**Synthesis of C₂₊ hydrocarbons by CO₂ hydrogenation over the
composite catalyst of Cu-Zn-Al oxide and HB zeolite using two-stage
reactor system under low pressure**

Masahiro Fujiwara,* Hiroaki Sakurai, Kumi Shiokawa, Yasuo Iizuka

National Institute of Advanced Industrial Science and Technology (Kansai center), 1-8-
31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Corresponding author:

*E-mail: m-fujiwara@aist.go.jp, Phone: +81-72-751-9525.

ABSTRACT

The combination of methanol synthesis and methanol-to-gasoline (MTG) reaction is a beneficial process to produce particular C_{2+} hydrocarbons from CO_2 and H_2 , because MTG reaction can produce C_{2+} hydrocarbons selectively without the formation of methane. However, the composite catalysts consisting of methanol synthesis catalyst and zeolite previously reported have produced C_{2+} hydrocarbons in poor yields especially under low pressure conditions. This paper reports the high yield production of C_{2+} hydrocarbons by CO_2 hydrogenation using a two-stage reaction system consisting of a Cu-Zn-Al oxide catalyst in the first reactor and a composite catalyst of the Cu-Zn-Al oxide and HB (zeolite beta) in the second reactor. The key points of this system are reversed water-gas-shift (RWGS) reaction in the first reactor and the following H_2O removal before the second reactor. The gas mixture supplied to the second reactor containing much amount of CO and little H_2O enhanced the methanol synthesis and suppressed the methanol decomposition to CO over the Cu-Zn-Al oxide catalyst in the composite catalyst, promoting the MTG reaction to produce C_{2+} hydrocarbons over HB zeolite. The highest yield of C_{2+} hydrocarbons reached to approximately 15 C-mol% under 0.98 MPa.

KEYWORDS: CO_2 hydrogenation; C_{2+} hydrocarbons; Methanol synthesis; MTG reaction; Composite catalyst; Two-stage reactor system

1. Introduction

The emission of a huge amount of CO₂ by using fossil fuels is believed to lead the anthropogenic global warming. The production of carbon fuels from CO₂ emitted from fossil fuels and H₂ obtained from renewable energies is a promising technology for the establishment of a carbon recycling system and for the creation of a sustainable society [1-3]. Since C₂₊ hydrocarbons such as propane gas (LPG), gasoline, and light diesel oils have been widely used as carbon fuels in modern society, their productions from CO₂ and H₂ must achieve the carbon recycling system rapidly. Although Fischer-Tropsch (F-T) type reaction has been studied for the hydrocarbon syntheses from CO₂, the high methane production and the poor hydrocarbon selectivity are inevitable drawbacks of the F-T process [4-7].

Methanol synthesis by CO₂ hydrogenation [1-3, 8-11] is a well-studied reaction, and methanol-to-gasoline (MTG) reaction over zeolite catalysts is known to produce some particular C₂₊ hydrocarbons without the by-production of methane [12-15]. The stepwise two-reaction process that combines the methanol synthesis as the first step and the MTG reaction as the second one is expected to be an effective C₂₊ hydrocarbon synthesis route [16,17]. However, it is well-known that the methanol synthesis from CO₂ has a strict thermodynamic limitation especially under low pressure conditions [18-21]. The simple equilibrium conversions of CO₂ to methanol at 250 and 300 °C under 1 MPa are 6.3 % and 3.7 %, respectively. On the other hand, the production of H₂O by reversed water-gas-shift (RWGS) reaction as an inevitable side reaction restricted the methanol synthesis more intensely, decreasing the equilibrium conversions to only 1.88 % (250 °C) and 0.34 % (300 °C) [20,21].

The composite catalyst process, where the methanol synthesis and the MTG reaction are carried out concurrently in one catalyst bed, is known to overcome the thermodynamic limitation of the methanol synthesis [22-28]. The irreversible MTG reaction shifts the equilibrium of the methanol synthesis to produce C_{2+} hydrocarbons free from the thermodynamic restriction as shown in Fig. 1. The CO_2 hydrogenation over the composite catalysts have been examined and revealed that the proper selections of methanol synthesis catalysts and zeolites achieved the good performances of C_{2+} hydrocarbon productions [22-34]. However, these good catalytic activities are generally exhibited at high temperature ($>350\text{ }^{\circ}C$) and under high pressure ($>3\text{ MPa}$). Nevertheless, as the MTG reaction requires no high pressure reaction and is often conducted under ambient pressure, the composite catalyst must have a high activity for the synthesis of C_{2+} hydrocarbons even under low pressure, as long as the equilibrium shift shown in Fig. 2 is achieved sufficiently [22].

It has been reported in the methanol synthesis from CO_2 that the partial conversion of CO_2 to CO by the RWGS reaction beforehand the methanol synthesis reaction is effective for enhancing the methanol yield using a two-stage reactor [10]. In this study, we have applied this two-stage reactor system for the production of C_{2+} hydrocarbons from CO_2 and H_2 over composite catalysts consisting of Cu-Zn-Al oxide and HB (proton type of zeolite beta). After many approaches, the two-stage reactor system consisting of the first reactor for the RWGS reaction and the second reactor for the production of C_{2+} hydrocarbons using the composite catalyst was found to be very effective for the C_{2+} hydrocarbon production from CO_2 and H_2 even under the pressure less than 1 MPa. In this paper, we wish to report our latest results on the CO_2 hydrogenation over the composite catalysts by using the two-stage reactor system,

where the yield of C_{2+} hydrocarbons reached to about 15 C-mol% beyond the equilibrium conversion of the methanol synthesis.

2. Materials and methods

2.1. Catalyst preparations

Among a number of Cu-Zn based methanol synthesis catalysts, we selected a Cu-Zn-Al oxide catalyst with an atomic composition of 6:3:1 in this study, which is analogous to the catalyst actually employed in commercial industrial processes for methanol production [10,35]. This Cu-Zn-Al oxide catalyst was prepared by a co-precipitation method using an aqueous solution of the corresponding metal nitrates and Na_2CO_3 . The mixed 1 M solution of Cu, Zn and Al nitrates (6:3:1 in molar ratio) was added at once into the 1 M solution of Na_2CO_3 at 80 °C. The amount of Na_2CO_3 was 1.2 equivalents to the total stoichiometric quantities of the nitrates. The precipitate was aged for 2 h at the same temperature, then filtered and washed 5 times with fresh distilled H_2O . The gel was dried at 120 °C for 12 h and finally calcined at 500 °C for 4 h or at 350 °C for 3 h in air. The resulting powder, Cu-Zn-Al (6:3:1) oxide, was physically mixed with HB zeolite [Tosoh corporation; HSZ-931HOA ($SiO_2/Al_2O_3=28.5$) or HSZ-940HOA ($SiO_2/Al_2O_3=41.6$)] by grinding about 1000 times in various weight ratios to give the composite catalysts. The Cu-Zn (3:7) oxide catalyst and its composite catalyst were prepared by the procedures similar to those described above.

The specific surface areas and the particle sizes of Cu-Zn-Al oxide catalysts were analyzed by BET method using nitrogen adsorption isotherms measured with Belsorp Mini instrument (Bel Japan) and by a laser diffraction particle analyzer (Shimadzu SALD-2300), respectively.

2.2. Catalytic reactions

The CO₂ hydrogenation was carried out by using a pressurized flow-type reactor. This system had two reactors connected in series and a trap cooled by ice-water mixture placed between these two reactors (Fig. 2). The Cu-Zn-Al (6:3:1) oxide catalyst (1 g) was packed in the first reactor, and used without changing for all catalytic tests. The composite catalysts loaded in the second reactor were replaced in each experiment. In a typical catalytic reaction, the each catalyst in the first and second reactors was reduced by H₂ stream (40 mL/min) at 250 °C approximately for 14 h under atmospheric pressure. After this pre-reduction, the temperatures of the catalyst beds of the two reactors were raised to the respective temperatures prescribed. Then, the mixed gas of CO₂ and H₂ with a composition of H₂/CO₂=3/1 was introduced and the pressure of the system was raised until 10 kgf/cm² (0.98 MPa). The cold trap was cooled to approximately 2 °C to remove the H₂O formed in the first reactor. In the experiments using only the first reactor, the vacant second reactor was heated at 300 °C. In the experiments using only the second reactor, the mixed gas was directly flowed into the second reactor. In the catalytic reactions without the cold trap, the tubing between the first and second reactors was heated at about 150 °C to prevent the condensation of any components.

All parts of tubing from the outlet of the second reactor to the inlet of online-gas chromatographs were heated at 100-150 °C to prevent the condensation of any products. All effluent gases were analyzed by on-line TCD and FID gas chromatographs. The former was equipped with an active carbon column for analyzing CO₂ and CO, and the latter with a plot column GS-Q (Shimadzu GLC) for evaluating all hydrocarbons,

methanol, and dimethyl ether (DME). The calculations for evaluating the catalytic performances were based on C-mol%, which means the amount of the products based on carbon mole: [(carbon number of the product)×(yield or selectivity of the product)].

3. Results and discussion

3.1. CO₂ hydrogenation over only the composite catalysts

Before examining the CO₂ hydrogenation by using the two-stage reactor system, the catalytic performance only over the composite catalysts using a single reactor (only the second reactor of the two-stage reactor system was used) was tested. The composite catalysts used were the physical mixtures of Cu-Zn-Al (6:3:1) oxide and HB zeolite (SiO₂/Al₂O₃=28.5). The runs 1-6 of Table 1 summarize the results of the CO₂ hydrogenation at 300 °C under 0.98 MPa. The composite catalyst with the equal weight of the both catalysts (0.9 g/0.9 g) gave only 0.16 C-mol% of C₂₊ hydrocarbons (run 1). When the amount of the Cu-Zn-Al oxide in the composite catalyst was reduced, the yields of C₂₊ hydrocarbons increased (runs 2 and 3). The best yield of C₂₊ hydrocarbons was found over the composite catalyst with 0.1 g of the Cu-Zn-Al oxide and 0.9 g of the HB zeolite (run 3). In these three cases, the conversions of CO₂ were approximately same, which were near to the equilibrium conversion of CO₂ to CO (about 23 %) at 300°C under 1 MPa [20]. Thus, 10 wt% of the Cu-Zn-Al oxide in the composite catalyst was almost sufficient to convert CO₂ to the equilibrium level under the conditions. For comparison, Cu-Zn (3:7) oxide as another representative methanol synthesis catalyst [35] was also employed for the composite catalyst. However, both the yield of C₂₊ hydrocarbons and the CO₂ conversion were lower (run 4).

(Table 1)

When the flow rate of the reaction gas was increased, the selectivities of C_{2+} hydrocarbons, methanol and dimethylether became higher with the decrease of CO selectivity (runs 3,5,6). We previously reported that the competition between the methanol decomposition over methanol synthesis catalyst and the methanol transportation to the zeolite particle is a crucial factor for determining the selectivity of C_{2+} hydrocarbons in the reaction over composite catalysts [29-33]. It is also known that Cu-Zn based oxide is an active catalyst of the decomposition of methanol to CO [36,37]. The decrease of the contact time of methanol with the Cu-Zn-Al oxide in the faster flow rates enhanced the transportation of methanol to the HB zeolite particle, increasing the yields of C_{2+} hydrocarbons (runs 5 and 6). The poor yields of C_{2+} hydrocarbons using the composite catalysts with higher Cu-Zn-Al oxide contents were caused from the preferential decomposition of methanol to CO by the longer contact times with the Cu-Zn-Al oxide (runs 1 and 2). These results suggested that (1) the suppression of the methanol decomposition to CO over the Cu-Zn-Al oxide and (2) the rapid transportation of methanol into the HB zeolite are essential for the high yield synthesis of C_{2+} hydrocarbons over the composite catalyst.

3.2. CO₂ hydrogenation over only the methanol synthesis catalyst of the first reactor

The runs 7-10 of Table 1 show the catalytic performances of Cu-Zn-Al (6:3:1) oxide packed in the first reactor for CO₂ hydrogenation. The yield of methanol at 250 °C was 2.66 C-mol%, which was higher than the equilibrium conversions of methanol synthesis in consideration of the RWGS reaction (1.88 %) [20,21]. The low conversion of the RWGS reaction (2.54 C-mol%) reduced the thermodynamic restriction of methanol synthesis (run 7). The elevation of the reaction temperature increased CO and

adversely decreased methanol (runs 8-10). The methanol yield became negligible at more than 400 °C, and the CO₂ conversion approximately reached the equilibrium conversion level of the RWGS reaction (runs 9-10) [21]. At 420 °C, CO was exclusively produced, whereas the methane formation evidently increased to about 0.15 C-mol% probably due to the F-T type reaction (run 10). Since one of the primary aims of the composite catalyst is to produce C₂₊ hydrocarbons with the minimum by-production of methane, 420 °C was chosen to the highest temperature of the first reactor.

3.3. Catalytic performance of the composite catalyst using the two-stage reactor system

Table 2 summarizes the results of CO₂ hydrogenation using the two-stage reactor system. In the second reactor, the catalytic reaction was carried out at 300 °C using the composite catalyst consisting of 0.1 g of Cu-Zn-Al (6:3:1) oxide, which was obtained by calcination at 500 °C, and 0.9 g of HB zeolite (SiO₂/Al₂O₃=28.5). The cold trap between the first and second reactors was equipped to remove H₂O formed in the first reactor unless otherwise noted. When the temperature of the first reactor was set at 250 °C as an optimal temperature for the methanol synthesis (see runs 7-10 of Table 1), the yield of C₂₊ hydrocarbons was only 1.19 C-mol% (run 1). In the catalytic reaction without the cold trap feeding all products formed in the first reactor including H₂O and methanol to the second reactor, C₂₊ hydrocarbons were obtained in 4.31 C-mol% yield (run 2). Since the yield of C₂₊ hydrocarbons was higher than that of methanol provided from the first reactor (2.66 C-mol%), this methanol also promoted the CO₂ hydrogenation reaction. When the reaction temperature of the first reactor was raised

with using the cold trap, the yields of C_{2+} hydrocarbons increased monotonically (runs 3-5). At over 400 °C (runs 4 and 5), the yields of C_{2+} hydrocarbons became higher than that of the reaction at 250 °C without the cold trap (run 2). The best yield of C_{2+} hydrocarbons (6.15 C-mol%) was observed in the reaction that the temperature of the first reactor was set at 420 °C after a time-on-stream of 1 h (run 5). This yield of C_{2+} hydrocarbons was greatly over the equilibrium conversion of CO_2 to methanol at 300 °C under 1 MPa (3.7 %). The yield of C_{2+} hydrocarbons diminished almost linearly with time to become 5.45 C-mol% after a time-on-stream of 6 h (run 6). This decrease was approximately equivalent to the increase of CO. It is thought that the degradation of the acidic site of the HB zeolite by coke formation [12-15] inhibited the MTG reaction to result in preferential decomposition of methanol to CO. When another HB zeolite with a SiO_2/Al_2O_3 ratio of 41.6 (HSZ-940HOA) was used for the composite catalyst, the yield of C_{2+} hydrocarbons was lower (1.28 C-mol%; run 7). Since considerable amounts of methanol and DME were yielded, the MTG reaction progressed insufficiently. These results suggested that the amount of acidic sites in HB zeolite is a crucial factor for the high yield production of C_{2+} hydrocarbons. On the other hand, the composite catalyst obtained from Cu-Zn (3:7) oxide had a lower catalytic activity even in the two-stage reactor system (run 8).

(Table 2)

The low methane yield and the predominant production of C_3 and C_4 paraffins (propane and butane) with a high iso-butane selectivity in all C_4 hydrocarbons (about 82 %) indicated that these hydrocarbons were obtained not by F-T type reaction but by the MTG reaction. It is also obvious that this MTG reaction was not caused by the methanol fed from the first reactor, because CO formation was exclusive in the first

reactor (see run 10 of Table 1). The methanol synthesis and the following MTG reaction produced these hydrocarbons in the second reactor. Although the simple MTG reaction over HB zeolite generally produces light olefins and C₅₊ hydrocarbons in considerable selectivities [13], both the yields of olefins and C₅₊ hydrocarbons were poor over the composite catalyst. We reported in our previous papers that the hydrogenation of light olefins obtained from the MTG reaction occurs over the methanol synthesis catalysts to afford the corresponding paraffins, inhibiting the olefin formation and the elongation of carbon chains in the composite catalysts [29-34]. The analogous reactions resulted in the predominant production of C₂-C₄ paraffins even in the two-stage reactor system.

3.4. Effect of water formed in the first reactor

The run 9 of Table 2 shows the result of the CO₂ hydrogenation at 420 °C without the cold trap for H₂O removal. The yield of C₂₊ hydrocarbons decisively decreased to 0.30 C-mol%. It is noteworthy that the CO₂ conversion was also reduced to 25 % despite about 37 % of CO₂ must be converted to CO in the first reactor according to the run 10 of Table 1. Since the equilibrium conversion of CO₂ to CO at 300 °C was about 23.4 % [20], CO was overabundance toward the equilibrium ratio under the conditions of the second reactor (300 °C, 0.98 MPa). The feeding of H₂O to the gas mixture without using the cold trap led to water-gas-shift (WGS) reaction to reduce the content of CO. It is thought that the poor production of C₂₊ hydrocarbons in the run 9 was caused from the decrease of CO abundance in the second reactor. On the other hand, when the cold trap was used, no WGS reaction progressed by the absence of H₂O (run 5). Thus, it is clear that the cold trap for removing H₂O is an essential component of this two-stage reactor system for the high yield production of C₂₊ hydrocarbons.

3.5. C_{2+} hydrocarbon production using the two-stage reactor system

Fig. 3 presents the CO_2 hydrogenation reaction taking place over the composite catalyst in the second reactor. There are two reaction behaviors of methanol that determine the yield of C_{2+} hydrocarbons. The first reaction leading to the high yield of C_{2+} hydrocarbons is the transportation of methanol to the HB zeolite particle and the following MTG reaction. The second one resulting in the poor yield of C_{2+} hydrocarbons is the decomposition of methanol to CO over the Cu-Zn-Al oxide [33]. In the case of the two-stage reactor system with the cold trap, the excess amount of CO toward the equilibrium composition in the second reactor suppresses the methanol decomposition to CO, because this reaction further increased the overabundance of CO. In addition, the high content of CO in the reaction gas is reported to be advantageous to the methanol synthesis from CO_2 thermodynamically [20]. Thus, the effective transportation of much more amount of methanol into HB zeolite particle takes place to produce C_{2+} hydrocarbons in higher yields. The consumption of methanol by the MTG reaction efficiently shifts the equilibrium of the methanol synthesis from CO_2 to accelerate the production of C_{2+} hydrocarbons (see Fig. 1). In the effective cases, the yields of C_{2+} hydrocarbons exceeded the equilibrium conversion of the methanol synthesis from CO_2 under 1 MPa.

3.6. Particle size effect on the production of C_{2+} hydrocarbons

In the last part of the section 3.1, we proposed that two essential requirements to the composite catalyst for the high yield production of C_{2+} hydrocarbons; (1) the suppression of the methanol decomposition to CO over the Cu-Zn-Al oxide and (2) the

rapid transportation of methanol into the HB zeolite. The results above indicated that the first requirement was achieved using the two stage reactor with the cold trap. On the other hand, the utilization of smaller particles of Cu-Zn-Al oxide for the composite catalyst is expect to respond to the second requirement, because the transfer of methanol from the smaller particle of Cu-Zn-Al oxide must occur more quickly from the larger one. When the calcination of the Cu-Zn-Al carbonate precursor was carried out at 350 °C, a Cu-Zn-Al oxide catalyst with smaller particle was obtained. This catalyst had the larger specific surface area (53 m²/g) and the smaller average particle size (1.747 μm) compared with the catalyst calcined at 500 °C used in the runs 1-9 of Table 2 (35 m²/g and 1.906 μm, respectively).

The composite catalyst obtained from the Cu-Zn-Al oxide calcined at 350 °C produced much higher C₂₊ hydrocarbons as shown in run 10 of Table 2. The yield of C₂₊ hydrocarbons was attained to 10 C-mol%. When the flow rate was decreased to 25 mL/min (SV=1500 mL/g-cat./h), the yield of C₂₊ hydrocarbons was further enhanced to about 15 C-mol% (run 11). As the conversions of CO₂ were approximately same between in the runs 10 and 11, the increase of C₂₊ hydrocarbons was compensated with the decrease of CO. Approximately 5 % of methanol that was decomposed to CO in the run 10 was converted to C₂₊ hydrocarbons by extending the contact with the composite catalyst. These results were well consistent with our reaction scheme that the inhibition of the methanol decomposition to CO and the immediate transportation of methanol to zeolite enhanced the C₂₊ hydrocarbon production (Fig. 3). The C₂₊ hydrocarbon yields observed in the runs 10 and 11 were much higher than the equilibrium conversion of CO₂ to methanol not only at 300 °C (3.7 %) but also at 250 °C (6.3 %) under 1 MPa. Therefore, these high yields are never achieved by the stepwise two-reaction process

separately combining the methanol synthesis and the MTG reaction [16,17].

Furthermore, even under 0.5 and 0.3 MPa, C₂₊ hydrocarbons were obtained in about 2.7 C-mol% or 1.9 C-mol%, respectively (runs 12 and 13). Thus, it was ascertained that the two stage reactor system satisfying the two requirements for the active composite catalyst produced C₂₊ hydrocarbons in high yields.

4. Conclusions

The two-stage reactor system consisting of the first reactor with the Cu-Zn-Al oxide for the RWGS reaction from CO₂ to CO and the second reactor with the composite catalyst (Cu-Zn-Al oxide + HB zeolite) for the methanol synthesis and the MTG reaction was found to be an effective reaction process for the synthesis of C₂₊ hydrocarbons from CO₂ and H₂. The installation of the cold trap between the two reactors for the removal of H₂O yielded in the first reactor was essential for the high yield synthesis of C₂₊ hydrocarbons. The main hydrocarbons obtained were propane and iso-butane. These distributions indicated that the hydrocarbons were produced by the MTG reaction mechanism. The RWGS reaction of CO₂ to CO in the first reactor and the following H₂O removal led the high content of CO in the second reactor. The high ratio of CO to CO₂ was thermodynamically advantageous for the synthesis of methanol from CO₂, and the overabundance of CO also inhibited the decomposition of methanol to CO. These effects promoted the efficient transportation of methanol to the HB zeolite particle and finally achieved the high yield production of C₂₊ hydrocarbons using the composite catalyst. The employment of the smaller particle of Cu-Zn-Al oxide increased the yield of C₂₊ hydrocarbons to about 15 C-mol%, which was higher than the equilibrium conversion of CO₂ to methanol even at 250 °C. Therefore, it was

demonstrated that the composite catalyst system is superior to the stepwise two-reaction process separately combining the methanol synthesis and the MTG reaction. The main products, C₃-C₄ paraffins, were the primary component of LPG and the high selectivity of branched hydrocarbons like iso-butane will be advantageous for the production of high octane value fuels. Thus, the two-stage reactor system that accomplished a breakthrough in the direct production of C₂₊ hydrocarbons from CO₂ will contribute to the construction of carbon recycle system using C₂₊ hydrocarbon fuels.

Acknowledgments

This work was partly supported by the Advanced Low Carbon Technology Research and Development Program from the Japan Science and Technology Agency (JST-ALCA).

References and notes

- [1] G. Centi, E.A. Quadrelli, S. Perathoner, Catalysis for CO₂ conversion: A key technology for rapid introduction of renewable energy in the value chain of chemical industries, *Energy & Environmental Science* 6 (2013) 1711–1731.
- [2] W. Wang, S. Wang, X. Ma, J. Gong, Recent advances in catalytic hydrogenation of carbon dioxide, *Chemical Society Review* 40 (2011) 3703–3727.
- [3] C. Song, Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing, *Catalysis Today* 115 (2006) 2–32.

- [4] U. Rodemerck, M. Holenňa, E. Wagner, Q. Smejkal, A. Barkschat, M. Baerns, Catalyst development for CO₂ hydrogenation to fuels, *ChemCatChem* 5 (2013) 1948–1955.
- [5] J. Wang, Z. You, Q. Zhang, W. Deng, Y. Wang, Synthesis of lower olefins by hydrogenation of carbon dioxide over supported iron catalysts, *Catalysis Today* 215 (2013) 186–193.
- [6] P. Kaiser, R.B. Unde, C. Kern, A. Jess, Production of liquid hydrocarbons with CO₂ as carbon source based on reverse water-gas shift and Fischer-Tropsch synthesis, *Chemie Ingenieur Technik* 85 (2013) 489–499.
- [7] H. Ando, Q. Xu, M. Fujiwara, Y. Matsumura, M. Tanaka, Y. Souma, Hydrocarbon synthesis from CO₂ over Fe-Cu catalysts, *Catalysis Today* 45 (1998) 229–234.
- [8] F. Studt, I. Sharafutdinov, F. Abild-Pedersen, C.F. Elkjær, J.S. Hummelshøj, S. Dahl, I. Chorkendorff, J.K. Nørskov, Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol, *Nature Chemistry* 6 (2014) 320–324.
- [9] X.-M. Liu, G.Q. Lu, Z.-F. Yan, J. Beltramini, Recent advances in catalysts for methanol synthesis via hydrogenation of CO and CO₂, *Industrial & Engineering Chemistry Research* 42 (2003) 6518–6530.
- [10] O.-S. Joo, K.-D. Jung, I. Moon, A.Y. Rozovskii, G.I. Lin, S.-H. Han, S.-J. Uhm, Carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction (the CAMERE process), *Industrial & Engineering Chemistry Research* 38 (1999) 1808–1812.
- [11] M. Fujiwara, H. Ando, M. Tanaka, Y. Souma, Hydrogenation of carbon dioxide over Cu-Zn-Cr oxide catalysts, *Bulletin of the Chemical Society of Japan* 67 (1994) 546–550.

- [12] U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Conversion of methanol to hydrocarbons: How zeolite cavity and pore size controls product selectivity, *Angewandte Chemie International Edition* 51 (2012) 5810–5831.
- [13] T. Mokrani, M. Scurrell, Gas conversion to liquid fuels and chemicals: The methanol route – Catalysis and processes development, *Catalysis Reviews* 51 (2009) 1–145.
- [14] J.F. Haw, W. Song, D.M. Marcus, J.B. Nicholas, The mechanism of methanol to hydrocarbon catalysis, *Accounts of Chemical Research* 36 (2003) 317–326.
- [15] M. Stöcker, Methanol-to-hydrocarbons: Catalytic materials and their behavior, *Microporous and Mesoporous Materials* 29 (1999) 3–48.
- [16] T. Inui, Recent advance in catalysis for solving energy and environmental problems, *Catalysis Today* 51 (1999) 361–368.
- [17] T. Inui, K. Fujioka, Y. Fujii, T. Takeguchi, H. Nishiyama, M-H. Inoue, W. Tanakulrungsank, Highly active catalysts for syngas production from natural gas and its consecutive conversion to methanol and more valuable hydrocarbons, *Studies in Surface Science and Catalysis* 81 (1994) 361–366.
- [18] E.L. Fornero, D.L. Chiavassa, A.L. Bonivardi, M.A. Baltanás, CO₂ capture via catalytic hydrogenation to methanol: Thermodynamic limit vs. ‘kinetic limit’, *Catalysis Today* 172 (2011) 158–165.
- [19] F. Gallucci, A. Basile, A theoretical analysis of methanol synthesis from CO₂ and H₂ in a ceramic membrane reactor, *International Journal of Hydrogen Energy* 32 (2007) 5050–5058.

- [20] W.-J. Shen, K.-W. Jun, H.-S. Choi, K.-W. Lee, Thermodynamic investigation of methanol and dimethylether synthesis from CO₂ hydrogenation, Korean Journal of Chemical Engineering 17 (2000) 210-216.
- [21] S. Ohyama, Possibility of catalytic conversion of carbon dioxide to methanol, Evaluation of catalytic conversion of carbon dioxide to methanol, Central Research Institute of Electric Power Industry Research Reports (1994) T93101.
- [22] C. Li, X. Yuan, K. Fujimoto, Direct synthesis of LPG from carbon dioxide over hybrid catalysts comprising modified methanol synthesis catalyst and β -type zeolite, Applied Catalysis A: General 475 (2014) 155–160.
- [23] X. Ni, Y. Tan, Y. Han, N. Tsubaki, Synthesis of isoalkanes over Fe–Zn–Zr/HY composite catalyst through carbon dioxide hydrogenation, Catalysis Communications 8 (2007) 1711–1714.
- [24] R. Bai, Y. Tan, Y. Han, Study on the carbon dioxide hydrogenation to iso-alkanes over Fe–Zn–M/zeolite composite catalysts, Fuel Processing Technology 86 (2004) 293–301.
- [25] Y.-K. Park, K.-C. Park, S.-K. Ihm, Hydrocarbon synthesis through CO₂ hydrogenation over CuZnOZrO₂/zeolite hybrid catalysts, Catalysis Today 44 (1998) 165–173.
- [26] J.-K. Jeon, K.-E. Jeong, Y.-K. Park, S.-K. Ihm, Selective synthesis of C₃–C₄ hydrocarbons through carbon dioxide hydrogenation on hybrid catalysts composed of a methanol synthesis catalyst and SAPO, Applied Catalysis A: General 124 (1995) 91–106.

- [27] T. Inui, K. Kitagawa, T. Takeguchi, T. Hagiwara, Y. Makino, Hydrogenation of carbon dioxide to C₁-C₇ hydrocarbons via methanol on composite catalysts, *Applied Catalysis A: General* 94 (1993) 31–44.
- [28] K. Fujimoto, T. Shikada, Selective synthesis of C₂-C₅ hydrocarbons from carbon dioxide utilizing a hybrid catalyst composed of a methanol synthesis catalyst and zeolite, *Applied Catalysis* 31 (1987) 13–23.
- [29] Y. Tan, M. Fujiwara, H. Ando, Q. Xu, Y. Souma, Syntheses of iso-butane and branched higher hydrocarbons from carbon dioxide and hydrogen over composite catalysts, *Industrial & Engineering Chemistry Research* 38 (1999) 3225–3229.
- [30] M. Fujiwara, R. Kieffer, H. Ando, Q. Xu, Y. Souma, Change of catalytic properties of Fe-ZnO/zeolite composite catalyst in the hydrogenation of carbon dioxide, *Applied Catalysis A: General* 154 (1997) 87–101.
- [31] M. Fujiwara, H. Ando, M. Matsumoto, Y. Matsumura, M. Tanaka, Y. Souma, Hydrogenation of carbon dioxide over Fe-ZnO/zeolite composite catalysts, *Chemistry Letters* (1995) 839–840.
- [32] M. Fujiwara, H. Ando, M. Tanaka, Y. Souma, Hydrogenation of carbon dioxide over Cu-Zn-Chromate/zeolite composite catalyst: Study on the effects of reaction behavior of olefins on hydrocarbon synthesis, *Applied Catalysis A: General* 130 (1995) 105–116.
- [33] M. Fujiwara, R. Kieffer, H. Ando, Y. Souma, Development of composite catalysts made of Cu-Zn-Cr oxide/zeolite for the hydrogenation of carbon dioxide, *Applied Catalysis A: General* 121 (1995) 113–124.

- [34] M. Fujiwara, Y. Souma, Hydrocarbon synthesis from carbon dioxide and hydrogen over Cu-Zn-Cr oxide/zeolite hybrid catalysts, *Chemical Communications* (1992) 767–768.
- [35] R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn, J.B. Bulko, T.P. Kobylinski, Catalytic synthesis of methanol from CO/H₂: I. Phase composition, electronic properties, and activities of the Cu/ZnO/M₂O₃ catalysts, *Journal of Catalysis* 56 (1979) 407–429.
- [36] Y. Matsumura, W.-J. Shen, Methanol decomposition and synthesis over palladium catalysts, *Topics in Catalysis* 22 (2003) 271–275.
- [37] W.-H. Cheng, Development of methanol decomposition catalysts for production of H₂ and CO, *Accounts of Chemical Research* 32 (1999) 685–691.

Table 1. CO₂ hydrogenation using single reactor^a

Run	Weight ratio (g/g) ^b	Temp. (°C)	Flow rate (mL/min)	CO ₂ conv. (%)	Selectivity (C-mol%)								C ₂₊ yield (C-mol%) ^c
					CO	C ₁	C ₂	C ₃	C ₄	C ₅₊	MeOH	DME	
1	0.9/0.9	300	50	22.8	94.2	<0.1	0.6	<0.1	<0.1	0	3.4	1.7	0.16
2	0.5/0.9	300	50	22.9	93.7	<0.1	1.0	<0.1	0	0	3.4	1.8	0.25
3	0.1/0.9	300	50	20.6	91.9	0.1	1.1	0.6	0.5	<0.1	3.6	2.1	0.47
4 ^d	0.1/0.9	300	50	9.6	98.4	0.1	0.3	0.9	0.4	0.0	0.0	0.0	0.15
5	0.1/0.9	300	100	15.9	87.8	0.2	0.7	1.7	1.7	0.2	4.5	3.2	0.68
6	0.1/0.9	300	150	12.7	86.6	0.2	0.5	2.0	2.1	0.3	4.7	3.6	0.62
7	1.0/0.0	250	50	5.2	48.9	0.0	0.0	0.0	0.0	0.0	51.1	0.0	0.00 (2.66)
8	1.0/0.0	300	50	17.7	88.6	<0.1	0.0	0.0	0.0	0.0	11.3	0.0	0.00 (2.00)
9	1.0/0.0	400	50	34.2	99.4	0.2	0.1	0.1	0.0	0.0	0.2	0.0	0.06 (0.07)
10	1.0/0.0	420	50	37.1	99.2	0.4	0.2	0.1	<0.1	0.0	<0.1	0.0	0.13 (0.02)

^a Reaction conditions: 0.98 MPa, H₂/CO₂=3, catalytic activity after a time-on-stream of 1 h, all Cu-Zn-Al (6:3:1) oxide catalysts were obtained by calcination at 500 °C for 4 h.

^b Weight ratio of Cu-Zn-Al (6:3:1) oxide/HB zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3=28.5$).

^c In parentheses, the yields of methanol.

^d Cu-Zn (3:7) oxide was used.

Table 2. CO₂ hydrogenation over Cu-Zn-Al (6:3:1) oxide + HB composite catalysts using two-stage reactor system^a

Run	Temp. of first reactor (°C)	Pressure (MPa)	Flow rate (mL/min)	CO ₂ conv. (%)	Selectivity (C-mol%)								C ₂₊ yield (C-mol%)
					CO	C ₁	C ₂	C ₃	C ₄	C ₅₊	MeOH	DME	
1	250	0.98	50	25.3	91.3	0.2	1.4	1.5	1.5	0.3	2.4	1.4	1.19
2 ^b	250	0.98	50	20.7	73.2	1.3	1.2	5.9	12.0	1.7	3.1	1.6	4.31
3	300	0.98	50	32.5	90.8	0.3	1.4	2.7	2.7	0.5	1.1	0.5	2.37
4	400	0.98	50	43.2	87.6	0.5	1.4	5.0	4.5	0.5	0.4	<0.1	4.92
5	420	0.98	50	45.9	85.4	0.8	1.3	5.9	5.6	0.6	0.3	<0.1	6.15
6 ^c	420	0.98	50	45.8	87.1	0.7	1.3	5.2	4.9	0.5	0.2	<0.1	5.45
7 ^d	420	0.98	50	45.8	89.3	0.4	0.6	0.7	1.2	0.3	2.4	5.1	1.28
8 ^e	420	0.98	50	45.2	95.2	0.4	0.7	1.6	1.8	0.2	0.1	<0.1	1.94
9 ^b	420	0.98	50	25.0	95.7	0.7	1.0	0.2	0.0	0.0	1.8	0.6	0.30
10 ^f	420	0.98	50	47.2	77.5	0.9	1.1	9.0	10.2	1.0	0.2	0.1	10.05
11 ^f	420	0.98	25	47.8	66.8	1.4	1.7	15.0	13.6	1.3	0.2	<0.1	15.10

12 ^f	420	0.5	50	45.2	93.5	0.3	0.5	2.6	2.5	0.4	0.1	0.1	2.71
13 ^f	420	0.3	50	43.2	95.3	0.2	0.4	1.8	1.8	0.3	0.1	0.1	1.86

^a Reaction conditions: catalyst in the first reactor 1 g of Cu-Zn-Al (6:3:1) oxide obtained by calcination at 500°C for 4 h, catalyst in the second reactor 0.1 g of Cu-Zn-Al (6:3:1) oxide obtained by calcination at 500°C for 4 h and 0.9 g of HB zeolite (SiO₂/Al₂O₃=28.5), 300 °C, 0.98 MPa, H₂/CO₂=3, catalytic activity after a time-on-stream of 1 h.

^b Without the cold trap.

^c After a time-on-stream of 6 h in run 5.

^d HB zeolite (SiO₂/Al₂O₃=41.6) was used.

^e Cu-Zn (3:7) oxide was used.

^f Cu-Zn-Al (6:3:1) oxide obtained by calcination at 350°C for 3 h was used.

Legends of Figures

Fig. 1 Reaction scheme of CO₂ hydrogenation over composite catalyst consisting of methanol synthesis catalyst and zeolite

Fig. 2 Schematic diagram of the two-stage reactor system

Fig. 3 Reaction passes of CO₂ hydrogenation over the composite catalyst consisting of methanol synthesis catalyst and zeolite

Figure 1 Masahiro Fujiwara et al.

Figure 2 Masahiro Fujiwara et al.

Figure 3 Masahiro Fujiwara et al.