

Structural analysis for supported-Pd catalysts effective for hydrodechlorination of chlorinated aromatics

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Introduction

The accumulation of chlorinated aromatic compounds in the environment represents an urgent problem nowadays. These compounds having strong resistance to physical, chemical or biological treatments cause hazardous influence on living organisms including human. The selective removal of chlorine atoms from their structure allows to reduce the toxicity of chloroaromatics. We have reported the selective hydrodechlorination of chloroaromatics over supported palladium [1]. The catalytic activity of the supported palladium was changed by the kinds of the supports. We consider that the structure of palladium on the supports determines the catalytic activity for the dechlorination.

In the study, we investigated the structure of palladium species on a variety of the supports by Pd K-edge XAFS.

Experimental

Supported-Pd (1 wt%) catalysts were prepared by impregnating the supports with an aqueous solution of PdCl₂ at 353 K, and drying up the impregnated sample. Then, the sample was dried at 373 K and calcined at 573 K in air, except for carbon-supported palladium. The samples were reduced by hydrogen at 573 K, prior to the measurement of XAFS.

X-ray absorption experiments were carried out on the beam line BL-10B at Photon Factory in Institute of Materials Structure Science for High Energy Accelerator Research Organization, Tsukuba, Japan, with a ring energy of 2.5 GeV and a stored current of 250 – 450 mA. The X-ray absorption spectra of the catalysts were recorded in a transmission mode with a Si(311) monochromater.

Results and discussion

Figure 1 shows the Fourier transforms of Pd K-edge EXAFS of Pd catalysts supported on various supports. The XANES spectra showed that Pd species was present as Pd metal in all the supported Pd catalysts. The Fourier transforms for all the catalysts had a peak due to Pd-Pd at 2.4 Å and the intensity of the peaks depended on the kind of the supports. Therefore, the crystallinity and/or particle size of Pd metal were different according to the kinds of the catalytic supports. Thus, we carried out the curve fitting of the EXAFS of the supported Pd catalysts to evaluate the coordination number of Pd-Pd. All the EXAFS shown in Fig. 1 could be fitted with a shell of Pd-Pd and the interatomic distances (2.74 ~ 2.76 Å) of Pd-Pd evaluated by the curve-fitting for all the catalysts were

almost the same as that of Pd metal. The coordination numbers of Pd-Pd were larger in order, Pd/Active carbon < Pd/SiO₂ < Pd/MgO < Pd/Al₂O₃ < Pd/CaO < Pd/TiO₂ < Pd/Carbon fiber.

We have already reported the effects of the kinds of the catalytic supports for Pd on the hydrodechlorination of 2,4-dichlorophenoxyacetic acid over the supported Pd catalysts [1]. The activities of the catalysts were higher in order, Pd/CaO < Pd/Active carbon < Pd/SiO₂ < Pd/Carbon fiber < Pd/MgO < Pd/Al₂O₃ << Pd/TiO₂. The tendency of the catalytic activity was not consistent with that of the coordination number of Pd-Pd. Therefore, we cannot speculate the difference of the catalytic activity according to the kind of the supports on the basis of the crystallinity and/or particle size of Pd metal. It is likely that the interface between Pd metal and the support is the active species for the hydrodechlorination of 2,4-dichlorophenoxyacetic acid.

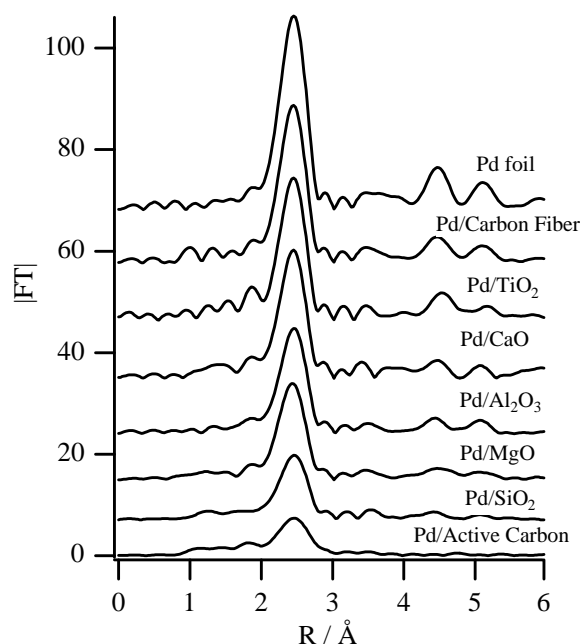


Fig.1 Fourier transforms of Pd K-edge EXAFS of supported Pd catalysts.

References

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