NW2A/2008C003

# Time-resolved DXAFS study on RedOx reactions of Pd supported on $Al_2O_3$ (II)

Yasuhiro NIWA*[1], Masao KIMURA [2], Yasuhiro INADA[1,3], Msaharu NOMURA[1]
[1]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan
[2]Adv. Tech. Res. Lab., Nippon Steel Corp., Futtsu, Chiba 293-8511, Japan
[3](Present) College of Life Sciences, Department of Applied Chemistry, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

## Introduction

Pd is used as the catalyst for many purposes, such as automobile exhaust purification and steam methane reforming. In methane reforming, the efficiency of PdO-based catalyst is strongly influenced by the chemical state of Pd [1]. Thus the evaluation of state of Pd during these reactions is very important to understand the catalysis function and to improve the efficiency. We have carried out the time-resolved DXAFS [2,3] measurements of reduction and oxidation (RedOx) processes of Pd to elucidate the reaction mechanism [4].

## Experiments

Powder specimens of 3 wt.% Pd supported on $Al_2O_3$ were prepared and set in the *in situ* cell. The specimen was reduced in $H_2$ ($P$ = 4.0 – 49.5 kPa) and then oxidized in $O_2$ ($P$ = 4.5 – 49.1 kPa) at $T$ = 623 and 673 K. Change of Pd states was measured by the *in situ* DXAFS technique at NW2A beam line (PF-AR)[3] at the vicinity of the Pd K edge. A Si(511) bent crystal (Laue type) was used as the polychromator with the bending radius of 0.9 m, and a photodiode array was used as the linear detector.

## Results and Discussion

Change of XANES spectra were clearly observed in a short time after introduction of $H_2$ or $O_2$. The spectrum before the reduction is consistent with that of PdO with the white line peak top at 24.363 keV. After the reduction by $H_2$, PdO is perfectly converted to metallic Pd. Some isosbestic points were clearly observed in the spectral change and they are independent on the reaction conditions. The reduced Pd(0) species is quantitatively oxidized to the initial PdO state by $O_2$. The observed isosbestic points are in agreement with those of reduction process. Redox reactions were thus found to occur reversibly in these conditions.

In the oxidation process, the absorbance at 24.363 keV (the white line peak top of PdO) increased exponentially on the reaction time ($t$) in a range of $t$ > 2 s (Fig.1). Reaction rates: $k_1$ were determined at each temperature and oxygen pressure as shown in Fig. 2.

When we assume the following reaction considering the formation of adsorbing chemical species $Pd(0)O_2$ scheme,

$$\mathrm{Pd(0)} + \mathrm{O_2} \underset{}{\overset{K}{\rightleftarrows}} \mathrm{Pd(0)\cdot_2} \xrightarrow{K} \mathrm{PdO} \qquad (1)$$

reaction rate: $k_1$ can be written as follows:

$$k_1 = \frac{k \cdot k \cdot P}{1 + k \cdot P} \quad , \qquad (2)$$

where $k$ is a reaction constant, $K$ is an equilibrium constant, and $P$ is the oxygen pressure.

Pressure dependence of reaction rates: $k_1$ are fitted well by curves calculated on the equation (2) (Fig.2), suggesting that the oxidation reaction follows the scheme (1). Adsorption and/or decomposition of oxygen gas are possible rate-determining processes.

It has been shown that DXAFS gives us crucial information on the mechanism of RedOx reaction of $Pd/Al_2O_3$ system.

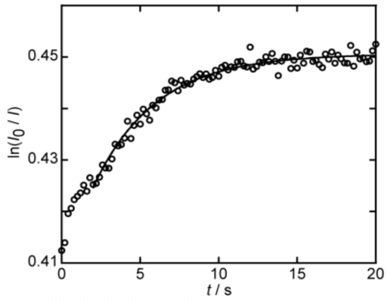

Fig.1 Change of absorbance at 24.363 keV in the oxidation reaction at $T$ = 673 K and $P$ = 32.7 kPa.

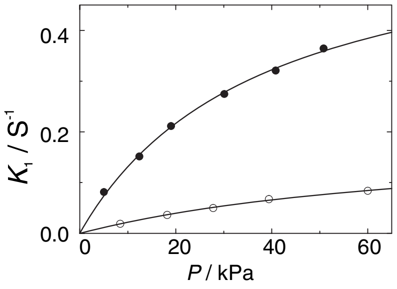

Fig.2 Pressure dependence of reaction rates: $k_1$ for $T$ = 673 K (closed) and 623 K (open). Solid lines were calculated based on (2).

## Reference

[1] S. Colussi *et al*., *Catal. Commun.*, **8**, 1263 (2007).
[2] T. Matsushita and R. P. Phizackerley: *Jpn. J. Appl. Phys.*, **20**, 2223 (1981).
[3] Y. Inada et al: *AIP Conf. Proc*., Vol.879, 1230(2006).
[4] Y. Niwa et al., *PF Act. Rep*., #25 PartB, 40 (2008)

* yasuhiro.niwa@kek.jp