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Time-resolved DXAFS study on redox mechanisms of Pd supported on Al_2O_3

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Introduction

Pd is used as the catalyst for many purposes, such as automobile exhaust purification and steam methane reforming. Especially in case of 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 the reaction is very important to understand the catalysis function and to improve the efficiency. In this study, we have carried out the time-resolved DXAFS measurements of the reduction and oxidation processes of Pd to elucidate the reaction mechanism.

Experiments

The sample used in this work, 3 wt% Pd supported on Al_2O_3, is set in the *in-situ* cell. The reduction by H_2 and the oxidation by O_2 were measured by the DXAFS instrument at NW2A beam line (PF-AR) 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. All measurements were carried out at 673 K.

Results and Discussion

An example of the XANES spectral change for the reduction and oxidation process is shown in Fig. 1 and 2, respectively. 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 are 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 as seen in Fig. 2. The observed isosbestic points are in agreement with those of reduction process. The redox reactions are thus found to occur reversibly at 673 K.

The change of absorbance at 24.363 keV (the white line peak top of PdO) was shown in Fig. 3 and 4 as a function of time for the reduction and oxidation reaction, respectively. The reduction with H_2 is completed within ca. 1 s under the H_2 pressure of 20.6 kPa at 673 K (Fig. 3). It is found that the absorbance is linearly changed vs. time, suggesting the zero-order reaction for Pd. This means that the Pd species does not contribute to the reaction before the system reaches to the transition state. The change in the H_2 species may be the rate-determining step for the reduction process of PdO on Al_2O_3. In contrast, the absorbance is exponentially changed for the oxidation process, indicating that the reaction is first-order for Pd. The oxidation of Pd(0) by O_2 is relatively slower than the reduction of PdO by H_2, but is completed within ca. 3 s under the O_2 pressure of 50.7 kPa at 673 K.

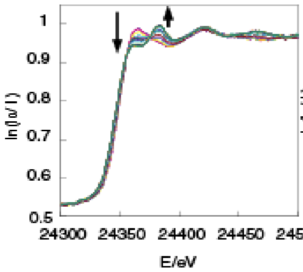

Fig. 1. Change of XANES spectra for the reduction process with H_2 (20.6 kPa) at 673 K.

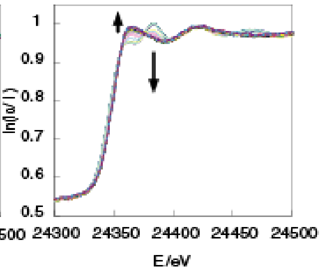

Fig. 2. Change of XANES spectra for oxidation process with O_2 (50.7 kPa) at 673 K.

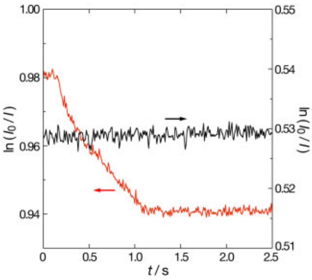

Fig. 3. Change of absorbance at 24.363 keV (red line) and 24.300 keV (black line, background region) for the reduction process.

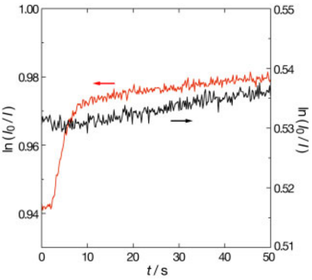

Fig. 4. Change of absorbance at 24.363 keV (red line) and 24.300 keV (black line, background region) for the oxidation process.

The redox reactions of Pd on Al_2O_3 proceed reversibly and the reaction rates are found to be dependent on the gas pressure for both reactions. The reaction mechanisms can be revealed by the kinetic analysis of the absorbance change and by the evaluation of the pressure dependence of the rate constants. The microscopic structure change during reactions will be clarified by the dynamic EXAFS analyses.

Reference

[1] S. Colussi *et al.*, *Catal. Commun.*, **8**, 1263 (2007).

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