BL-9C/2020G039

In situ XAFS Analysis of Supported Pt Catalysts During Partial Oxidation of Methane

Kyoko K. BANDO[1,*], Vibin VARGHEESE[2], S. Ted OYAMA[2]
[1]Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[2]Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

1 Introduction

Catalytic partial oxidation of methane with a molecular oxygen under mild conditions is an extremely difficult reaction. Although it has been investigated for decades, a practical process has not been developed yet. Recently we have found that it is possible to activate oxygen atoms in an oxygen molecule homogeneously and use it as an oxidant to convert methane to dimethyl either (DME) under ambient pressure at around 300℃ over supported Pt catalysts [1]. Catalytic performance varies with the kind of support. Pt/Y_2O_3 produced solely DME at temperatures from 275℃ to 375℃, whereas over Pt/TiO_2, the main oxygenate product changed from DME (275℃ - 325℃) to formaldehyde (325℃ - 375℃). In order to elucidate the reaction mechanism, in situ XAFS analysis was conducted and the active structure was compared between Pt/Y_2O_3 and Pt/TiO_2.

2 Experiment

The Pt catalysts were synthesized by an incipient wetness impregnation method. The concentration of Pt was 2 wt% of Pt. After the impregnation, the sample was dried and calcined at 400 ºC. In situ measurements of Pt L_{III}-edge XAFS were conducted at BL-9C equipped with a Si(111) double crystal monochromator in a transmittance mode with ionizing chambers (15%Ar + 85%N_2 for I_0 and 50%Ar+50%N_2 for I). A pelletized sample was set in a gas flow cell developed by the PF-XAFS group [2]. A gas flow rate controlling system (Fujikin Co., Ltd.) was used to change the composition of the reaction gas mixture.

3 Results and discussion

Fig.1 shows the first peak (the white line) area of the normalized Pt L_{III}-edge XANES spectra under various conditions observed for Pt/TiO_2 and Pt/Y_2O_3. The peak height is thought to reflect the oxidation state of Pt.

For the calcined Pt/TiO_2, judging from the intensity of the white line ($\mu t = 2.4$), the electronic state of Pt was in an almost fully oxidized state (Pt^{4+}), whereas the oxidation state of Pt in Pt/Y_2O_3 was a little lower compared to Pt in Pt/TiO_2, since the intensity of the white line was weaker ($\mu t = 2.1$).

The catalysts was activated by reduction at 400℃. Pt in Pt/TiO_2 was deeply reduced to Pt^0 ($\mu t = 1.3$), but Pt in Pt/Y_2O_3 was not reduced to Pt^0 ($\mu t = 1.5$).

After the reduction, various reaction gas mixtures were introduced to the catalyst. For Pt/TiO_2, when the gas mixture changed between oxidative (CH_4+NO+O_2 or NO+O_2) and reductive (CH_4) conditions, corresponding changes in the white line intensity were observed, indicating the oxidation state of Pt fluctuated between Pt^0 and Pt^{2+} (estimated from the white line intensity). On the contrary, for Pt in Pt/Y_2O_3, when the reaction gas mixture was introduced to the catalyst, Pt was oxidized to the Pt^{2+} state. After that, the electronic state of Pt remained in Pt^{2+} regardless of the conditions. In other words, it was found that the Pt^{2+} state was significantly stabilized in Pt/Y_2O_3, which might be the reason for high selectivity to DME.

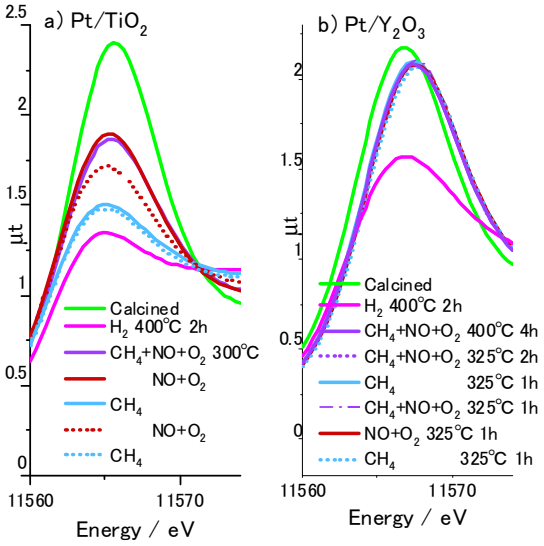

Fig.1 In situ Pt L_{III}-edge XAFS spectra for Pt/TiO_2 and Pt/Y_2O_3. The conditions are as follows: CH_4+NO+O_2 indicates CH_4:NO:O_2:He =20:1:1:78, NO+O_2 indicates NO:O_2:He =:1:1:98, and CH_4 indicates CH_4:He =20:80.

Acknowledgement

This work was supported by Japan Science and Technology Agency under the CREST program, Grant Number JPMJCR16P2. We thank all the members of the CREST team involved in the XAFS experiments for their support and cooperation.

References

[1] V. Vargheese, J. Murakami, K. K. Bando, I. T. Ghampson, G.-N. Yun, Y. Kobayashi, S. T. Oyama, *J. Catal.*, **389** (2020) 352–365.
[2] M. Kimura, K. Uemura, T.Nagai, Y.Niwa, Y.Inada, M.Nomura, *J. Phys.: Conference Series* **190** (2009) 012163.

* kk.bando@aist.go.jp