metal Rh took place up to 633K. After completely reduction of Rh oxide, the CN of the Rh-Rh bond kept a constant value at 5.3. A similar pattern in the change of the CN of the Rh-Rh bond was observed in figure 2. From the fact, it is revealed that crystal structure of the USY affect the formation of the stable metal Rh\textsubscript{13} clusters.

![Figure 4](image-url)

**Figure 4.** Dependence of coordination number of Rh-O (☐) and Rh-Rh (●) on the temperature measured in an 10 % H\textsubscript{2} flow after pre-treatment in an 10 % O\textsubscript{2} flow; (a) Rh / H-USY, (b) Rh / Na-USY.

### 4. Conclusions

In the present work, the structural changes in Rh loaded on the H-USY and the Na-USY zeolite were investigated by means of Rh K-edge EXAFS using an in \textit{in-situ} Quick XAFS technique. The conclusions are, as follows:

1. The generation of stable Rh\textsubscript{13} cluster was observed on both USY. From this result, it is revealed that crystal structure of the USY affect the formation of the stable metal Rh clusters.
2. The dispersion of Rh oxide particles was observed on the H-USY in O\textsubscript{2} flowing. On the other hand, Rh oxide particles on the Na-USY did not disperse. The fact reveals that the interaction of Rh oxide species with acid sites of zeolite promoted dispersion of Rh.
3. In the reduction process, a pattern of change structure of the metal Rh on the H-USY after O\textsubscript{2} processing was different from that of Na-USY and directly reduced H-USY. This result indicates that interaction of acid site in USY with highly dispersed Rh oxide enhances the stability of Rh oxide particles.

### References

[1] K. Yuzaki, T. Yarimizu, K. Aoyagi, S. Ito, K. Kunimori 1998 *Catalysis Today* \textbf{45} 129
[2] M. Sugioka, C. Tochiyama, F. Sado, N. Maesaki 1995 *Catalysts in Petroleum Refining and Petrochemical Industries* 551
[3] P. Reyes, I. Concha, M.E. Konig, J.L.G. Fierro 1993 *Applied Catalysis A* \textbf{103} 5-16
[4] T.J. McCarthy, G.-D. Lei, and W.M.H. Sachtler 1996 *Journal of catalysis* \textbf{159} 90-98
[5] H. Tanaka, S. Ito, S. Kameoka, K. Tomishige, K. Kunimori 2003 *Applied Catalysis A* \textbf{250} 255