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In-situ XAFS observation of silica– and alumina–supported Pd–Pt catalysts

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Introduction

Supported bimetallic catalysts including Pd and Pt as active metal species are known to have high ability for hydrogenation of aromatic species (hydrodearomatization = HDA) of diesel fuel even in the presence of sulfur, which often becomes a serious poison for noble metal catalysts. It is important to elucidate the mechanism which gives the catalysts high sulfur tolerance. For this purpose structural analysis of sulfur tolerant noble metal catalysts was carried out using in-situ XAFS analysis. It was already found that Al_2O_3–supported Pd-Pt catalysts (Pd-Pt/Al_2O_3) showed higher HDA activity than SiO_2–supported Pd-Pt catalysts (Pd-Pt/SiO_2). In this paper we present different structural changes of metal particles during reduction process observed for Pd-Pt/Al_2O_3 and Pd-Pt/SiO_2 .

Experimental

Silica and Alumina supported Pd-Pt (molar ratio of Pd/Pt = 4) catalysts were prepared by the impregnation method. The precursors used for Pd and Pt were $Pd(NH_3)_4Cl_2 \cdot xH_2O$ (41.21 wt% Pd) and $Pt(NH_3)_4Cl_2\ xH_2O$ (55.6 wt% Pt), respectively. The total metal content was 2 wt%. The impregnated samples were calcined at 573 K for 3 h. The catalyst (0.3 g) was pressed into a disk with a diameter of 10 mm, and set in an in-situ EXAFS cell [1]. The reduction treatment of the catalyst was carried out in-situ under a flow of diluted H_2 (20% H_2 / Ar). The flow rate was 120 ml/min.

Measurements of Pd K-edge XAFS spectra were conducted in a transmittance mode at BL-10B.

Results and Discussion

Figures 1 (a) and (b) show changes in Fourier transform of EXAFS ($k^3\chi(k)$) spectra observed for (a) Pd-Pt/SiO_2 and (b) Pd-Pt/Al_2O_3 ,respectively. In the as-calcined state (indicated by solid lines), one broad peak at 0.18 nm assigned to Pd-O and Pd-Cl was observed for both catalysts. Upon introduction of diluted H_2 at r.t. to the catalysts, different changes were observed (indicated by broken lines) for the two catalysts. For Pd-Pt/SiO_2, the first peak at 0.18 nm almost disappeared and a strong peak at 0.24 nm due to Pd-Pd scattering emerged, which implied that almost all the Pd atoms were reduced even at r.t. under hydrogen. On the other hand, for Pd-Pt/Al_2O_3, the first peak decreased to 91 % of that of the as-calcined one and a peak assigned to Pd-Pd scattering appeared at 0.24 nm was very weak. Therefore most part of Pd atoms still remained in a similar state to that of the calcined ones under H_2 atmosphere at r.t.. Further reduction of metal species was carried out by a subsequent treatment at 573 K under diluted H_2 (indicated by dotted lines). For Pd-Pt/SiO_2, intensity of the peak at 0.24 nm increased to 117 % of that observed at r.t. under H_2. This fact suggested that formation of Pd metal particles was almost completed at r.t. under H_2. On the other hand, for Pd-Pt/Al_2O_3, the first peak at 0.18 nm disappeared after reduction at 573 K and a strong peak due to Pd-Pd scattering appeared at 0.24 nm. Therefore gradual reduction of Pd atoms upon heating under H_2 occurred on Pd-Pt/Al_2O_3. In the present work, a significant difference in structural change during reduction process was found between silica- and alumina-supported Pd-Pt catalysts by in-situ XAFS analysis.

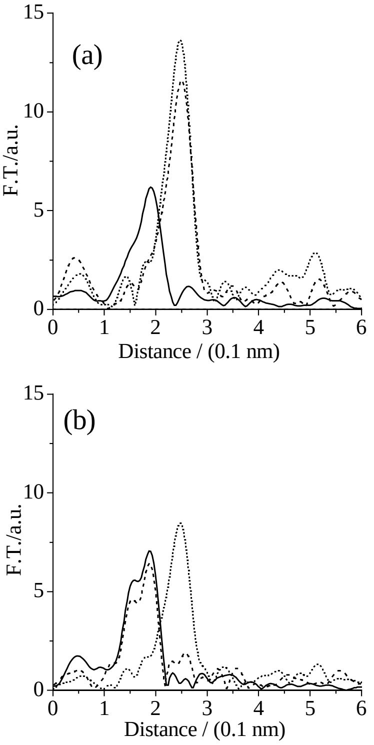

Fig.1 Change of Fourier Transform of EXAFS spectra observed for (a) Pd-Pt/SiO_2 and (b) Pd-Pt/Al_2O_3 . After calcination (solid lines), under a flow of 20 % H_2 at r.t. (broken lines) and after reduction at 573 K measured at r.t. (dotted lines).

Reference

[1] K. K. Bando, et al, J. Sync. Rad., 8, 581 (2001).

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