

Characterization of the K-Pt/Al₂O₃ Catalyst for Preferential CO oxidation

Masatoshi KURIYAMA*¹, Yuji MINEMURA¹, Shin-ichi ITO¹,
Kazu OKUMURA², Keiichi TOMISHIGE¹, Kimio KUNIMORI¹

¹Institute of Materials Science, Univ. of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

²Department of Materials Science, Tottori Univ., Koyama-cho, Minami, Tottori 680-8552, Japan

Introduction

Hydrogen is a promising energy carrier related to the fuel cell technology, and generally hydrogen can be produced by the reforming of methanol and hydrocarbons. In this case, the produced gases always contain some amounts of CO. Preferential CO oxidation (PROX) in H₂ rich mixtures is an important reaction in the fuel cell technology in term of the purification of the fuel gas. Recently, our group has reported that K-Pt/Al₂O₃ was very effective in the PROX reaction [1]. In this research, we have carried out the characterization of K-Pt/Al₂O₃.

Experimental

The Pt/Al₂O₃ catalyst was prepared by impregnation the Al₂O₃ support with an aqueous solution of Pt(NO₂)₂(NH₃)₂ (Soekawa). After the impregnation, the sample was dried at 383 K for 12 h, and then calcined in the air at 773 K for 1 h. The loading amount of Pt was 2 wt%. The Pt/Al₂O₃ catalyst modified with potassium ion was prepared, by the following method. After the impregnation with aqueous solution of Pt(NO₂)₂(NH₃)₂, the sample was dried at 383 K for 12 h. And then the sample was impregnated again with an aqueous solution of KNO₃ (Wako), dried at 383 K for 12 h, and calcined at 773 K for 3 h. The loading amount of potassium ion is described in the molar ratio to Pt (K/Pt) with the ratio of 10 (denoted as K-Pt/Al₂O₃ (10)).

The catalyst was crushed and pressed to the disk (0.5 mm thickness, 10 mm ϕ) for EXAFS measurements. The samples were pretreated at 773 K under H₂ flow for 1 h. After the treatment, the sample disk was transformed to the measurement cell without exposing to air. Pt L_{III}-edge EXAFS spectra were measured by transmission mode at room temperature. After back ground subtraction, k^3 weighted EXAFS functions were Fourier transformed into R space and the one or two-shell fitting were analyzed by curve fitting.

Results and Discussion

Fig. 1 shows the Fourier transform of EXAFS for Pt/Al₂O₃ (a) and K-Pt/Al₂O₃ (10) (b). And table 1 shows the fitting results of EXAFS data. From the fitting result of EXAFS data of Pt/Al₂O₃ catalyst, we Pt-Pt and Pt-O species were necessary for the good agreement. Contribution of Pt-O is quite small and that of Pt-Pt is large. The contribution suggests that Pt particle has a strong interaction with Al₂O₃ support. In addition, from the result of TEM observation, Pt particles were highly dispersed and could not be observed (<1 nm). On the other hand, in the case of K-Pt/Al₂O₃ (10) catalyst, we

have used only Pt-Pt species was enough to fit the spectra. There was no contribution of Pt-O, and the contribution of Pt-Pt became larger than that with Pt/Al₂O₃ catalyst, and this suggests that some amount of Pt particles aggregated. Similarly, Pt particle was observed (2 nm) of TEM [1]. From TEM observation, Pt particle in K-Pt/Al₂O₃ (10) were estimated to be 2 nm, which corresponds to 0.55 dispersion. We also calculated the size of Pt particles by measuring the amount of CO adsorption. From the result of CO adsorption, the dispersion of Pt in K-Pt/Al₂O₃ (10) should be smaller than 0.55. This difference suggests that the surface of Pt metal particle can be covered with potassium ion.

Although the addition of potassium ion caused the decrease in the number of active site due to covering the surface of Pt, catalytic performance for the PROX was enhanced by the modification of the surface structure of the Pt particles.

The results of EXAFS analysis support that more effective active site on Pt particle for the PROX must be formed by the addition of potassium ion.

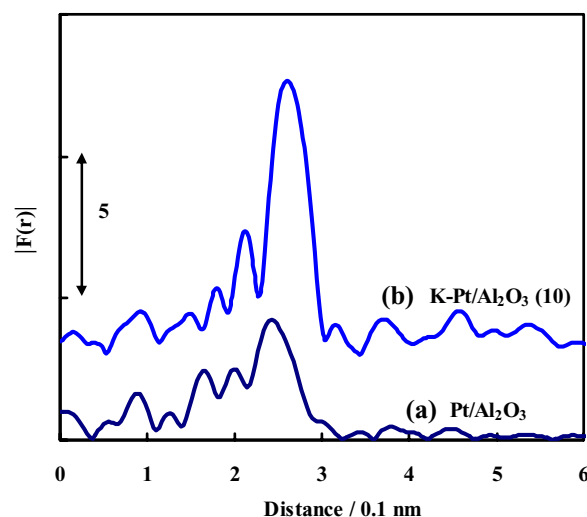


Fig. 1 Fourier transform of EXAFS
(a) Pt/Al₂O₃, (b) K-Pt/Al₂O₃ (10)

Table 1 EXAFS Parameters of Pt-Pt Shell and Pt-O Shell

Catalyst	Shells	CN	$R / 10^{-1} \text{ nm}$	$\sigma / 10^{-1} \text{ nm}$
Pt/Al ₂ O ₃	Pt-Pt	5.8±0.8	2.65±0.008	0.094±0.008
	Pt-O	0.5±0.2	2.04±0.022	0.050±0.045
K-Pt/Al ₂ O ₃ (10)	Pt-Pt	8.5±0.5	2.74±0.003	0.079±0.003

Reference

[1] Y. Minemura et al. *Chem. Commun.*, (2005) 1429

*s-k-m-8783@ims.tsukuba.ac.jp