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In situ XAFS Study on In/SiO_2 Catalyst for Non-Oxidative Coupling of Methane Dynamic Structure Change during the Activation Process

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The structure of In /SiO_2 catalyst for the non-oxidative coupling of methane(CH_4)was studied by *in situ* X-ray absorption fine structure (XAFS) during the activation process under CH_4 flow. We found a drastic morphological change during the activation process under CH_4 flow such as melting to liquid at 430 K, the formation of a new structure with In-X(X=C or O) bond at 873 K and In metal reproduction at the reaction conditions at 1173 K.

1 Introduction

A catalyst for non oxidative coupling of methane(CH_4) to higher hydrocarbons (NOCM) is important to use the CH_4, a main ingredient of natural gases as feedstock. The In supported on SiO_2 is an active catalyst for the NOCM reaction[1]. Systematic studies of In/SiO_2 using *in situ* XAFS methods are required to gain further insights into the structural changes of In/SiO_2 during the activation process in order to reveal the active site. The main purpose of this work is to investigate the structural change during the activation process of the In/SiO_2 under the CH_4 flow conditions using the *in situ* XAFS spectroscopy.[2]

2 Experimental

An impregnation method was applied to the synthesis of In/SiO_2 catalysts according to the reported way[1]. The In K-edge spectra were calibrated against In metal foil with the maximum in the first derivative of the K-edge set to 27.94 KeV. *Operando* XAFS measurements of In/SiO_2 were carried out in a transmission mode at the beamline NW-10A, KEK-IMSS-PF (Tsukuba, Japan) using a Si (311) double crystal monochromator. All XAFS experiments were recorded with 40 s time intervals from 300 K to 1173 K under the CH_4 flow conditions.

3. Results and discussion

Figure 1 represents the Fourier transforms(FT) of k^3-weighted $\chi(k)$ signals at the In K-edge of the In/SiO_2 under the CH_4 flow activation. The sudden change in the XAFS oscillation was found at ~ 430 K where the peak top was shifted to the lower side, indicating that In was melt to liquid. We found another prominent peak at ca. 873 K at ca. 1.56 Å in the FT, indicating that the formation of In -X (X is a lighter element such as carbon or oxygen) [2]. At the reaction temperature (1173 K), the In-X peak disappeared, and the only In-In bond was found indicating that metallic In was reproduced.

The In/SiO_2 catalyst exhibits the high catalytic activity for NOCM in the CH_4 flow activation process. *In situ* XAFS revealed the melting of In metal at 473 K, In-X(X=O,C) formation at 873 K. The reproduced In metal at 1173 K was the active structure for NOCM reaction. In catalyst was activated after the dynamic structure changes.

1) Nishikawa, Y.; Ogihara, H.; Yamanaka, I., ChemistrySelect 2017, 2 (16), 4572-4576.
2) Kashaboina, U.; Nishikawa, Y.; Wakisaka, Y.; Sirisit, N.; Nagamatsu, S.; Bao, D.; Ariga-Miwa, H.; Takakusagi, S.; Inami, Y.; Kuriyama, F.; Dipu, A. L.; Ogihara, H.; Iguchi, S.; Yamanaka, I.; Wada, T.; Asakura, K., Chem. Lett. 2019, 48 (9), 1145-1147.

Research Achievements

1. High temperature XAFS studies under the real working conditions were successfully carred out
2. Dynamic change of In catalyst was revealed during the activation process.
3. Active site structure was determined.

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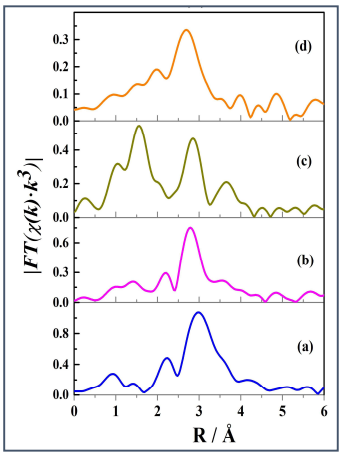

Figure 1: k^3-weighted EXAFS $\chi(k)$ signals during the activation conditions under CH_4 flow, at different temperatures; (a) 300 K, (b) 473 K, (c) 873 K, (d) 1173 K