

# CO<sub>2</sub> hydrogenation activity over iron carbide catalysts having different crystal structures derived from iron oxalate

Akihide YANAGITA, Daisuke KOMIZU, Haruki HORIKOSHI, Keigo TASHIRO, <u>Shigeo SATOKAWA\*</u> Seikei University, Faculty of Science and Technology, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo 180-8633, Japan. \* e-mail satokawa@st.seikei.ac.jp

e man satokana es

#### Significance and Relevance

An iron carbide catalyst having  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> structure allows both RWGS and FTS reactions to proceed on a single crystal surface, whereas an iron carbide catalyst having  $\vartheta$ -Fe<sub>3</sub>C structure only allows RWGS. Since the CO production rates and the apparent activation energies of the two catalysts are different, it was inferred that the reaction mechanisms are different with each other due to the differences in the microstructure of the crystal surface.

## **Introduction and Motivations**

Conversion of carbon dioxide (CO<sub>2</sub>) to liquid fuels by catalytic reactions is an important technology for realizing a carbon-neutral society. An alkali-containing iron carbide is known as a catalyst that can obtain liquid fuels from CO<sub>2</sub> via reverse water gas shift (RWGS) and Fisher-Tropsch Synthesis (FTS). It has been reported that Fe<sub>3</sub>O<sub>4</sub> is the active site for the RWGS reaction and  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> is the active site for the FTS reaction in this catalyst.<sup>1</sup>

We have previously reported that the catalyst with the highest liquid component yield can be obtained by adding 0.8 wt% alkali to  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>.<sup>2</sup> This result not only shows that a catalyst with a high liquid component yield has been found, but also that the RWGS reaction also proceeds on  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>, and that the Fe<sub>3</sub>O<sub>4</sub> phase is not necessary. In this study, we focused on the RWGS reaction occurring on iron carbide and aimed to experimentally prove the difference in activity of iron carbides ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>,  $\vartheta$ -Fe<sub>3</sub>C) for the RWGS reaction proposed in computational study.<sup>3</sup>

### **Materials and Methods**

Catalyst preparation and reaction tests were carried out using a fixed-bed flow reactor. Commercially available iron oxalate dihydrate powder was mixed with quartz sand as a diluent and packed into a reactor, then heat-treated at 350 °C or 500 °C for 4 h under a 30% CO/N<sub>2</sub> gas flow to prepare iron carbide catalysts, FeCx-350 or FeCx-500, respectively. Catalytic activity tests were carried out with a catalyst amount of 0.3 g-Fe, reaction gas composition  $CO_2/H_2/N_2 = 1/3/1$ , reaction gas flow rate 120-600 mL min<sup>-1</sup>, pressure 0.1-1.0 MPa(a), reaction temperature 200-320 °C. The outlet gas composition was analyzed using a gas chromatograph equipped with a TCD detector (Agilent 990MCGC).

### **Results and Discussion**

It was confirmed that the FeCx-350 and FeCx-500 were iron carbides with crystal structures mainly composed of the  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> phase and the  $\vartheta$ -Fe<sub>3</sub>C phase, respectively by the XRD analysis. When the RWGS reactivity of each catalyst was evaluated at different reaction temperatures, the selectivity of CO<sub>2</sub> to CO was almost 100%. Since no significant changes were observed in the crystal structure of the catalyst before and after the reaction, it was confirmed that the RWGS reaction proceeds on the surface of iron carbides.

The catalytic activity of each catalyst was compared. FeCx-500 had a higher CO production rate per catalyst surface area than FeCx-350. In addition, the apparent activation energy (*Ea*) was calculated using the Arrhenius plots (Figure 1). The *Ea* values of FeCx-350 and FeCx-500 were calculated to be 92.9 kJ mol<sup>-1</sup> and 70.4 kJ mol<sup>-1</sup>, respectively. It was considered that these differences were due to the difference in the reaction mechanism of the RWGS reaction on the  $\vartheta$ -Fe<sub>3</sub>C and  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> crystal surfaces. Effect of reaction pressure for the CO<sub>2</sub> hydrogenation reaction were evaluated. It was found that, the generation of C2-C4 hydrocarbons became prominent as the pressure increased in FeCx-350. On the



other hand, this tendency was not observed in FeCx-500. It was confirmed that the crystal structure of iron carbide has a significant effect not only on RWGS reactivity but also on FTS reactivity.



Figure 1 Arrhenius plots of the RWGS reaction over iron carbide catalysts.

## References

- B. Yao, T. Xiao, O. A. Makgae, X. Jie, S. Gonzalez-Cortes, S. Guan, A. I. Kirkland, J. R. Dilworth, H. A. Al-Megren, S. M. Alshihri, P. J. Dobson, G. P. Owen, J. M. Thomas, P. P. Edwards, *Nat. Commun.* 2020, 11(1), 6395.
- 2. A. Yanagita, S. Furuya, H. Horikoshi, K. Tashiro, S. Satokawa, J. Jpn. Petrol. Inst. 2024, 67(4), 136-145.
- 3. S. J. Han, S.-M. Hwang, H.-G. Park, C. Zhang, K.-W. Jun, S. K. Kim, J. Mater. Chem. A, 2020, 8, 13014-13023.

### Acknowledgements

This study has been conducted under a contract with the New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to express our gratitude to NEDO.