Characterization of the active site structure of Pd and Pd-promoted Mo sulfide catalysts by means of XAFS

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Recently, noble metal catalysts are noted as promising candidates for new super-deep-hydrodesulfurization (HDS) catalysts. In this study, we investigated the structure of Pd particles supported on zeolite and Al_2O_3 under a sulfidation or reduction condition. From EXAFS analysis, it was found for sulfided Pd catalysts that small Pd sulfide clusters are formed without sintering. It was also revealed that no extensive growth of metal Pd particles occurs in Pd/NaY sulfide catalysts even after a treatment with H_2 at 673 K. The dispersion of Pd metal particles is improved by H_2/H_2S treatment. These results indicate that in the presence of H_2S, Pd shows high resistance against particle growth.

A comparison of the Mo and Pd K-edge EXAFS spectra for MoS_x/Pd-NaY and Pd-NaY catalysts revealed the existence of Mo-Pd bondings by the addition of Mo sulfide, indicating a direct interaction between Mo and Pd sulfides.

Keywords: hydrodesulfurization, noble metal, zeolite

1. Introduction

Recently, legislation of sulfur content in gasoline has become severer to reduce particulate materials and SO_x in exhaust. The sulfur content in gasoline is proposed by EU to be reduced to 50 ppm by 2005. Al_2O_3-supported Co-Mo sulfide catalysts have been extensively used for hydrodesufurization (HDS) of petroleum feedstocks (Topsøe *et al.*, 1996; Kabe *et al.*, 1999). In spite of extensive studies, the activities of conventional Co-Mo catalysts are not sufficiently improved to meet the future legislation. Recently, it is recognized that noble metal catalysts show high performance for HDS reaction (Kabe *et al.*, 1999). Because of high hydrogenation activity, noble metal catalysts are expected to be a new catalyst system for super-deep-HDS.

In this study, we investigated the structure of Pd particles supported on zeolite and Al_2O_3 under sulfidation or reduction conditions by means of XAFS techniques. We also investigated the catalytic properties and structures of Pd-promoted Mo sulfide catalysts.

2. Experimental

2. 1. *Catalyst preparation*

Pd/NaY catalysts were prepared by an ion-exchange method using aqueous solutions of $[Pd(NH_3)_4]Cl_2$. Pd/Al_2O_3 catalysts were prepared by an impregnation method using aqueous solutions of $Pd(CH_3COO)_2$. The Pd loadings were 1 and 5wt%. The sample was dried and calcined in an O_2 flow for 5 h at 673 K. The sample thus obtained was sulfided in an H_2/H_2S (9/1, 100 $cm^3 \cdot min^{-1}$) flow at 673 K. The sulfided Pd catalyst was treated in an H_2 flow at 673 K. NaY zeolite-supported Mo sulfide catalysts (MoS_x/NaY) were prepared by a CVD method using $Mo(CO)_6$ as the precursor. MoS_x/Pd/NaY (1wt% Pd) was prepared by introducing $Mo(CO)_6$ into Pd/NaY, followed by sulfidation. Detailed preparation methods of MoS_x/NaY were described in our previous study (Okamoto *et al.*, 1999).

2. 2. *Catalytic reaction*

The HDS reaction of thiophene was performed using a closed circulation system at 623 K. In the case of the HDS reaction, a vapor pressure of thiophene at 273 K was used and the thiophene/H_2 ratio (1/10, total pressure; 30 kPa) was kept almost constant during the reaction. The reactants and products were analyzed by gas chromatography.

2. 3. *XAFS measurements*

Pd K-edge and Mo K-edge EXAFS spectra for Pd/NaY, Pd/Al_2O_3 and MoS_x/Pd/NaY were measured in situ at BL01B1 in SPring-8 in a transmission mode. The synchrotron radiation was monochromatized by a Si(311) monochromator. The sulfided sample was evacuated at 673 K for 1 h and transferred to an EXAFS cell with two Kapton windows without contacting with air. The empirical parameters for Pd-S and Pd-Pd bondings were obtained by using PdS and Pd metal as the reference compounds. The parameters of Mo-S and Mo-Mo were obtained from crystalline MoS_2. The Mo-Pd parameters were estimated by using the parameters for Pd-Pd bondings. The coordination numbers and bond lengths were determined within the accuracies of ±10% and ±0.002 nm, respectively.

3. Results and Discussion

3. 1. *Structure of sulfided Pd particles*

Figure 1 shows Fourier transforms(FT) of Pd K-edge EXAFS oscillation functions for Pd/NaY and Pd/Al_2O_3 catalysts after sulfidation or reduction. Table 1 shows the curve-fitting results of EXAFS for the sulfided and reduced catalysts. For the reduced samples, a peak at 0.274 nm is observed, indicating the formation of Pd metal particles. It is evident from curve-fittings that the Pd-Pd coordination number for Pd/NaY (9.9) is somewhat smaller than that for Pd/ Al_2O_3 (12.0), indicating a higher dispersion of Pd metal particles in Pd/NaY. For the sulfided samples two peaks are observed at 0.232 and 0.274 nm. The peak at 0.232 nm corresponds to Pd-S bondings, and the peak at 0.274 nm is regarded as Pd-Pd metal bondings, indicating that Pd sulfide clusters are formed. It is considered that the Pd sulfide cluster has Pd metal "core" in its center, since Pd-Pd metal bondings are present. It is apparent from Table 1 that the particle size of PdS increase in the order, 1wt% Pd/NaY < 5wt% Pd/NaY ≤ 5wt% Pd/ Al_2O_3.

Figure 2 shows the FT of Pd K-edge EXAFS oscillation functions for 5wt% Pd/NaY after an H_2 treatment following the usual sulfidation. The intensity of the FT peak due to Pd-Pd bonding at 0.274 nm increases by the H_2 treatment and that due to

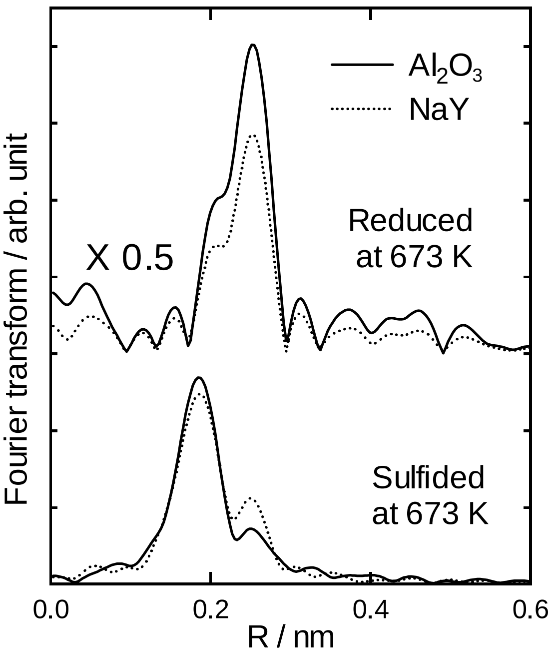

Figure 1
Fourier transforms of k^3-weighted Pd K-edge EXAFS functions for sulfided and reduced 5wt% Pd/NaY(dotted line), and Pd/Al$_2$O$_3$(solid line).

Table 1
Curve-fitting results of EXAFS for sulfided and reduced Pd catalysts.

			N	R / nm	E_0 / eV	$\Delta\sigma^2$*	R_f / %
1wt% Pd/NaY	Sulf	Pd-S	3.8	0.234	2.1	3.5	0.1
		Pd-Pd	2.5	0.270	-1.6	10.1	
5wt% Pd/NaY	Sulf	Pd-S	3.1	0.232	-2.8	5.8	0.4
		Pd-Pd	3.0	0.274	0.3	7.2	
	Red	Pd-Pd	9.9	0.274	9.1	3.6	0.8
5wt% Pd/Al$_2$O$_3$	Sulf	Pd-S	3.3	0.234	-1.0	5.0	0.3
		Pd-Pd	3.3	0.275	0.5	11.5	
	Red	Pd-Pd	12.0	0.275	9.5	2.5	0.6

$\Delta\sigma^2$: Debye-Waller factor / 10^{-5} nm^2

Pd-S bonding decreases. The structural parameters are summarized in Table 2. These results indicate the growth of Pd metal core by removal of bulk sulfur atoms. However, the intensity of Pd-Pd peak is almost restored by the re-sulfidation for 30 min. It is considered from these results on Pd/NaY that highly dispersed PdS particles turn into Pd metal particles covered with sulfur atoms and that in the presence of H_2S, Pd shows resistance against particle growth. With Pd/ Al$_2$O$_3$, analogous observations were made. The structure changes for Pd catalysts are schematically proposed in Figure 3. The H_2-reduced 5wt% Pd/NaY and Pd/ Al$_2$O$_3$ were subjected to the H_2/H_2S treatment at 673 K. The EXAFS results are summarized in Table 3, suggesting that the dispersion of Pd metal particles are improved by the sulfidation.

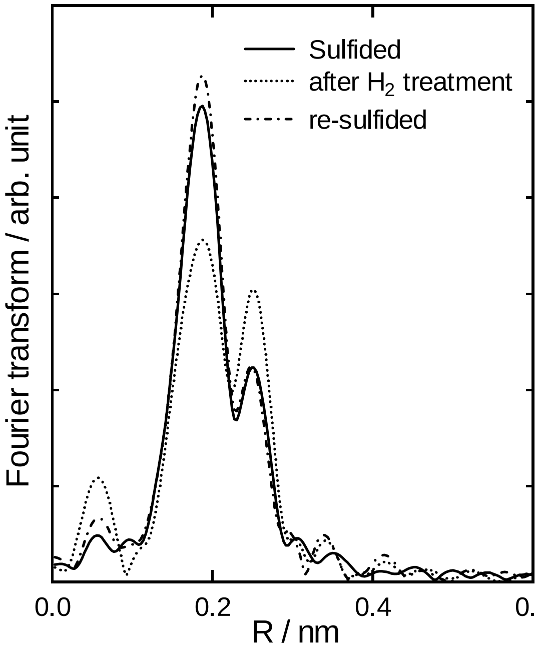

Figure 2
Fourier transforms of k^3-weighted Pd K-edge EXAFS functions for sulfided 5wt% Pd/NaY; sulfided(solid line), H_2 treated after the sulfidation(dotted line), re-sulfided after the H_2-treatment(broken line).

Table 2
Curve-fitting results of EXAFS for sulfided and H_2 treated 5wt% Pd/NaY.

		N	R / nm	E_0 / eV	$\Delta\sigma^2$	R_f / %
Sulf.	Pd-S	3.1	0.232	-2.8	5.8	0.4
	Pd-Pd	3.0	0.274	0.3	7.2	
H_2 treat.	Pd-S	2.4	0.230	-4.8	6.8	0.7
	Pd-Pd	3.8	0.275	0.8	6.4	
re-Sulf.	Pd-S	3.5	0.233	-1.1	6.2	0.4
	Pd-Pd	3.3	0.272	-1.4	8.1	

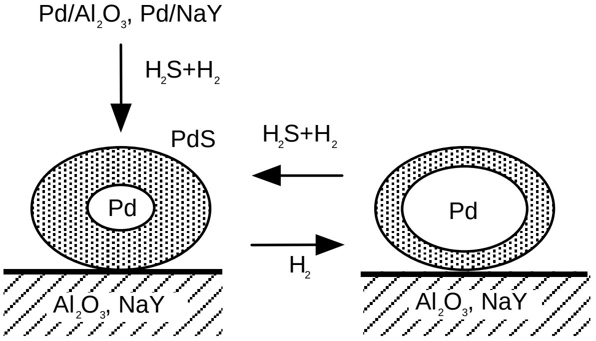

Figure 3
Scheme of the structure change of Pd sulfide clusters.

Table 3
Curve-fitting results of Pd K-edge EXAFS for Pd/NaY and Pd/Al_2O_3 after sulfidation following H_2-reduction.

		N	R / nm	E0 / eV	$\Delta\sigma2$	Rf / %
Pd/NaY	Pd-S	3.1	0.232	-3.2	6.4	0.3
	Pd-Pd	4.2	0.276	-0.4	8.7	
Pd/Al_2O_3	Pd-S	3.1	0.233	-1.3	3.4	0.3
	Pd-Pd	4.0	0.274	0.0	13.3	

3. 2. *Catalytic properties and structures of Pd-promoted Mo sulfide catalysts*

It was revealed previously that the addition of Pd to NaY supported Co, Mo, and Co-Mo sulfide catalysts promote their HDS activities (Okamoto *et al.*, 2000). This was explained by the hydrogen activation by sulfided Pd. Figure 4 shows the Fourier transforms of Mo and Pd K-edge EXAFS for MoS_x/Pd/NaY and Pd/NaY catalysts. The structural parameters are shown in Table 4. A small FT peak (0.25 nm, phase shift; uncorrected) of the Mo K-edge was found to be curve fitted only by assuming Mo-Pd bondings. On the basis of the parameters for sulfided Pd/NaY and MoS_x/Pd/NaY, it is considered that the Mo-Pd bondings are formed by the co-presence of Pd and Mo sulfide clusters. The formation of Mo-Pd bondings clearly indicate the direct interactions between Mo and Pd sulfides. This is supported by a complete loss of the extremely high hydrogenation activity of PdS by the presence of Mo sulfide clusters, as shown in Figure 5.

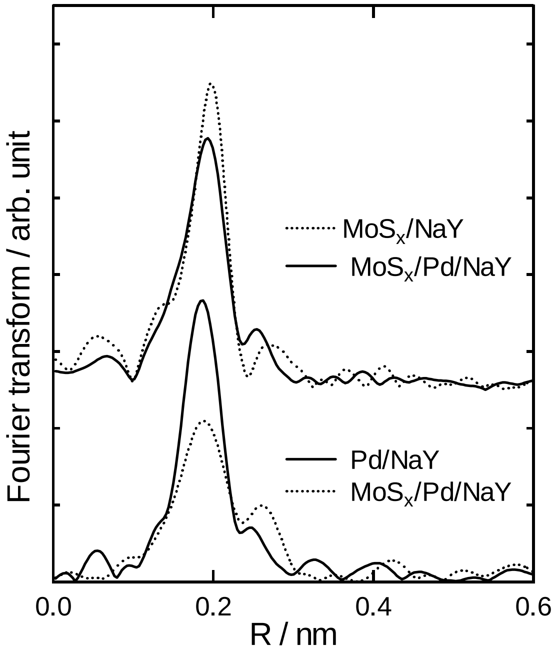

Figure 4
Fourier transforms of k^3-weighted Mo K-edge and Pd K-edge EXAFS functions for Pd-promoted and unpromoted MoS_x/NaY and Pd/NaY catalysts(Pd 1wt%).

Table 4
Curve-fitting results of Pd and Mo K-edge EXAFS for Pd/NaY and MoS_x/Pd/NaY.

		N	R / nm	E0 / eV	$\Delta\sigma2$	Rf / %
MoS_x/NaY	Mo-S	4.7	0.240	-2.3	4.8	/
	Mo-Mo	1.1	0.315	-2.0	8.9	
MoS_x/Pd/NaY	Mo-S	5.8	0.239	-0.9	10.3	0.7
	Mo-Pd	2.1	0.273	4.2	6.0	
	Pd-S	3.4	0.233	-2.3	5.2	1.3
	Pd-Pd	2.9	0.278	-0.1	5.6	

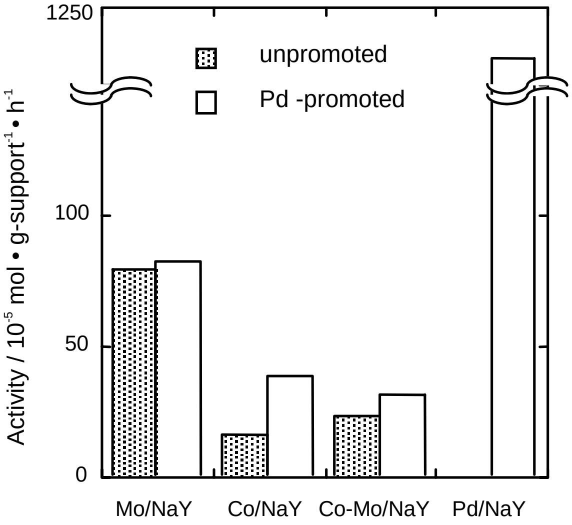

Figure 5
HYD activities of Pd-promoted and unpromoted Co, Mo and Co-Mo/NaY catalysts prepared by a CVD method

The absence of the Mo-Mo contribution for MoS_x/NaY (Table 4) may suggest a formation of highly dispersed Mo sulfide species.

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