Effect of additional metal ion on state of platinum on MCM-41

Masashi TANAKA, Akiko KOGA, Fumitaka HAYASHI, Masakazu IWAMOTO* Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Introduction

The deNO_x catalysts for diesel exhaust gas should work at 473-773 K under the presence of water and excess oxygen. Various Pt-loaded mesoporous materials have recently been tested as catalysts for HC-SCR of NO under the presence of excess oxygen [1,2] but their activities were not greatly improved in comparison with the previously reported ones [3]. Lowering of the reaction temperature and increase in the N₂ selectivity are still the subjects of deNO_x catalysts. On the SCR of NO by $C_{2}H_{4}$, we found that the catalytic performance was improved by the pore structure and the addition of Ce or Nb on the support, while it was suppressed by Ni or Cu addition. In the present study the effect of additional metal ions on the states of Pt on MCM-41 were examined by using XAFS spectroscopy.

Experimental

Metal ion-loaded MCM-41 were prepared by the template ion-exchange method [4] and employed as a support. The Si/Metal ratio was adjusted to 20. Pt (2 wt%) was impregnated by using an H_2PtCl_6 solution, followed by calcinations at 873 K for 6 h in air. The obtained samples are denoted as Pt/Metal-M41. The XAFS spectra of Pt L_3 -edge were measured in transmission mode under ambient conditions at beam line 9C of PF-KEK.

Results and discussion

Figure 1a shows the XANES spectra of Pt/Metal-M41 and those of the Pt foil and PtO_2 as reference samples. The spectra of Pt/M41, Pt/Ce-M41, and Pt/Nb-M41 were identical to that of Pt foil. On the other hand, the spectra of Pt/Ni-M41 and Pt/Cu-M41 showed the intense white line due to the oxidized Pt state with electron vacancy in the d-orbital, indicating that the loaded Pt existed as the PtO, species.

The EXAFS spectra of Pt/Metal-M41 and Pt reference compounds are shown in Figure 1b. Pt/M41, Pt/Ce-M41, and Pt/Nb-M41 exhibited the band at about 2.6 Å (no phase-shift correction), which was due to the Pt–Pt shell in metallic platinum. In contrast, on the spectrum of Pt/Ni-M41 the band at 2.6 Å was small and another band at 1.7 Å (no phase-shift correction) was observed. The latter was assigned to Pt–O shell and was also observed on the spectrum of Pt/Cu-M41. However, for Pt/Cu-M41 there was no band at near 2.6 Å. Therefore, the EXAFS analysis also revealed that the Pt species on Pt/Ni- and Pt/Cu-M41 were oxidized.

In summary, the Pt species on Pt/Ce- and Pt/Nb-M41, which exhibit the high catalytic performance for HC-SCR reaction, existed as metallic platinum after calcination at 873 K in air. In contrast, the Pt species on Pt/Ni- and Pt/Cu-M41 with low catalytic activity were the oxidized state. It follows that the enhancement of catalytic activity and N_2 selectivity would arise from the stabilization of metallic platinum by additional metal ions (Ce or Nb). The effect of metal ions introduced could be dependent on the electrophilicity of the ions.

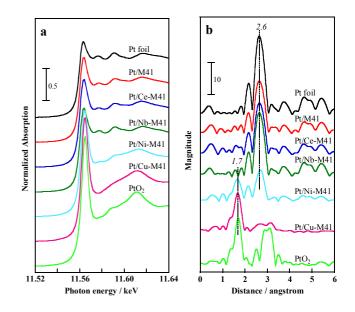


Figure 1: (a) XANES and (b) EXAFS spectra of Pt/Metal-M41.

References

[1] a) A. Jentys et al., Catal. Today 59, 313 (2000). b) J. Y. Jeon et al., Appl. Catal. B 44, 311 (2003). c) L. Jang et al., Appl. Catal. A 286, 36 (2005).

[2] T. Komatsu et al., Catal. Today 116, 244 (2006).

[3] a) M. Iwamoto et al., Chem. Lett. 2235 (1992); Catal. Today 26, 13 (1995). b) R. Burch and P.J. Millington,

Catal. Today 26, 185 (1995).

[4] M. Iwamoto and Y. Tanaka, Catal. Surv. Jpn. 5, 25 (2001).

* iwamoto@res.titech.ac.jp