

## State of Mn in the CuMn-spinel derived catalyst for the DME steam reforming

Nobuyuki ICHIKUNI\*<sup>1</sup>, Tetsuya FUKUNAGA<sup>1</sup>, Takayoshi HARA<sup>1</sup>, Shogo SHIMAZU<sup>1</sup>  
<sup>1</sup>Chiba University, Inage-ku, Chiba 263-8522, Japan

### Introduction

Fuel cells have attracted much attention as clean and high efficient power generators for stationary and mobile use. From the viewpoint of reformability, dimethyl ether (DME) is one of the most promising fuels<sup>1</sup>.

CuMn-spinel combined with acidic oxides, *i.e.* H-ZSM-5, showed very high activity with good selectivity toward steam reforming of DME<sup>2</sup>. To clarify the reason for the high activity, the nature of CuMn spinel should be identified. It is revealed that Cu species were reduced to zero-valent under the working state. In this study, Mn *K*-edge XAFS measurements were carried out to investigate the state of Mn in CuMn spinel.

### Experimental

The spinel CuMn (CuMn<sub>2</sub>O<sub>4</sub>) was prepared by calcination of CuMn mixed oxide powder at 1173 K. The non-spinel CuMn was obtained by calcination of the same powder at 573 K. Molar ratio of Cu:Mn is regulated to 1:2 in both samples. The as prepared catalyst and the hydrogen-reduced catalyst were denoted as (ox) and (red), respectively.

Mn *K*-edge XAFS spectra were collected at BL-7C and BL-12C with Si(111) double crystal monochromator in a transmission mode. The (ox) catalyst was pressed into a self-supporting disk. The (red) catalyst was transferred into the aluminum cell without contacting air, sealed with Kapton at the both ends of the X-ray path. The collected XAFS data were analyzed by the program REX2000 (Rigaku Co.).

### Results and discussion

The spinel derived catalyst showed the higher activity toward methanol steam reforming reaction than the non-spinel derived catalyst did. The CuMn catalysts were treated with hydrogen to reduce the Cu before reaction. It is revealed that the spinel derived Cu<sup>0</sup> cluster is smaller than the non-spinel derived one<sup>3</sup>.

Figure 1 shows the  $k^3$ -weighted Mn *K*-edge EXAFS oscillations and the XANES spectra for hydrogen reduced CuMn catalysts and the Mn foil. EXAFS functions of both spinel and non-spinel derived catalyst showed different shape from those of Mn foil. The shapes of Mn *K*-edge XANES of the catalysts were not similar to that of Mn foil. Thus, the catalysts were not fully reduced to Mn<sup>0</sup> state.

FTs of  $k^3$ -weighted Mn *K*-edge EXAFS oscillations are shown in Fig. 2. Although the FT profiles of reduced CuMn catalysts resembled each other, the profiles show the resemblance neither in Cu foil nor in oxidized form.

The peak intensity attributed to Mn-Mn coordination for spinel derived catalyst is smaller than that for non-spinel derived one. It can be concluded that Mn species were partially reduced and the smaller Mn clusters maintain the Cu particle being small.

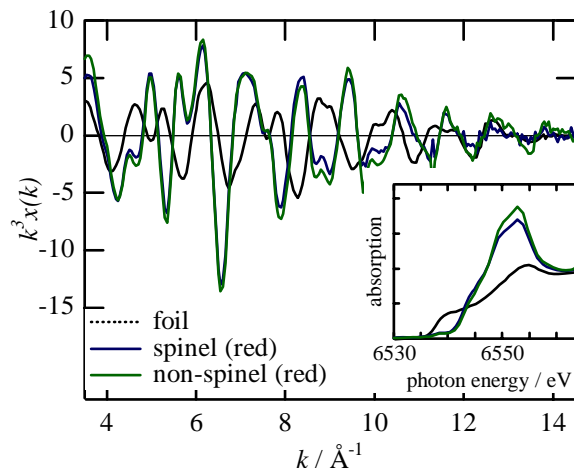


Figure 1.  $k^3$ -weighted Mn *K*-edge EXAFS oscillations for Mn foil and reduced CuMn catalysts. The inset shows the Mn *K*-edge XANES spectra.

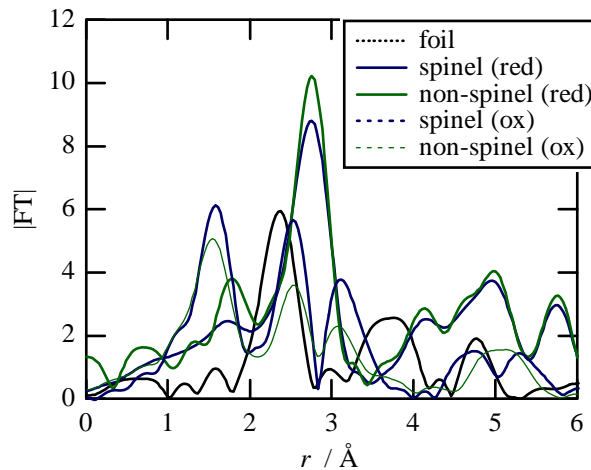


Figure 2. FT of Mn *K*-edge EXAFS spectra for Mn foil and CuMn catalysts.

### References

- [1] T. A. Semelsberger, R. L. Borup, H. L. Greene, *J. Power Source*, 156, 497 (2006).
- [2] T. Fukunaga, N. Ryumon, *Stud. Surf. Sci. Catal.*, 172, 577 (2006); Y. Tanaka, R. Kikuchi, T. Takeguchi, K. Eguchi, *Appl. Catal. B*, 57, 211 (2005).
- [3] T. Fukunaga, N. Ryumon, N. Ichikuni, S. Shimazu, *submitted*.

\* ichikuni@faculty.chiba-u.jp