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In-situ fluorescence EXAFS analysis of Pt/SnO_2 catalyst for micro gas sensor

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1 Introduction

Gas sensor for methane and natural gases is important to ensure the safety in our daily life. In order to increase the number of gas sensors employed in households, battery-driven type or cordless models are in demand for their appearance and ease of installation. Recently, Pt-promoted SnO_2 thin film device was prepared by MEMS (Micro Electro Mechanical System). It showed high sensitivity with low power driven which will provide the new pathway to realize low power consumption gas sensors. We have been studied the local structure of Pt in the highly active SnO_2 film base sensor by ex-situ XAFS. We found the methane and hydrogen oxidation activity increases with the increase of Pt content while Pt took a solid solution structure.[1] However, the structures of catalysts under reaction conditions are often different from those before the reactions and thus the *in-situ* characterization must be necessary to confirm the real active structure and reaction mechanism. Fluorescence mode is required in this study for *in-situ* XAFS measurement, because of Pt concentration into SnO_2 thin film is a few at% and the thickness of film is equal to or lower than 1 μm. An *in-situ* experiment with a large detection solid angle was required to measure fluorescent X-ray effectively. We have proposed a cell with a wide detection solid angle as shown in figure 1 where the sample was placed close to the Kapton window without any water cooling. We measured successfully the XAFS spectra of Pt/SnO_2 thin film on the Si substrate under methane and hydrogen flow conditions.

2 Experimental

Pt doped SnO_2 on the Si substrate was prepared as described before.[1] For the measurement, a 1 cm^2 sample was loaded in the cell and heated to 703 K at 100 K/min. Experiments were carried out in two steps. In the first step, sample was heated to 703 K under 200 ml/min of a dry air gas flow. In the second step the cell was refilled with the 1% H_2 and CH_4 gas (dry air base) in the same flow rate.

3 Results and Discussion

Figure 2 shows the oscillation $\chi(k)$ in the EXAFS oscillation of Pt/SnO_2 before (a) and after (b) the H_2 gas introduction. This oscillation could be fitted with Pt-O with the distance 2.000 ± 0.005 Å. The Pt-O coordination numbers before and after of H_2 gas reduction are 6.0 ± 0.5 and 5.0 ± 0.5, respectively. In order to derive the subtle change during the reaction, we took difference spectrum between them. We found a small but distinctive oscillation in the difference spectrum as shown in Figure 2(c). The change was due to the reduction of Pt-O and no evidence was found that the formation of Pt-Pt. On the other hands, we can't find the difference during the CH_4 gas reaction. The cell with a large fluorescence window allows a precise measurement of fluorescence X-ray and the observation of the subtle change of the absorption spectra. We are now deriving the reaction mechanism on the Pt/SnO_2 thin film from the *in situ* fluorescence XAFS.

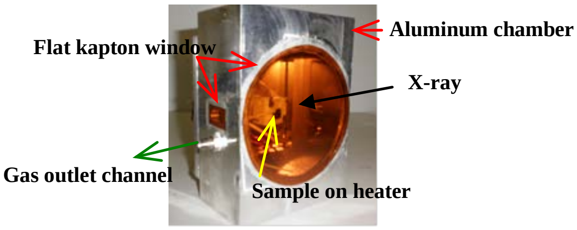

Figure 1. *In-situ* cell for fluorescence XAFS

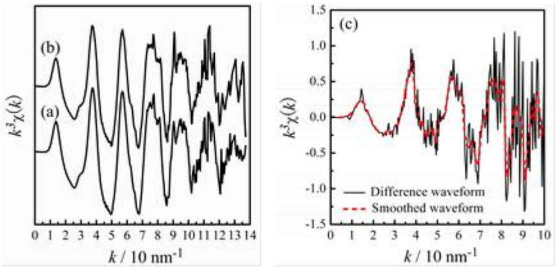

Figure 2. Illustration of the $\Delta\chi(k)$ technique. Pt/SnO_2 before (a) and after the H_2 reaction (b) and their difference spectrum $\Delta\chi(k)$ (c)

Reference

[1] N. Murata, T. Suzuki, M. Kobayashi, F. Togoh, K. Asakura, *Phys. Chem. Chem. Phys.*, in press

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