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Study on Fine Structure of Clay-supported Pd Complex Catalysts for Alcohol Oxidation

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Introduction

The selective oxidation of alcohols is widely recognized as one of the most fundamental organic transformations in both laboratory and industrial synthetic chemistry, because the resulting carbonyl compounds are of paramount importance as synthetic intermediates for fine chemicals and pharmaceuticals. Due to ever-growing environmental concerns, there is a strong need for the establishment of promising catalytic protocols using molecular oxygen as a sole oxidant, which is readily available and produces only water as a by-product [1]. For that reason, many transition metal-catalyzed aerobic processes, both homogeneous and heterogeneous, have been developed [2].

Clay materials occur richly in nature and their ion-exchange properties have been developed for catalytic applications through decades. Because of their great potentiality for the design of high-performance heterogeneous catalysts, various strategies have been widely reported in recent years.

In this study, we will report a noble clay-supported Pd(II) complex acts as an effective catalyst toward aerobic alcohol oxidation. The local structure of Pd species in the interlayer of clay was characterized by Pd K-edge EXAFS.

Experimental

Layered Ni-Zn mixed basic salt, $Ni_{0.78}Zn_{0.44}(OAc)_{0.44}(OH)_2{\cdot}0.86H_2O$ (NiZn), was synthesized according to the published procedure [3]. The intercalation of $[Pd(OH)_4]^{2-}$ species into NiZn was performed in water to obtain Pd/NiZn catalyst (Pd loading: 0.2 wt%). The catalytic reaction was carried out in Schlenk tube equipped with a condenser under air flow.

Pd K-edge XAFS spectra were collected at NW10A in PF-AR (IMSS, KEK) with Si(311) double crystal monochromator in a fluorescence mode with Lytle detector (Proposal No. 2007G662).

Results and discussion

The features of the Pd K-edge XANES spectrum and the edge position of Pd/NiZn catalyst did not resemble those of Pd foil but were similar to those of Pd oxide. This means that all Pd species in the Pd/NiZn are divalent. Fig. 1 shows the FT of k^3-weighted EXAFS for Pd/NiZn catalysts. In the second coordination sphere of the Pd/NiZn, no peaks due to Pd-Pd and Pd-O-Pd bonds, observed in those of Pd foil and Pd oxide at around 0.25 and 0.3 nm, were detected. The inverse FT of the peaks at around 0.1-0.2 nm for Pd/NiZn catalysts was well fitted with five oxygen atoms at a Pd-O distance of 0.201 nm (Table 1). Furthermore, the Pd species on the recovered Pd/NiZn maintained a divalent oxidation state and was not aggregated into Pd black even after the catalytic reaction.

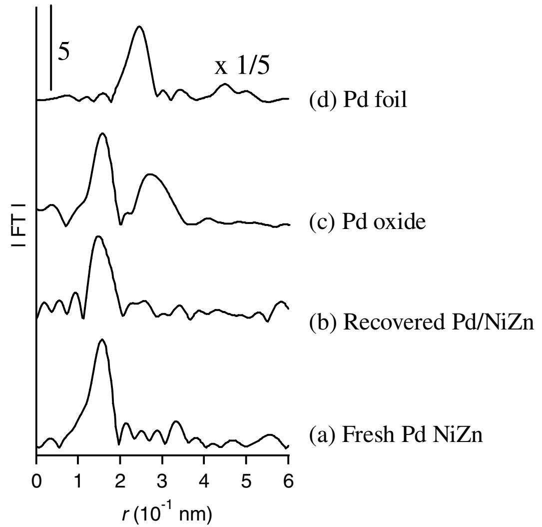

Fig 1. FT of Pd K-edge EXAFS spectra for various Pd catalysts

Table 1: The results of curve-fitting analysis[a]

sample	shell	CN [b]	r [c] (nm)	σ [d] (nm)
Fresh Pd/NiZn	Pd-O	5.2	0.201	0.00476
Recovered Pd/NiZn	Pd-O	5.1	0.201	0.00325
Pd foil[e]	Pd-Pd	12	0.274	
Pd oxide[e]	Pd-O	4	0.202	
	Pd-(O)-Pd	4	0.303	
	Pd-(O)-Pd	8	0.342	

[a] Inverse Fourier transforms were performed for the regions of 0.116-0.196 nm of the Pd/NiZn. [b] Coordination number. [c] Bond distance. [d] Debye-Waller factor. [e] Data from X-ray crystallography.

References

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