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Effect of noble metal particle size on the sulfur tolerance of monometallic Pd and Pt catalysts supported on high-silica USY zeolite

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Abstract

The size effect of monometallic Pd and Pt clusters was investigated for the sulfur tolerance of these noble metal catalysts supported on high-silica USY zeolite, using the CO adsorption method and the extended X-ray adsorption fine structure (EXAFS) method. Both Pd and Pt particles show the highest surface sulfur tolerance in the form of <20 Å-diameter particles, although the bulk phase of these clusters is subject to penetration by adsorbed sulfur atoms. For noble metal particles >25 Å in diameter, the bulk phases of the Pd and the Pt particles approach that of the metallic structure. With increased cluster size, the surface sulfur tolerance of Pt particles decreases gradually, while that of Pd particles decreases rapidly. For large noble metal particles >50 Å in diameter, EXAFS spectra show that sulfidation in the bulk phase of the noble metal particles is suppressed for Pt but promoted for Pd.

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1. Introduction

Aromatic compounds in diesel fuel have been identified as precursors of particulates in diesel engine exhaust, which are major sources of environmental damage [1–3]. Thus, the development of catalytic technology for deep aromatic saturation is urgently required. Noble metal catalysts have high aromatic hydrogenation activity under the mild conditions of low temperature and low pressure. However, these catalysts are prone to poisoning by sulfur compounds that are often present in oil feedstock. Recently, much attention has been focused on the high sulfur tolerance of noble metal catalysts when used for hydrogenation of aromatics. Many factors that affect the hydrogenation activity and the sulfur tolerance of noble metal catalysts have been studied and reported. The solid acidity of the supports is known to be one of the enhancing factors [2,4–11]. However, our previous measurements [12] have confirmed that highly dispersed Pd, Pt, and Pd–P particles supported on a high-silica USY zeolite and silica having small mesopores (pore diameter = 30 Å) showed relatively high sulfur tolerance, and had high aromatic hydrogenation activities, in spite of these supports having little acidity. This suggests that multi-contact between the noble metal particles and non-acidic supports affects the sulfur tolerance of noble metals. The size of noble metal particles also affects the sulfur tolerance and hydrogenation activity of the catalyst. The effects of the particle size of noble metals on catalytic activity have been extensively reported [13–19]. However, the effect of particle size of noble metals on sulfidation behavior and sulfur tolerance has not yet been studied.

In this study, we investigated the effect of particle size of noble metal particles on the sulfur tolerance of monometallic Pd and Pt catalysts supported on high-silica

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USY zeolite. Here, the sulfur tolerance of noble metal particles was investigated from two angles: one is the surface sulfur tolerance of the noble metal particles, which might be directly linked to aromatic hydrogenation activity, and the other is the sulfur tolerance of the bulk of the noble metal particles. Both these aspects of sulfur tolerance of Pd and Pt catalysts were investigated, using the CO adsorption method for surface sulfur tolerance, and quantitative sulfur analysis and EXAFS for bulk-phase sulfur tolerance.

2. Experimental

2.1. Preparation of catalyst

USY zeolite ($SiO_2/Al_2O_3 = 390$, hereafter called USY (390)) was obtained from Tosoh Co. and used as received (total surface area = 631 $m^2 g^{-1}$, mesopore surface area = 71 $m^2 g^{-1}$). This high-silica USY zeolite was used to eliminate the effect of acidity on the sulfur tolerance of noble metals. Monometallic Pd and Pt catalysts supported on USY (390) were prepared by incipient wetness impregnation with an aqueous solution containing appropriate amounts of $[Pd(NH_3)_4]Cl_2$ and $[Pt(NH_3)_4]Cl_2$. The total amount of metal loading was 1.2, 2.0 or 3.0 wt.% for each catalyst, respectively. The impregnated samples were dried under vacuum at 333 K for 6 h, pressed into a wafer, crushed into 310–700 μm chips, and then calcined in an oxygen stream for 3 h. The particle size (d_p) of the noble metal particles was controlled by changing the calcination temperature (403–573 K), the heating rate (5–20 K min^{-1}) and the O_2 flow rate (0.1–2 $dm^3 min^{-1}$).

2.2. Elemental analysis of sulfur for sulfided catalysts

Quantitative sulfur analysis of the sulfided Pd and Pt clusters supported on the USY (390) zeolite was performed using a LECO S-144R sulfur analyzer. The precalcined samples of Pd and Pt catalysts were first reduced in an H_2 stream (200 $cm^3 min^{-1}$) at 573 K for 3 h in a Pyrex tube, then sulfided in a stream of 500 vol. ppm H_2S–H_2 gas (200 $cm^3 min^{-1}$) at 553 K for 3 h. The USY (390) zeolite itself was also analyzed in the same way as the Pd/USY (390) and Pt/USY (390) catalysts, as a blank.

2.3. Dispersion of noble metals using the CO adsorption method

Metal dispersions of the Pd/USY (390) and Pt/USY (390) catalysts were determined from the measured amount of chemisorbed CO. The calcined sample (ca. 100 mg) was reduced in an H_2 stream (30 $cm^3 min^{-1}$) at 573 K for 1 h and then purged in He at the same temperature for 10 min. Pulses (0.5 cm^3) of 10.1% CO (in He) were injected into the He carrier gas stream (30 $cm^3 min^{-1}$) and contacted the catalyst at 323 K. The CO concentration in the gas stream was analyzed using a thermal conductivity detector. The stoichiometry of CO to either Pd or Pt was assumed to be unity. The average metal particle size was estimated using the equation $d = 5/\rho S$ (d is the metal particle size, ρ the density of the metal and S the surface area of the metal). The cross-sectional areas of Pd and Pt were assumed to be 0.0787 and 0.0800 nm^2, respectively [20]. To measure the surface thioresistance of the Pd and Pt/USY (390) catalysts, the dispersions of sulfided catalysts, i.e., amount of adsorbed CO (mol g^{-1}) after sulfidation divided by total amount of noble metal (mol g^{-1}), were also analyzed by CO chemisorption measurements. The sample was sulfided in a 500 vol. ppm H_2S–H_2 stream at 553 K for 1 h after reduction.

2.4. EXAFS analysis

The EXAFS of Pt L_{III}-edge (11.6 keV) and Pd K-edge (24.3 keV) were measured for samples of each catalyst using a double-crystal monochromator at the Photon Factory (BL-7C, 10B) of the Institute of Material Structure Science (KEK-PF, Tsukuba, Japan), and the SPring-8 (BL01B1) of the Japan Synchrotron Radiation Research Institute (Sayo-gun, Hyogo, Japan). All measurements were done at room temperature.

Reduced and sulfided samples (250 mg for the Pt L_{III}-edge measurement and 450 mg for the Pd K-edge measurement) were prepared for EXAFS measurement. For reduced samples, the precalcined monometallic Pd and Pt catalysts were reduced in a hydrogen stream (200 $cm^3 min^{-1}$) at 573 K for 3 h in a Pyrex tube that had vacuum taps and an EXAFS cell, and cooled to room temperature. For sulfided samples, catalysts were first reduced under the same conditions as the reduced samples, then sulfided in 500 vol. ppm H_2S–H_2 stream (200 $cm^3 min^{-1}$) at 553 K for 3 h, and then cooled in an H_2S–H_2 stream to 423 K, and finally in an H_2 stream to room temperature. After this treatment, the Pyrex tubes were evacuated, and the samples were transferred to the connected EXAFS cell, which had polyimide film windows and an optical path length of 8 mm (for the Pt L_{III}-edge measurement) and 15 mm (for the Pd K-edge measurement), and were sealed under vacuum (10^{-3} Torr).

The EXAFS data were analyzed using REX2000 software (Rigaku Co.). Fourier transformation of the k^3-weighted EXAFS data was done in the Δk range of 3–16 $Å^{-1}$ for the Pd K-edge and the Pt L_{III}-edge with square window damping of 5% at either side of the range using a Hanning function. Parameters for backscattering amplitudes and phase shift functions of the metal–metal bonds were derived from the oscillations of standard substances (Pd-foil, Pt-foil) observed at the same temperature as the ex situ measurement. For the analysis of the metal–S bonds, simulations by FEFF calculation [21] with the crystal structure of PtS and PdS [22,23] were used.

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