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Operando XAFS studies on In/ZSM-5 catalysts for dehydrogenative conversion of methane

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1. Introduction

With the shortage of petroleum resources, the use of natural gas has attracted the research interest. As the methane is a main ingredient of the natural gas, the methane activation has been a hot topic in the field of catalysis since the end of the last centuries. In 2017, Yamanaka et al. found that 10wt% In/SiO_2 catalyst is the most effective for dehydrogenative conversion of methane（DCM）reaction among many other SiO_2-supported metal catalysts [1]. Recently they found that In/Na-ZSM-5 provided higher conversion of CH_4 with larger ethylene/ethane ratio than that on SiO_2. In this study, Operando QXAFS (Quick X-ray absorption fine structure) is applied to the In/Na-ZSM-5 catalysts to reveal the structures of the catalysts during DCM reactions.

2.Experiments and analysis methods

This experiment was carried at the NW-10A beamline in the Photon Factory Advanced Ring, High Energy Accelerator Research Organization-(KEK-IMSS-PF-AR). The samples were also heated to 1173K under the condition of 100 % methane flow, and then cooled to 50 °C. The XAFS spectra were measured every 40s by a quick mode and were analyzed by REX2000 and FEFF8.

3.Results and discussion

XAFS analysis of 2 wt% In /ZSM-5 indicated that the Indium species was present in a monomer structure. The first nearest neighbor around In seemed to be the Si judging from the R -factor and the bond distance. The In monomer structure was confirmed by the HAADF-STEM.

Figure 1 shows the Fourier transform of 10 wt% In/SiO_2 species under the reaction conditions. We could explain the XAFS data of 10 wt% In/SiO_2 species by the atomically dispersed In species found in the 2wt% In/Na-ZSM-5 (87%) and that metallic indium (13 %). Further discussion must be necessary to identify the active structure.

Acknowledgement

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[1] Nishikawa, Y.; Ogihara, H.; Yamanaka, I., ChemistrySelect 2017, 2 (16), 4572-4576.

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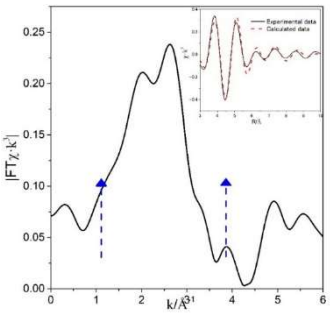

Fig.1 In K-edge EXAFS results for 10wt% In/Na-ZSM-5 at 1173K. (a)Fourier Transform (FT) and (b) associated EXAFS (solid line) and the best fit (dot line).