

# Oxidative methane conversion by CeO<sub>2</sub>- and NiO-supported MFI zeolite

**Mami Horie,<sup>a</sup> Fumiya Muto,<sup>a</sup> Yusuke Kunitake,<sup>b</sup> Masafumi Nakaya,<sup>a</sup> Toshiyuki Yokoi,<sup>b</sup> Kiyoshi Kanie,<sup>a</sup> Atsushi Muramatsu<sup>a,c,\*</sup>**

<sup>a</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku Univ., Sendai, 980-8577, Japan

<sup>b</sup>Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, 226-8503, Japan

<sup>c</sup>JST-CREST, Tokyo, 102-0076, Japan

\*Corresponding author: +81-(0)22-217-5165, mura@tohoku.ac.jp

**Abstract:** Methane is a natural resource and widely exist in natural gas, methane hydrate and so on. Therefore, development of methane conversion reaction has been expected to obtain petroleum products. Zeolite could control its acid strength, by introducing a metal element into its framework. In this study, we prepared CeO<sub>2</sub>- and NiO-supported MFI zeolite catalysts. The Al atoms in the framework was partly substituted by Fe atoms to optimize the acid strength. The activity of oxidative coupling methane (OCM) reaction was investigated. All catalysts showed for OCM activity. The CeO<sub>2</sub>-supported catalyst exhibited higher C<sub>2</sub> yield than the NiO-supported catalyst.

**Keywords:** Oxidative methane conversion, MFI Zeolite, Catalyst.

## 1. Introduction

There is a large amount of methane on the earth as a natural gas and methane hydrate. Preparation of C<sub>2</sub> chemical product by use it as starting material is strongly required. Oxidative coupling of methane (OCM) is one of the reaction of the famous methane-conversion reactions. However, methane is stable molecule and difficult to activate without high performance catalyst. Therefore, the development of the catalyst with high activity and selectivity toward OCM has been required.

Zeolite has attracted attention as the catalyst for OCM. Because its amount and strength of acid points can be controlled by introduction of metal elements into its framework. The reaction of methane conversion might depend on the amount and strength of acid points. In addition, molecular sieve effect of zeolite is expected to show high selectivity for C<sub>2</sub> compounds. In this study, we have designed and synthesized CeO<sub>2</sub>- and NiO-supported MFI zeolite catalysts. The Al atoms in the framework was partly substituted by Fe atoms to optimize the acid strength. We have also investigated the catalytic activity of the resulting MFI zeolite on OCM reactions.

## 2. Experimental

[Al, Fe]-MFI zeolite was prepared by hydrothermal synthesis. All precursors were mixed and stirred at room temperature. 6.0 M HCl and 40% tetrapropylammonium hydroxide solution (TPAOH) were added into that solution and stirred at room temperature for 10 min. Tetraethyl orthosilicate (TEOS) was added into the solution and stirred at 0 °C for 6 h and then at room temperature for 42 h. This solution was treated at 160 °C for 5 days. The resulting materials was calcined.

CeO<sub>2</sub> and NiO nanoparticles were supported on [Al, Fe]-MFI by the following method. The resulting [Al, Fe]-MFI zeolite and metal precursors were added into ethanol at room temperature and stirred for 2 h. Then the solution was evaporated. The obtained powder was dried at 60 °C and then calcined at 540 °C for 3 h.

The catalytic activity of the resulting catalysts were evaluated in a fixed bed reactor (Fig. 1). 100 mg of the catalyst (0.5-1 mm sieved fraction) was loaded in a 6 mm i.d. quartz tubular reactor with quartz wool. The reaction was performed at 300-600 °C under flow of the reactant feed gases: methane, oxygen, and argon (CH<sub>4</sub>: O<sub>2</sub>: Ar = 16: 4: 5, total flow rate :25 SCCM). The reaction products were measured by gas-chromatograph (GC-TCD and GC-FID).

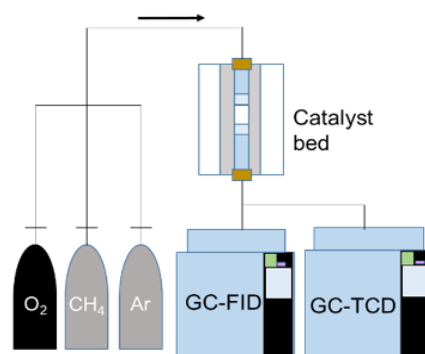


Fig. 1 Activity evaluation equipment

### 3. Results and discussion

Figure 2 and 3 show XRD patterns of the resulting MFI. The crystal structure of the all as-synthesized zeolite catalysts were identified with MFI type zeolite regardless of the presence or absence of metal oxide. Change of the XRD patterns of NiO/MFI was observed after the OCM reaction. NiO was reduced to Ni by the OCM reaction. On the other hand, the crystal structural change of CeO<sub>2</sub>/MFI was not observed after the reaction. The state of CeO<sub>2</sub> was maintained during the reaction.

Figure 4 shows TEM images of the MFI zeolites. It was observed that the CeO<sub>2</sub> and NiO nanoparticles were supported on the zeolite. After the reaction, the aggregation of the nanoparticles was observed in both CeO<sub>2</sub> and NiO supported MFI zeolites.

Figure 5 and 6 show catalytic activity of OCM reaction over NiO- or CeO<sub>2</sub>-supported MFI. When the activity was compared with that of MFI, the increase of the conversion was observed. In addition, the increase of C<sub>2</sub> yield was also observed by supporting NiO and CeO<sub>2</sub>. The oxygen active species might be increased by the addition of the metal oxide.

The generation of CO, CO<sub>2</sub> and ethane as a C<sub>2</sub> compounds were observed when NiO/MFI and CeO<sub>2</sub>/MFI were used as catalysts. In the case of use of CeO<sub>2</sub>/MFI, ethylene was detected. Especially CeO<sub>2</sub>/[Fe]-MFI, showed higher conversion at 500°C than other CeO<sub>2</sub>/MFI. However, there were not significant difference NiO/[Fe]-MFI and NiO/[Al,Fe]-MFI. When the catalytic activities of NiO/MFI was compared with CeO<sub>2</sub>/MFI, CeO<sub>2</sub>/MFI showed higher yield of C<sub>2</sub>H<sub>6</sub>. CeO<sub>2</sub> supported catalyst was suitable for OCM reaction.

### 4. Conclusion

In conclusion, all the resulting zeolites showed activity toward OCM. NiO/MFI showed higher activity than that of CeO<sub>2</sub>/MFI. Focus on C<sub>2</sub> yield, CeO<sub>2</sub> supported catalysts showed higher than that of NiO supported one. NiO/MFI produced only ethane as C<sub>2</sub> compounds. On the other hand, CeO<sub>2</sub>/MFI produced ethane and ethylene.

### References

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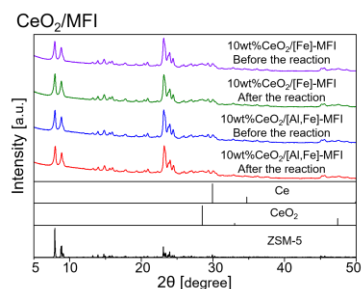


Fig. 2 XRD patterns of CeO<sub>2</sub>/MFI

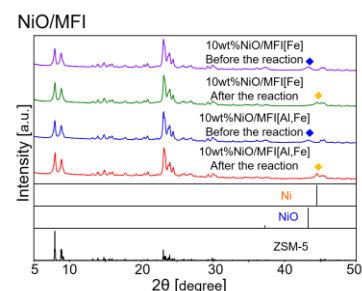


Fig. 3 XRD patterns of NiO/MFI

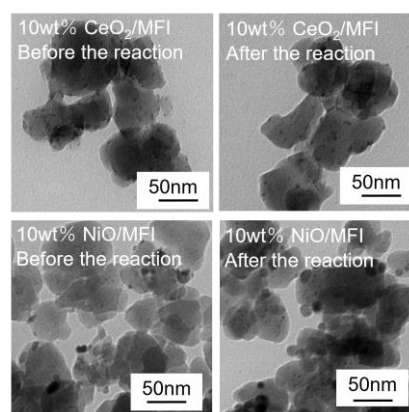


Fig. 4 TEM images of MFI catalyst

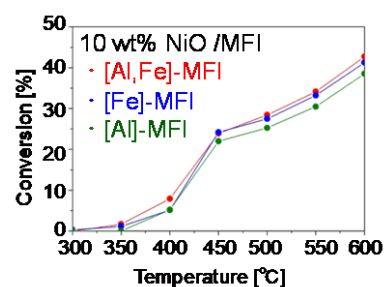


Fig. 5 Conversion of NiO/MFI

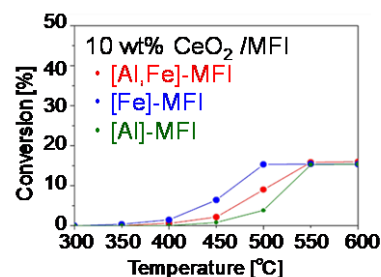


Fig. 6 Conversion of CeO<sub>2</sub>/MFI