

## Effect of Yb on the structure of bimetallic Pd-Pt particles supported on USY Observed by an in-situ XAFS method

Kyoko K. BANDO\*, Takashi MATSUI, Yuichi ICHIHASHI, Tomoaki TANAKA, Motoyasu IMAMURA, Yuji YOSHIMURA

National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki305-8565, Japan

### Introduction

Ultra stable Y-type zeolite (USY) supported Pd-Pt (Pd-Pt/USY) catalysts are efficient catalysts for hydrodearomatization (HDA) of diesel fuel. However, in the long term of the reaction, serious deactivation occurs due to poisoning of active metal species by sulfur. Recently we found that addition of Yb to Pd-Pt/USY greatly improved the sulfur tolerance of the catalysts [1]. But the mechanism how Yb additive worked during the reaction is yet to be known. In this work, in-situ XAFS (X-ray Absorption Fine Structure) analysis was applied to Pd-Pt/USY and Pd-Pt/Yb/USY to elucidate the effect of Yb on the structure of Pd-Pt metal particles.

### Experimental

A USY zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13.9$ ) was used as a support. The impregnation of metals was carried out successively, that is, firstly Yb was supported on USY and after drying the catalyst, Pd and Pt was added to it. The metal content was 5 wt % for Yb and 1.2 wt% for Pd-Pt. The atomic ratio of Pd/Pt was 4. The impregnated samples were dried and then calcined under  $\text{O}_2$  at 573 K for 3 hrs. A round disk of 0.3 g was made of a calcined sample and set in an in-situ XAFS cell [2]. Pd K-edge and Pt L<sub>III</sub>-edge XAFS spectra were successively measured in-situ during reduction (under a flow of 20 %  $\text{H}_2/\text{He}$  at a flow rate of 120 ml/min) and subsequent sulfidation (under a flow of 100ppm  $\text{H}_2\text{S} + 20\% \text{H}_2/\text{He}$  at the flow rate of 120 ml/min) processes. XAFS spectra were observed by a step-scanning mode with a data accumulation time of 0.5 – 1 sec for each step. Analysis of the data was conducted with commercially available software (REX, Rigaku Co.). Parameters for curve-fitting analysis were extracted from spectra observed of standard substances at the reaction temperature.

Some of the reactant gases were flammable and toxic. They were removed with absorbers and an exhaust gas burner attached at the end of the reaction system [3].

### Results and Discussion

Figure 1 shows change of coordination numbers (CN) during the reduction process. The CN of Pd-Pd became smaller and the CN of Pt-Pd became larger by addition of Yb to Pd-Pt/USY, which indicates that more uniformly mixed alloy metal particles were formed in Pd-Pt/Yb/USY compared with those in unpromoted Pd-Pt/USY. In addition to that, the CN(Pt-Pd) for Pd-Pt/Yb/USY increased with the temperature, suggesting

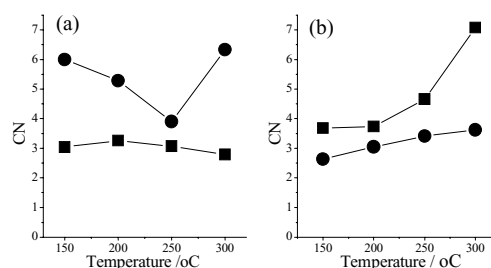


Fig.1 Change of coordination numbers during reduction. (a) CN(Pd-Pd) and (b) CN(Pt-Pd). Circles indicate Pd-Pt/USY and squares indicate Pd-Pt/Yb/USY.

that Pt atoms were dissolved in Pd particles with the temperature. The averaged CN for the metal-metal scattering was 6.9 for reduced Pd-Pt/USY and 7.1 for reduced Pd-Pt/Yb/USY. Therefore, the averaged particle size was mostly the same for the two catalysts. Addition of Yb has a influence on the arrangement of metal atoms in the particle without changing its size.

Table 1 shows the CN of metal-sulfur scattering observed after sulfidation at 553 K. The sulfur tolerance as a whole was promoted by Yb, because contribution of sulfur decreased in both edges by addition of Yb. This effect is more significant in Pt L<sub>III</sub>-edge. The CN(Pt-S) decreased from 6.3 to 2.7 due to the presence of Yb. Pt atoms in Pd-Pt/Yb/USY is buried inside Pd particles, meanwhile, Pt atoms in unpromoted Pd-Pt/USY formed small Pt particles outside of Pd particles [3]. As a result, sulfur easily came into contact with Pt atoms in Pd-Pt/USY, but not in the case of Pd-Pt/Yb/USY.

Table 1 CN of metal-sulfur after sulfidation.

Cat.	CN(Pd-S)	CN(Pt-S)
Pd-Pt/USY	1.9	6.3
Pd-Pt/Yb/USY	1.6	2.7

### References

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\* kk.bando@aist.go.jp