

## Characterization of the K-Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst for Preferential CO oxidation

Masatoshi KURIYAMA<sup>\*1</sup>, Yuji MINEMURA<sup>1</sup>, Shin-ichi ITO<sup>1</sup>,  
Kazu OKUMURA<sup>2</sup>, Keiichi TOMISHIGE<sup>1</sup>, Kimio KUNIMORI<sup>1</sup>

<sup>1</sup>Institute of Materials Science, Univ. of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

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

### Introduction

Hydrogen is a promising energy carrier associated with the fuel cell technology, where one of hydrogen production methods is the steam reforming reaction of hydrocarbons and oxygenates. In this case, the product of gases can contain CO as an impurity, and this can be regarded as a poison for the anode catalyst. Preferential CO oxidation in H<sub>2</sub>-rich mixtures is an important reaction in terms of the purification of the fuel gas.

Our group has reported that the optimized K-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was very effective in decreasing CO concentration below 10 ppm in the fuel gas [1,2]. In this research, we investigated the effect of potassium on catalytic properties in the preferential CO oxidation and we attempted to elucidate the promoting mechanism of potassium on Pt/Al<sub>2</sub>O<sub>3</sub> in the preferential CO oxidation was discussed.

### Experimental

Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnating the Al<sub>2</sub>O<sub>3</sub> with an aqueous solution of Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> (Soekawa). After the impregnation, the sample was dried at 383 K for 12 h, and then calcined in air at 773, 823 and 873 K for 3 h. Calcination temperature of the catalysts is denoted as Pt/Al<sub>2</sub>O<sub>3</sub> [773]. The loading amount of Pt was 2 wt%. The Pt/Al<sub>2</sub>O<sub>3</sub> catalysts modified with potassium were also prepared, and the modification method was as follows. After the impregnation with the aqueous solution of Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>, the sample was dried at 383 K for 12 h. After the further impregnation of the dried sample with an aqueous solution of KNO<sub>3</sub> (Wako), it was dried again at 383 K for 12 h, and calcined at 773 K for 3 h. The loading amount of potassium is described in the molar ratio to Pt (K/Pt=10). The Pt/Al<sub>2</sub>O<sub>3</sub> catalysts modified with potassium are denoted as K-Pt/Al<sub>2</sub>O<sub>3</sub> (10).

The catalyst was crushed and pressed to the disk (0.5 mm thickness, 10 mm $\phi$ ) for EXAFS and XANES measurements. The samples were pretreated at 773 K under H<sub>2</sub> flow for 1 h and the sample disks were transformed to the measurement cell without exposing to air. Pt L<sub>III</sub>-edge EXAFS and XANES spectra were measured by transmission mode at room temperature. After back ground subtraction, k<sup>3</sup> weighted EXAFS functions were Fourier transformed into R space and the one or two-shell fitting were analyzed by curve fitting. In the analysis of XANES spectra, the normalized spectra were obtained by subtracting the pre-edge background from the raw data with a modified Victoreen's equation and normalizing them by the edge height.

### Results and Discussion

Figure 1 shows the relation between the coordination number of the Pt-Pt bond obtained from EXAFS and the relative electron deficiency from XANES for discussion about the electronic state of the catalysts considering the Pt metal particlesize. In the case of the Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, the relative electron deficiency decreased gradually with increasing the coordination number of the Pt-Pt bond. In contrast, K-Pt/Al<sub>2</sub>O<sub>3</sub> (10) is far from the relation of the Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, and this means that Pt metal particles in K-Pt/Al<sub>2</sub>O<sub>3</sub> (10) have higher electron deficiency for the large Pt-Pt coordination number, and this can be caused by the modification of potassium. As is usually known, the additive effect of alkali metal to metal surfaces is explained by the electron transfer from the alkali metal to the metal surface. This tendency is opposite to the results above. The difference is due to the chemical state of alkali metal. We found that here potassium was present as a cation, not metallic.

The addition of potassium to Pt/Al<sub>2</sub>O<sub>3</sub> enhanced the activity of the preferential CO oxidation activity in H<sub>2</sub>-rich stream remarkably, and the results of EXAFS and XANES analyses support that the addition of potassium ion leads the formation of more effective active site on Pt particle for the PROX.

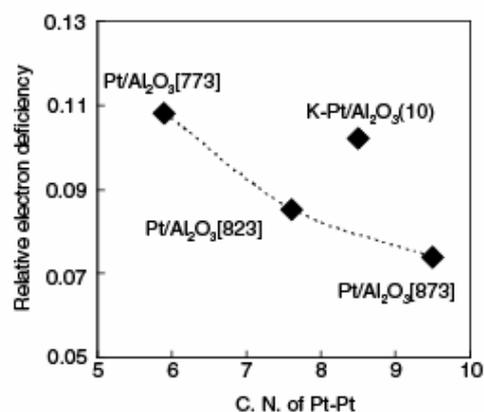


Fig. 1 Relation between the relative electron deficiency from XANES and the coordination number of the Pt-Pt bond from EXAFS of K-Pt/Al<sub>2</sub>O<sub>3</sub> (10) and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.

### Reference

- [1] Y. Minemura et al. *Chem. Commun.* (2005) 1429.
- [2] Y. Minemura et al. *Catal. Commun.* 7 (2006) 623.

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