

## Time-resolved structure change of Pt/MCM-41 by the adsorption of Hydrogen and Oxygen

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### Introduction

Platinum catalysts are easily reduced by hydrogen and also oxidized by oxygen at RT. Although the oxidized and reduced species were studied intensively, the reaction mechanism was not clarified yet. We have clarified the adsorption and release mechanism of hydrogen to/from Pt clusters on an MCM-41 surface by the dispersive XAFS (DXAFS) technique.

### Experimental

3.5 wt % Pt/MCM-41 catalyst was prepared by ion-exchange method using an aqueous solution (pH 9) of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  (Soekawa Chemical Co.). The obtained sample was dried in an oven at 353 K overnight and calcined at 573 K in a flow of  $\text{O}_2$  (200ml/min).

The DXAFS measurements were performed at NW2A. A Si(111) crystal was bent into the radius of 3 m. The DXANES spectra were recorded every 60ms. Data analysis was performed by using UWXAFS package and the backscattering amplitudes, phase shift and mean free paths were calculated with the FEFF8 code.

### Results and Discussion

The DXAFS spectra can be analyzed up to  $k = 140 \text{ nm}^{-1}$ . Fig.1 shows the variation of XANES at the PtLIII edge during the reduction process of Pt/MCM-41 under 20 Torr of  $\text{H}_2$  at 298 K. With the increase of  $\text{H}_2$  exposure time, the XANES spectra were dramatically changed between 11564 and 11584 eV. The intensity of white line (marked A) decreased and a shoulder appeared in the region of 11574-11584 eV (marked B). This shoulder increases as the increase of adsorbed hydrogen and was ascribed to the multiple scattering from Pt-H. The DXAFS study revealed that the structural transformation during  $\text{H}_2$  adsorption and desorption proceeds through several steps. After the adsorption of hydrogen, the icosahedral Pt13 cluster with an average Pt-Pt distance of 0.273 nm is formed. When the hydrated cluster is exposed to  $\text{O}_2$ , hydrogen is released at first (900 ms) and the cluster becomes smaller (1.8s), then  $N(\text{Pt-O})$  increases from 0.3 to 1.1 rapidly (4s). It is suggested that the formation of small Pt cluster is driven not by the adsorbed oxygen but by hydrogen desorption. After that,  $N(\text{Pt-O})$  slowly

increases (120s). On the other hand, when  $\text{H}_2$  is introduced to the oxidized cluster,  $N(\text{Pt-O})$  decreases and Pt-H interaction increases within 1s and this reaction is the driving force of reaction. Then  $N(\text{Pt-O})$  decreases from 1.6 to 0.7 (2s) and  $N(\text{Pt-Pt})$  increases, suggesting the formation of Pt cluster frame (4s). Pt-Pt interaction increases and its distance become longer by the adsorbed hydrogen and finally forms Pt13 cluster (160s).

The present study clarified the dynamic change of Pt cluster framework by DXAFS.

### Acknowledgement

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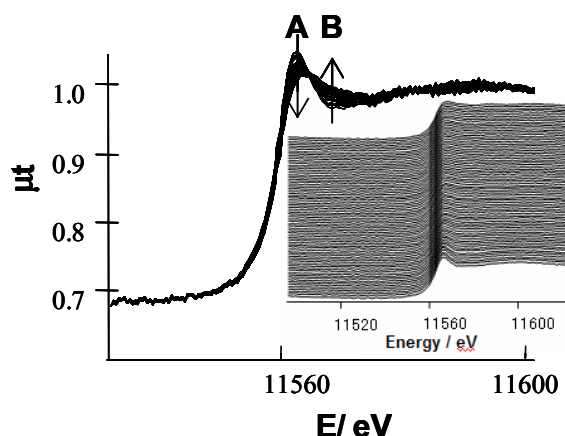


Figure 1. A series of Pt  $L_{III}$ -DXANES spectra at Pt  $L_{1}$ -edge of 3.5 wt% Pt/MCM-41 under the reduction process.

[1] K. Asakura, T. Kubota, N. Ichikuni and Y. Iwasawa *Proc. 11th Int. Congres on Catalysis, Baltimore, Stud. Sur, Sci. Catal*, Vol. 101, 911 (1996).

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