Studies on the Formation and Structure of Highly Dispersed PdO Interacted with Brønsted Acid Sites of Zeolite by EXAFS

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The degree of the dispersion of PdO was highly dependent on the Al content of HZSM-5. This is due to the strong interaction between Brønsted acid sites and PdO as demonstrated by the reversible transformation from aggregated metal Pd to highly dispersed PdO upon the successive reduction and oxidation treatments. The role of Brønsted acid sites was considered to keep the dispersed state of PdO.

Recently, much attention has been directed to the metal loaded zeolite catalyst using hydrocarbons as reductant. Methane is most preferable reductant because it is the main component of natural gas. As for catalyst component, palladium is one of the most active and durable elements for $NO\text{-}CH_4\text{-}O_2$ reaction.[1] Among supports for palladium, zeolite is especially favorable to retain the active structure for Pd due to the existence of micropore and Brønsted acid sites.[2] It is widely believed that the acid sites of zeolite keep the Pd^{2+} cation, and this was assigned to the active center for the $NO\text{-}CH_4\text{-}O_2$ reaction.[3-5] However, the formation and structure of the active Pd species or its precursor and the role of the Brønsted acid sites associated with Pd are rather ambiguous. In this study, H-form of ZSM-5 zeolites with different Al content were employed as supports for palladium and the structure of Pd was followed by Pd K-edge EXAFS measurement. EXAFS is a powerful tool to analyze the structure of metal oxides dispersed inside zeolite pore system, which is otherwise difficult to study.[6]

ZSM-5 with different Al content were synthesized (Si/Al_2=55) or supplied from Tosoh Co.(Si/Al_2=24), Nikki Co.(Si/Al_2=38), and Mobil Catal. Co. Japan (Si/Al_2=75). HZSM-5 was prepared by an ion exchange of ZSM-5 with NH_4NO_3 solution, followed by calcination under N_2 at 773 K for 4 h. Pd/HZSM-5 was prepared by an ion exchange method using $Pd(NH_3)_4Cl_2$ solution. The catalysts were calcined in a N_2 flow at 773 K as the pretreatment. The chemical composition of the Pd loaded catalyst was measured by ICP method. The loading of Pd was calculated to be 0.20-0.23 wt%.

Pd K-edge EXAFS was measured at BL01B1 station of Japan Synchrotron Radiation Research Institute (SPring-8). The storage ring was operated at 8 GeV with a ring current of 44-65 mA. Si(311) single crystal was used to obtain monochromatic X-ray beam. For the measurement of Pd K-edge spectra, two ion chambers filled with Ar and Kr were used as detectors of I_0 and I, respectively. The sample was transferred to glass cells with two Kapton windows connected to a flow reaction system without contacting air. In spite of the low concentration of Pd, fairly good spectra were obtained. For extended X-ray absorption fine structure (EXAFS) analysis, the oscillation was first extracted from the EXAFS data by a spline smoothing method.[7] The oscillation was normalized by the edge height around 50 eV above the threshold. The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to r space was performed over the range 30-155 nm^{-1} to obtain a radial distribution function. The inversely Fourier filtered data were analyzed by a usual curve fitting method. For the curve fitting analysis, the empirical phase shift and amplitude functions for Pd-O and Pd-Pd were extracted from the data for PdO and Pd foil, respectively. CdS was used as a reference for the Pd-Si/Al according to the literature.[8] Errors in the analysis were estimated by R factor (R_f).

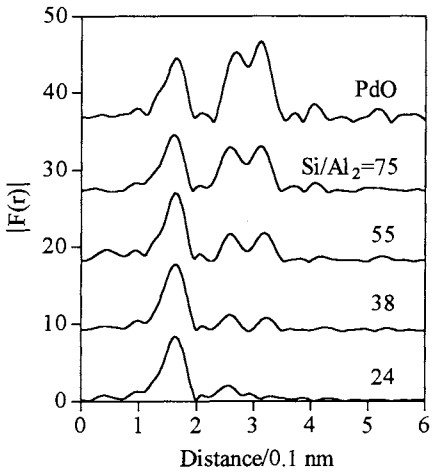

Figure 1. Pd K-edge EXAFS Fourier transforms for PdO and Pd/HZSM-5 oxidized at 773 K.

Table 1. Curve fitting results of Pd K-edge EXAFS for Pd/HZSM-5 oxidized at 773 K

Si/Al_2	Scatter atom	CN[a]	r/nm[b]	ΔE_0/eV[c]	σ/nm[d]	R_f/%[e]
24[f]	O	4.3±0.9	0.202±0.001	6	0.0069	3.6
	Al	1.4±0.7	0.305±0.004	-3	0.0063	
38[g]	O	4.5±0.9	0.202±0.002	8	0.0069	4.7
	Pd	0.7±0.5	0.302±0.003	-6	0.0064	
	Pd	0.9±0.6	0.342±0.002	6	0.0062	
55[g]	O	4.4±0.9	0.202±0.001	8	0.0065	4.2
	Pd	1.5±0.6	0.304±0.002	1	0.0049	
	Pd	1.8±0.8	0.342±0.002	4	0.0044	
75[g]	O	3.5±0.6	0.201±0.001	0	0.0061	3.6
	Pd	2.9±0.5	0.303±0.001	-8	0.0057	
	Pd	3.9±1.2	0.344±0.001	0	0.0055	
PdO[h]	O	(4)	(0.202)			
	Pd	(4)	(0.304)			
	Pd	(8)	(0.342)			

[a]coordination number, [b]bond distance, [c]difference in the origin of photoelectron energy between the reference and the sample(±4 eV), [d]Debye-Waller factor (±0.0020 nm), [e]residual factor, [f]Fourier filtering range: 0.11-0.31 nm, [g]Fourier filtering range: 0.11-0.35 nm, [h]data from X-ray crystallography.[9]

Figure 1 shows the Fourier transforms of the $k^3\chi(k)$ EXAFS for Pd/HZSM-5 with different Al content. All samples were oxidized under the oxygen flow at 773 K for 3 h before the measurement. In the spectrum of Pd/HSM-5 (Si/Al_2=75), two intense Pd-Pd peaks appeared at 0.26 and 0.31 nm. Accompanied by the increase in the Al content of HZSM-5, the intensity of these Pd-Pd peaks gradually lowered, and finally disappeared on the Pd/HZSM-5 with highest Al content (Si/Al_2=24), where high activity toward the NO-CH_4-O_2 reaction was observed. The curve fitting analysis of the small peak observed at 0.25 nm in Figure 1(a) was not successful assuming that the peak was due to the Pd backscatter. However, a fairly good result was obtained by using parameters extracted from CdS. Therefore, this peak may be assigned to the contribution from Al or Si in zeolite framework. The decrease in Pd-Pd is also depicted in the Pd-Pd coordination number change calculated by curve fitting analysis in Table 1. The present results indicated that the size of PdO is the function of the amount of Brønsted acid in HZSM-5 and it decreases with increase in the acid amount of HZSM-5, since the intensity of Pd-Pd shell seems to reflect the size of PdO.

On the other hand, as for Pd-O bond observed at 0.16 nm (phase shift uncorrected) in Figure 1, the spectra for bulk PdO and highly dispersed PdO on HZSM-5 are quite similar. In addition, the coordination number and bond distance of Pd-O determined by the curve fitting analysis on highly dispersed PdO agreed well with those on bulk PdO as shown in Table 1, implying the local structure of highly dispersed PdO is closely similar to that of bulk PdO. Therefore, it can be noted that the role of Brønsted acid sites of HZSM-5 is not to provide the ion-exchange sites for Pd^{2+}, but to stabilize the dispersed state of PdO. Based on the analysis, the local structure of Pd in the oxidized Pd/HZSM-5 (24) was proposed as shown in Figure 2, where Pd was surrounded by four oxygen atoms, a part of which came from zeolite structure. Judging from the XANES regions, the valence of the highly dispersed PdO was same as that for bulk PdO because of the coincidence of the edge energy.

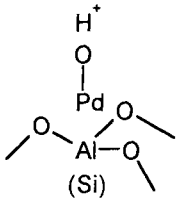

Figure 2. Schematic picture of the local structure of Pd in Pd/HZSM-5 (24) oxidized at 773 K.

To confirm the ability for Brønsted acid sites of zeolite to anchor PdO, the regeneration of dispersed PdO upon the repetition of reduction and oxidation treatments was followed by EXAFS. The experiment was conducted on the Pd/HZSM-5 (24) where highly dispersed PdO was observed by the oxidation treatment as explained above. Figure 3(b) shows the EXAFS FT spectrum measured after the reduction of previously oxidized Pd/HZSM-5 (24). The formation of metal Pd was confirmed from the appearance of intense peak at 0.24 nm (phase shift uncorrected). The particle size of the metal Pd calculated from the Pd-Pd coordination number (CN=10.6) was estimated to be >3 nm,[10] which was far larger than zeolite pore diameter. Thus on account of the treatment under H_2, the highly dispersed PdO was reduced and migrated to form aggregated Pd metal particle on zeolite outer surface. The reduced sample was successively oxidized under oxygen flow at 773 K for 3 h again. The spectrum measured after oxidation was identical with that measured after initial oxidation treatment as shown in Figure 3(c). Therefore, the aggregated Pd disrupted and returned to the HZSM-5 pore as the highly dispersed PdO. This behavior of Pd demonstrates the high mobility of PdO and the presence of strong interaction between Brønsted acid sites of HZSM-5 and PdO.

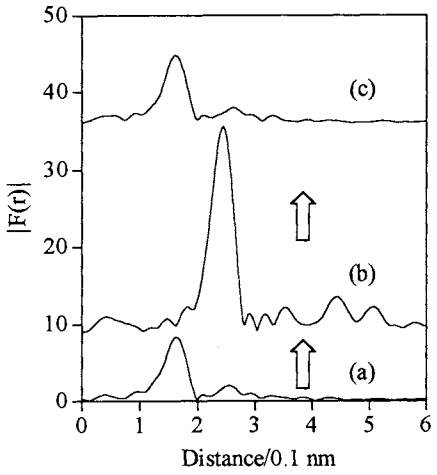

Figure 3. Pd K-edge EXAFS Fourier transforms for Pd/HZSM-5; (a) oxidized, (b) reduced by H_2, and (c) successively oxidized; treatments were conducted at 773 K.

It is meaningful to consider the driving force for the formation of highly dispersed PdO on Brønsted acid sites of zeolite. In our opinion, it comes from the basic character of PdO. That is, the acid-base interaction between highly dispersed PdO and Brønsted acid sites of zeolite promoted the disruption and fixation of highly dispersed PdO. In practice, PdO was categorized to the basic oxide as described in the text on Inorganic Chemistry.[11]

References

1 Y. Nishizaka and M. Misono, *Chem. Lett.*, **1993**, 1295.
2 Y. Nishizaka and M. Misono, *Chem. Lett.*, **1994**, 2237.
3 B. J. Adelman and W. M. H. Sachtler, *Appl. Catal. B: Environmental*, **14**, 1 (1997).
4 C. Descorme, P. Gélin, C. Lécuyer, and M. Primet, *J. Catal.*, **177**, 352 (1998).
5 M. Ogura, M. Hayashi, and E. Kikuchi, *Catal. Today*, **45**, 139 (1998).
6 A. Ali, W. Alvarez. C. J. Loughran, and D. E. Resasco, *Appl. Catal. A: Generarl*, **14**, 13 (1997).
7 B. K. Teo, "EXAFS: Basic Principles and Data Analysis," "Inorganic Chemistry Concepts 9," Springer-Verlag, Berlin (1986).
8 K. Moller, D. C. Koningsberger, and T. Bein, *J. Phys. Chem.*, **93**, 6116 (1989).
9 G. Lunde, *Metallwirtschaft*, 7, 417 (1928).
10 D. Guillemot, M. Polisset-Thfoin, and J. Fraissard, *J. Phys. Chem. B*, **101**, 8243 (1997).
11 R. T. Sanderson, "Inorganic Chemistry," Reinhold Publishing Corporation, New York (1967).