

EXAFS study of local structure of platinum species in platinum on mesoporous silica catalysts

Yasumasa TAKENAKA¹, Takahiro KIYOSU², Kyoko K. BANDO¹, Jun-Chul CHOI¹,
Toshiyasu SAKAKURA¹, Hiroyuki YASUDA*¹

¹National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

²Wako Pure Chemical Industries, Ltd., 1633 Matoba, Kawagoe, Saitama 350-1101, Japan

Introduction

Organic hydroxylamines are useful compounds in a wide variety of applications, including intermediates in the synthesis of biologically active substances and reagents for organic synthesis. Selective catalytic hydrogenation of nitro compounds is an ideal process to produce hydroxylamines because hydrogen is a relatively cheap reductant and the sole by-product is water. However, reduction of a nitro group using noble metal catalysts usually continues until an amino group is produced. We have recently found that platinum nanoparticles supported on ordered mesoporous silica modified with an aminopropyl group exhibit high catalytic activities for the selective hydrogenation of nitroaromatics in the presence of dimethyl sulfoxide. In this study, we attempted to elucidate the local structure of platinum species and the role of the immobilized aminopropyl group by using an EXAFS technique.

Experimental

SBA-15, an ordered mesoporous silica, was prepared according to the literature [1]. The 4.9 wt% platinum on SBA-15 catalyst (Pt/SBA-15) was prepared by an incipient wetness impregnation method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as the Pt precursor. The 5.1 wt% platinum catalyst supported on SBA-15 modified with an *N,N*-dimethylaminopropyl (DMAP) group (Pt/DMAP/SBA-15) was prepared as follows. SBA-15 was treated with (*N,N*-dimethylaminopropyl)trimethoxysilane in toluene at reflux for 24 h. The SBA-15 modified with a DMAP group was then contacted with an aqueous solution of K_2PtCl_4 and reduced by NaBH_4 . The EXAFS spectra of Pt L_{III}-edge (11.56 keV) for the catalysts were measured using a Si(111) double-crystal monochromator at BL-12C of KEK-PF. Data analysis was conducted with commercially available software (REX2000, Rigaku Co.).

Results and Discussion

Figures 1(a) and 1(b) show the Fourier transforms of Pt L_{III}-edge EXAFS spectra for the Pt/DMAP/SBA-15 and Pt/SBA-15 catalysts, respectively. The structural parameters were calculated by curve-fitting analysis of the EXAFS spectra. The coordination number of the platinum particles in Pt/DMAP/SBA-15 was much smaller than that of Pt/SBA-15. TEM images also showed

that the particle size of platinum in Pt/DMAP/SBA-15 was smaller compared with Pt/SBA-15. These results suggest that the DMAP groups on SBA-15 assist the formation of platinum fine particles. Additionally, the peak due to the Pt-N bond was observed at around 1.6 Å for the Pt/DMAP/SBA-15 catalyst (Figure 1(a)), indicating that the immobilized DMAP ligands partly coordinate to the platinum particles. It is possible that the electron-donating DMAP ligands increase the hydride character of hydrogen on platinum and promote the attack of the activated hydride species to the nitrogen-oxygen bond in nitroaromatics.

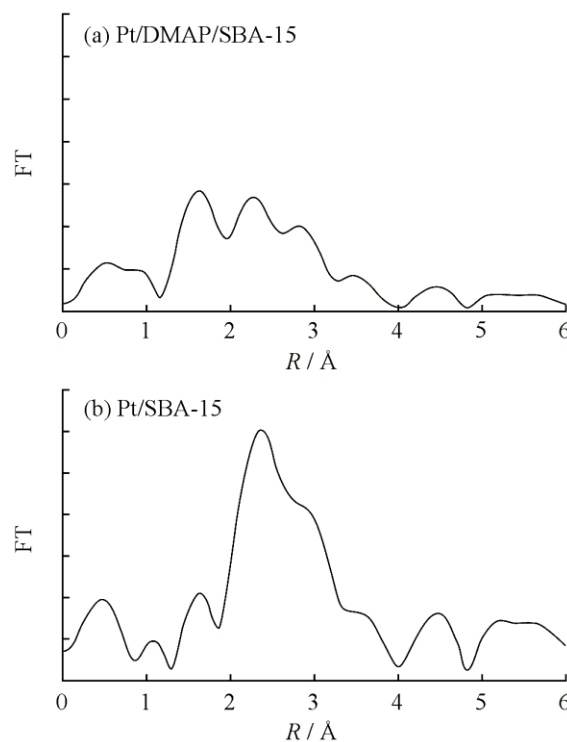


Figure 1: Fourier transforms of Pt L_{III}-edge EXAFS spectra for (a) Pt/DMAP/SBA-15 and (b) Pt/SBA-15 catalysts.

References

[1] G. D. Stucky et al., *J. Am. Chem. Soc.* 120, 6024 (1998).

* h.yasuda@aist.go.jp