

## Slurry-Phase CO<sub>2</sub> Hydrogenation to Hydrocarbons over a Precipitated Fe-Cu-Al/K Catalyst : Investigation of Reaction Conditions

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**Abstract**—The hydrogenation of CO<sub>2</sub> to hydrocarbons over a precipitated Fe-Cu-Al/K catalyst was studied in a slurry reactor for the first time. Reducibility of the catalyst and effect of reaction variables (temperature, pressure and H<sub>2</sub>/CO<sub>2</sub> ratio of the feed gas) on the catalytic reaction performance were investigated. The reaction results indicated that the Fe-Cu-Al/K catalyst showed a good CO<sub>2</sub> hydrogenation performance at a relatively low temperature (533 K). With the increase of reaction temperature CO<sub>2</sub> conversion and olefin to paraffin (O/P) ratio in C<sub>2</sub>-C<sub>4</sub> hydrocarbons as well as the selectivity to C<sub>2</sub>-C<sub>4</sub> fraction increased, while CO and CH<sub>4</sub> selectivity showed a reverse trend. With the increase in reaction pressure, CO<sub>2</sub> conversion and the selectivity to hydrocarbons increased, while the CO selectivity and O/P ratio of C<sub>2</sub>-C<sub>4</sub> hydrocarbons decreased. The investigation of H<sub>2</sub>/CO<sub>2</sub> ratio revealed that CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity increased while CO selectivity and O/P ratio of C<sub>2</sub>-C<sub>4</sub> decreased with increasing H<sub>2</sub>/CO<sub>2</sub> ratio.

Key words : CO<sub>2</sub> Hydrogenation, Hydrocarbon Synthesis, Precipitated Fe-Cu-Al/K Catalyst, Slurry Phase Reactor, Reaction Conditions

### INTRODUCTION

Recently, the global warming problem has received increasing attention, and extensive efforts have been made to explore the possible ways for fixation and disposal of greenhouse gases [Choi et al., 1996; Jun et al., 1998; Lee et al., 1996, 1998]. Conversion of greenhouse gases to useful chemicals may be one of the promising ways to mitigate the problem. Carbon dioxide is the most important greenhouse gas arising from human activities. Increases in CO<sub>2</sub> concentrations contribute over half of the enhanced green house effect, the rest being mainly due to increases in the concentrations of methane, halocarbons and nitrous oxide [Edwards, 1995]. Therefore, development of the technologies for hydrogenation of CO<sub>2</sub> to valuable chemicals such as hydrocarbons and alcohol is of great significance, which may provide an effective way not only to curtail the growing amount of carbon dioxide emission, but also to improve economic benefits.

In recent years, several studies on CO<sub>2</sub> hydrogenation to hydrocarbons have been published, which can be categorized into two groups according to the catalyst and reaction route. One is the CO<sub>2</sub> hydrogenation to hydrocarbons via methanol synthesis [Park et al., 1995, 1997; Souma et al., 1995] conducted using composite catalysts (i.e. methanol synthesis catalysts+zeolite); and the other is the CO<sub>2</sub> hydrogenation to hydrocarbons via Fischer-Tropsch synthesis conducted using iron-based catalysts [Dziembaj et al., 1992; Weatherbee and Bar-

tholomew, 1984; Trovarelli et al., 1993; Kaspar et al., 1994; Choi et al., 1996; Lee et al., 1992]. Previous studies were exclusively conducted on fixed-bed reactors and at relatively high temperatures (above 573 K). A thermodynamic study showed that CO<sub>2</sub> hydrogenation to hydrocarbons is very exothermic (100-125 KJ/mol) and that it is desirable for the reaction to be conducted at temperatures not exceeding 550 K [Paushkin et al., 1988].

Previous studies indicated that hydrogenation of CO<sub>2</sub> to hydrocarbons over iron-based catalysts via two consecutive steps [Lee et al., 1989, 1992]. CO<sub>2</sub> first reacts with H<sub>2</sub> to form CO and H<sub>2</sub>O, the so-called reverse water gas shift reaction (RWGS) followed by Fischer-Tropsch (F-T) CO hydrogenation reaction. Since iron-based catalysts are widely used in both WGS and F-T reactions, iron-based catalysts seem to be the potential catalysts for hydrogenation of CO<sub>2</sub> to hydrocarbons. On the other hand, copper and potassium are two important promoters for iron-based catalysts, of which copper is reportedly able to promote the reduction of catalysts while potassium enhances the basicity of the catalysts [Dry, 1981].

In this study, a slurry-bed reactor system which is known to have a better heat transfer efficiency and many other advantages compared to the fixed-bed reactors was used, and a precipitated Fe-Cu-Al/K catalyst was employed for the CO<sub>2</sub> hydrogenation to hydrocarbons.

### EXPERIMENTAL

#### 1. Catalyst Preparation

The catalyst preparation involved two steps : preparation of the Fe-Cu-Al precursor followed by potassium impregnation. The Fe-Cu-Al precursor was prepared by continuous precipi-

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**Table 1. Composition and physical properties of the catalyst**

Composition (on a mass basis)	100Fe : 8.7Cu : 15.7Al : 8 K
BET surface area (m <sup>2</sup> /g)	134.3
Pore volume (cc/g)	0.19
Mean pore diameter (Å)	56.8*

\*: Pore diameter = (4 × pore volume)/surface area

tation from an aqueous solution of metal nitrates with ammonium hydroxide at a constant pH value. The resulting precipitate was subjected to multiple filtration and washing cycles, then dried in air at 383 K for 24 hour. Atomic absorption spectroscopy (AAS) was conducted for the dried sample to determine the composition of precursor as well as the amount of potassium needed. After potassium impregnation by incipient wetness technique, the catalyst was dried at 383 K for 48 hr, and then calcined at 723 K for 5 hr. The sample thus obtained was crushed and sieved to the required particle size (< 75 μm). The composition and physical properties of the final catalyst are shown in Table 1.

## 2. Temperature-Programmed Reduction (TPR) of the Catalyst

Reduction of catalyst *in-situ* is preferable for most of the process. But for slurry-phase reactors the catalyst requires to be reduced at temperatures much lower than the boiling point of the reaction medium employed. In order to get the reduction feature of the catalyst and to check whether the Fe-Cu-Al/K catalyst is suitable for *in-situ* reduction, thermo-gravimetric analysis (TGA) of the catalyst during temperature programmed and isothermal reduction was carried out in a SET-ARAM TGDTA 92 instrument.

## 3. Reaction Procedures and Product Analysis

Hydrogenation reactions were conducted in a 500-cm<sup>3</sup> continuous stirred tank reactor (CSTR). The system process diagram is shown in Fig. 1. In a typical experiment, 15 g of the catalyst (< 200 mesh) and 200 g of squalane as a reaction medium were loaded into the reactor. Prior to reaction the cat-

alyst was reduced *in-situ* with N<sub>2</sub>/H<sub>2</sub> (10 % of H<sub>2</sub>) mixture at standard reduction conditions of 533-573 K and 81 psig unless otherwise stated. The reason for performing the reduction at an elevated pressure is to minimize the loss of reaction medium during reduction. The reduction process was monitored by an on-line GC, in which the same N<sub>2</sub>/H<sub>2</sub> mixture was used as the reference gas for detecting H<sub>2</sub> consumption with a thermal conductivity detector (TCD). For the reactions, the flow rates of the reactant gases (H<sub>2</sub> and CO<sub>2</sub>) as well as of internal standard gas (Ar) were controlled by thermal mass flow controllers (LOKAS automation). After flow regulation, the three gases were mixed in a 600-cm<sup>3</sup> pressure vessel prior to their entering the reactor. The mixed gases then were introduced into the bottom of reactor through a nozzle tube. After leaving the reactor, the exit gas passed through a high-pressure cold-trap (275 K) to condense liquid products. The non-condensable gases from the cold-trap passed through a backpressure regulator to reduce the pressure of exit product steam to atmospheric pressure, then divided into two paths: the one vented directly and the other flowed to the on-line gas chromatograph (GC). The flow to the on-line GC sampling valves was kept at 30 cc/min.

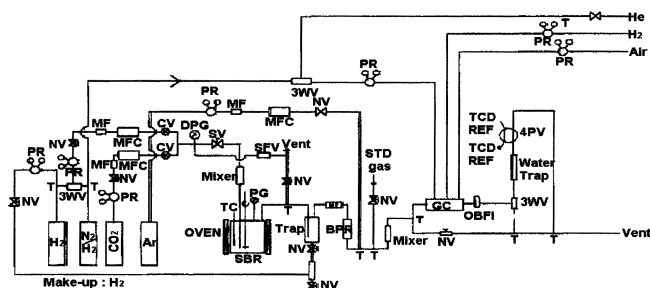
The feed-gas and non-condensable products were analyzed on-line with a DS 6200 GC: Ar, CO<sub>2</sub>, CO and CH<sub>4</sub> were analyzed with a 6-foot carbosphere column and a TCD, while light hydrocarbons (C<sub>1</sub>-C<sub>3</sub>) were analyzed with a 30-meter GS-Q capillary column and a flame ionization detector (FID). Liquid hydrocarbons and water collected in the trap were weighed and analyzed off-line with a Hewlett Packard 5890 series II GC equipped with a SPB-1 capillary column and FID.

Because Ar was added as an internal standard, CO<sub>2</sub> conversion could be calculated directly by comparison of differences in the CO<sub>2</sub>/Ar peak ratio in the feed and during the reaction. CO and CH<sub>4</sub> flow in the effluent were calculated by using the calibration curve obtained prior to the reaction. The assumption made is that the volume of Ar is the same in the feed gas and in exit gas. The analysis of CH<sub>4</sub> was used as the link to correlate the peaks of FID and TCD.

## RESULTS AND DISCUSSION

### 1. Reducibility of the Catalyst

TPR profiles of the catalyst are shown in Fig. 2. It is seen that there were four weight loss peaks in TG-DTA spectra. The first peak (ca. 343 K) was probably attributed to de-moisture of the catalyst. The ensuing three peaks were interpreted to be formed by the reduction of the catalyst, which is in good accordance with the three-step reduction mechanism of Fe<sub>2</sub>O<sub>3</sub>: Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → FeO → Fe [Shroff et al., 1995]. Due to the introduction of the reduction promoter (Cu), the initial reduction temperature was decreased to about 413 K. Another point that can be inferred from Fig. 2 is that the catalyst can be reduced to FeO at about 523 K-weight loss was corresponding to ca. 15 %. The FeO phase is reported to be responsible for the initiation of CO hydrogenation [Bukur et al., 1995]. Based on the above-obtained results, the *in-situ* isothermal reduction of the catalyst with N<sub>2</sub>/H<sub>2</sub> mixture (10 mole % of H<sub>2</sub>)

**Fig. 1. Diagrammatic flow sheet of the reactor system.**

- |                                 |                           |
|---------------------------------|---------------------------|
| BPR: Back pressure regulator    | CV: Check valve           |
| DPG: Digital pressure gauge     | MF: Microfilter           |
| GC: Gas chromatography          | MFC: Mass flow controller |
| MV: Metering valve              | NV: Needle valve          |
| OBFI: Oil bubble flow indicator | PG: Pressure gauge        |
| PR: Pressure regulator          | SV: Stop valve            |
| SBR: Slurry bed reactor         | SFV: Safety valve         |
| 3WV: 3-way valve                | 4PV: 4-port valve         |
| TC: Thermocouple                |                           |

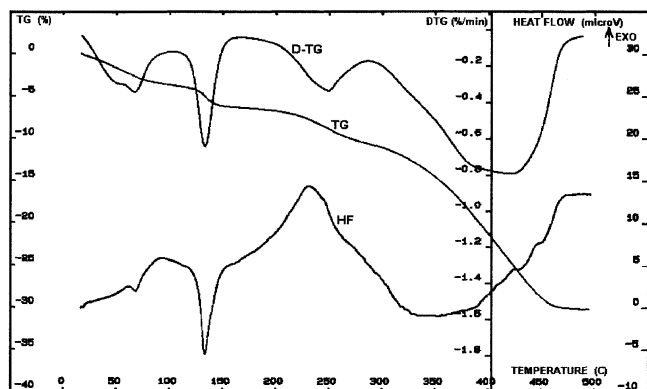


Fig. 2. TPR profiles of the catalyst.

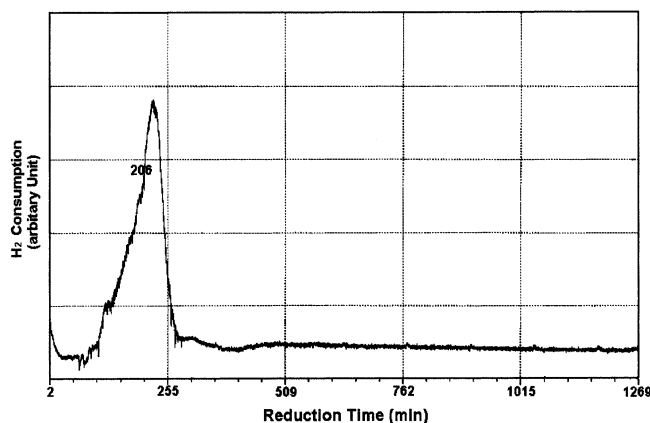


Fig. 3. Reduction curve of the catalyst.

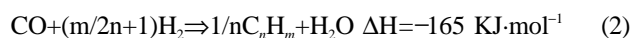
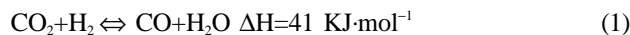
(reduction conditions : T=533 K, P=81 psig, W/F=15 g-cat./h/mol N<sub>2</sub>+H<sub>2</sub>)

was conducted in a slurry-bed reactor at 533 K and 81 psig. The consumption of H<sub>2</sub> during reduction was monitored and curved continuously (Fig. 3). It is easily found from the reduction curve of the catalyst that reduction process of the catalyst can be finished at 533 K within 8 hours. This indicates that the catalyst is suitable for *in-situ* reduction.

## 2. Effect of Reaction Temperature

The results of CO<sub>2</sub> hydrogenation over the Fe-Cu-Al/K catalyst at different temperatures in terms of CO<sub>2</sub> conversion, CO selectivity, hydrocarbon (HC) distribution and olefin/paraffin (O/P) ratio are shown in Table 2. It is obvious that CO<sub>2</sub> conversion and O/P ratio increased with the increase in reaction temperature, but CO and CH<sub>4</sub> selectivity showed a reverse trend. As for the hydrocarbon distribution, C<sub>2</sub>-C<sub>4</sub> fraction showed a positive response to temperature, while C<sub>5+</sub> decreased with increasing reaction temperature.

As mentioned in the introduction, CO<sub>2</sub> hydrogenation over iron-based catalysts proceeds via two sequential steps :



The first step is a reverse water gas shift reaction (RWGS) which converts CO<sub>2</sub> to CO ; and the subsequent step is CO hydrogenation to hydrocarbons (Fischer-Tropsch synthesis), with CO being the intermediate. Therefore, the CO selectivity depends not only on the CO<sub>2</sub> conversion (RWGS) rate but also on the CO hydrogenation (Fischer-Tropsch synthesis) rate. For a reversible reaction of Eq. (1), increasing temperature would favor the reaction toward the endothermic direction. It is reasonable that CO<sub>2</sub> conversion increases kinetically as well as thermodynamically with increasing temperature as observed in Table 2, because RWGS is an endothermic reaction. The decrease in selectivity to CO with increasing temperature indicates that influence of temperature on CO hydrogenation reaction is more pronounced than on the CO<sub>2</sub> hydrogenation under the conditions employed. As for the O/P ratio in the product, it is well established that the O/P ratio depends not only on the primary olefin selectivity in F-T synthesis but also on the activity of secondary hydrogenation of the primary product [Dry, 1981]. Both steps are related to the adsorbed H/C ratio on the catalyst surface. The higher the surface H/C ratio, the higher the saturation degree of the product. This is because the enhanced CO and CO<sub>2</sub> hydrogenation resulting from increasing temperature would consume more adsorbed H species than C species on the catalyst surface stoichiometrically, which makes the adsorbed H/C ratio relatively lower. Consequently, a secondary reaction of olefin hydrogenation was inhibited, thereby the increased O/P ratio and decreased CH<sub>4</sub> selectivity were observed. With regards to the hydrocarbon distribution, it is easily understood that selectivity toward C<sub>2</sub>-C<sub>4</sub> fraction increased while selectivity to C<sub>5+</sub> decreased with temperature ; because the Fischer-Tropsch polymerization reaction is an exothermic reaction, increase of reaction temperature always shifts the product towards lower carbon number hydrocarbons.

## 2. Effect of Reaction Pressure

Table 3 shows the effect of reaction pressure on the CO<sub>2</sub> conversion and the product selectivity, in which it is seen that with the increase in reaction pressure CO<sub>2</sub> conversion as well as the selectivity to hydrocarbon products increased, while CO selectivity and O/P ratio of C<sub>2</sub>-C<sub>4</sub> hydrocarbons decreased.

In the two-step reaction mechanism, the first step reverse water gas shift reaction is not reaction pressure-dependent, because the number of molecules on the reactant side is the same

Table 2. Effect of reaction temperature on CO<sub>2</sub> hydrogenation performance\*

Temp. (K)	CO <sub>2</sub> conv. (%)	CO sel. (%)	CH <sub>4</sub> sel. (%)	Hydrocarbon distribution (C-atom %)					O/P ratio (molar)		
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5+</sub>	C <sub>2</sub> =/C <sub>2</sub> <sup>o</sup>	C <sub>3</sub> =/C <sub>3</sub> <sup>o</sup>	C <sub>4</sub> =/C <sub>4</sub> <sup>o</sup>
533	13.1	35.4	12.2	17.5	14.1	17.5	12.8	38.1	1.8	3.1	2.4
543	16.4	26.7	11.5	15.7	15.8	20.0	15.3	33.2	2.6	7.3	4.6
553	17.8	25.3	11.2	15.4	17.0	21.5	16.7	29.4	3.1	5.7	11.3

\* : Reaction conditions : P=240 psig, W/F=10 g-h/mol, H<sub>2</sub>/CO<sub>2</sub>=3/1, reductant gas : pure H<sub>2</sub>.

**Table 3. Effect of reaction pressure\***

Pressure (Psig)	CO <sub>2</sub> conv. (%)	CO sel. (%)	CH <sub>4</sub> sel. (%)	Hydrocarbon distribution (C-atom %)					O/P ratio (molar)		
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5+</sub>	C <sub>2</sub> =/C <sub>2</sub> <sup>o</sup>	C <sub>3</sub> =/C <sub>3</sub> <sup>o</sup>	C <sub>4</sub> =/C <sub>4</sub> <sup>o</sup>
145	15.7	30.6	11.2	15.6	12.0	14.2	10.3	47.9	3.2	8.5	3.7
220	18.4	28.3	11.4	14.7	11.9	14.0	10.1	49.3	2.9	8.1	3.5
295	19.5	21.4	11.5	13.7	11.9	15.7	11.8	46.9	2.7	7.7	3.4

\* : Reaction conditions : T=538 K, W/F=10 g-cat.h/mol (CO<sub>2</sub>+H<sub>2</sub>), H<sub>2</sub>/CO<sub>2</sub>=3, reduction gas : H<sub>2</sub>/N<sub>2</sub> mixture.

**Table 4. Effect of H<sub>2</sub> to CO<sub>2</sub> feed ratio\***

H <sub>2</sub> /CO <sub>2</sub> (%)	CO <sub>2</sub> conv. (%)	CO sel. (%)	CH <sub>4</sub> sel. (%)	Hydrocarbon distribution (C-atom %)					O/P ratio (molar)		
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5+</sub>	C <sub>2</sub> =/C <sub>2</sub> <sup>o</sup>	C <sub>3</sub> =/C <sub>3</sub> <sup>o</sup>	C <sub>4</sub> =/C <sub>4</sub> <sup>o</sup>
2/1	10.1	34.0	9.8	13.9	12.5	15.4	11.6	46.6	3.7	10.5	4.0
3/1	18.4	28.3	11.4	14.7	11.9	14.0	10.1	49.3	2.9	8.1	3.5
4/1	19.2	30.5	14.9	22.0	19.4	22.8	16.1	19.7	2.9	7.9	3.5

\* : Reaction conditions : T=538 K, P=220 psig, W/F=10 g-cat.h/mol (CO<sub>2</sub>+H<sub>2</sub>), reduction gas : H<sub>2</sub>/N<sub>2</sub> mixture.

as that on the product side. Hence, pressure has no effect on CO<sub>2</sub> conversion according to the chemical equilibrium theory, for the second step (F-T reaction) that the number of product molecules is less than the number of reactant molecules, is pressure dependent. Therefore, it is easily understood that the increase of reaction pressure would promote the F-T reaction, which consequently leads to a decrease in CO selectivity and an increase in hydrocarbon formation rate. As for the increased CO<sub>2</sub> conversion with pressure, which seems to be in disagreement with the chemical equilibrium theory, it can be interpreted by the following two aspects. It is well known that gas absorption into solvent is, within a certain range, proportional to the partial pressure of the gas. With increasing gas pressure, the concentration of the gas in the solvent also increased. As a result of the increase in concentration of reactant, the CO<sub>2</sub> conversion increased naturally. On the other hand, the enhancement of the F-T reaction caused by an increase in pressure would consume more CO. This, in turn, would cause a shift of equilibrium toward the reverse water gas shift reaction direction, which also can increase the CO<sub>2</sub> conversion.

### 3. Effect of H<sub>2</sub>/CO<sub>2</sub> Ratio

The effect of H<sub>2</sub>/CO<sub>2</sub> feed ratio on CO<sub>2</sub> conversion and product distribution is illustrated in Table 4, where it can be seen that CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity increased while CO selectivity and O/P ratio of C<sub>2</sub>-C<sub>4</sub> decreased with the increase of H<sub>2</sub>/CO<sub>2</sub> ratio. It can be visualized easily that with the increase in H<sub>2</sub>/CO<sub>2</sub> feed ratio, adsorbed H<sub>2</sub>/CO<sub>2</sub> ratio on catalyst surface also increased. As a result, hydrogenation reactions for CO<sub>2</sub> and CO as well as for the secondary hydrogenation of olefin were promoted. Therefore, an increase in CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity and a decrease in CO selectivity and O/P ratio were observed.

## CONCLUSIONS

The following conclusions can be obtained from the present study.

1. The precipitated Fe-Cu-Al/K catalyst used in this study

is suitable for *in-situ* reduction in the slurry-bed reactor and active for the reaction at low temperatures.

2. With the increase in reaction temperature CO<sub>2</sub> conversion, selectivity toward C<sub>2</sub>-C<sub>4</sub> hydrocarbons and O/P ratio increased, but CO selectivity decreased.

3. In the cases studied, CO<sub>2</sub> conversion and the selectivity to hydrocarbon products increased, while the CO selectivity and O/P ratio decreased with increasing reaction pressure.

4. H<sub>2</sub>/CO<sub>2</sub> feed ratio can influence both CO<sub>2</sub> conversion and product selectivity. In the cases studied, CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity increased with H<sub>2</sub>/CO<sub>2</sub> feed ratio while CO selectivity and O/P ratio showed the reverse trend.

Based on the above conclusions, the CO<sub>2</sub> hydrogenation reaction should be conducted at different conditions depending on the aim-product. In order to enhance the selectivity to olefins the CO<sub>2</sub> hydrogenation reaction should be carried out at higher temperature, medium pressure and lower H<sub>2</sub>/CO<sub>2</sub> ratio.

## REFERENCES

- Bukur, D. B., Koranne, M., Lang, X. S., Rao, K. R. P. M. and Huffman G. P., "Pretreatment Effect Studies with a Precipitated Iron Fischer-Tropsch Catalyst," *Appl. Catal. A: General* **126**, 85 (1995).
- Choi, P.-H., Jun, K.-W., Lee, S.-J., Choi, M.-J. and Lee, K.-W., "Hydrogenation of Carbon Dioxide over Alumina Supported Fe-K Catalysts," *Catal. Lett.*, **40**, 115 (1996).
- Dry, M. E., "Fischer-Tropsch Synthesis," *Catalysis-Science and Technology*, Anderson, J. R. and Boudart, M., eds., Springer-Verlag, **1** (1981).
- Dziembaj, R., Makowski, W. and Papp, H., "Carbon Dioxide Hydrogenation on Fe-Mn Oxide Catalyst Doped with Rh and La," *J. Mol. Catal.*, **75**, 81 (1992).
- Edwards, J. H., "Potential Sources of CO<sub>2</sub> and the Options for Its Large-Scale Utilisation Now and in the Future," *Catalysis Today*, **23**, 59 (1995).
- Jun, K.-W., Shen, W.-J., Rama Rao, K. S. and Lee, K.-W., Residual Sodium Effect on the Catalytic Activity of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> in Methanol Synthesis from CO<sub>2</sub> Hydrogenation," *Appl. Catal. A* :

- General*, **174**, 231 (1998).
- Kaspar, J., Graziani, M., Rahaman, A. M., Trovarelli, A., Vichi, E. J. S. and Silva, E. C. da, "Carbon Dioxide Hydrogenation over Iron Containing Catalysts," *Appl. Catal. A : General*, **117**, 125 (1994).
- Lee, E.-K., Kim, S.-B. and Hahm, H.-S., "Two Stage Strategy to Improve Methanol Yield in the Carbon Dioxide Hydrogenation Reaction," *HWAHAK KONGHAK*, **36**, 821 (1998).
- Lee, H.-J., Park, J.-W. and Hahm H.-S., "Methanol Synthesis by the Hydrogenation of Carbon Dioxide," *HWAHAK KONGHAK*, **34**, 716 (1996).
- Lee, J. F., Chern, W. S. and Lee, M. D., "Hydrogenation of Carbon Dioxide on Iron Catalysts Doubly Promoted with Manganese and Potassium," *The Can. J. Chem. Eng.*, **70**, 511 (1992).
- Lee, M. D., Lee J. F. and Chang C. S., "Hydrogenation of Carbon Dioxide on Unpromoted and Potassium Promoted Iron Catalysts," *Bull. Chem. Soc. Jpn.*, **62**, 2756 (1989).
- Park, S. E., Nam, S. S., Choi, M. J. and Lee, K.W., "Catalytic Reduction of Carbon Dioxide-The Effects of Catalysts and Reductants," *Energy Convers. Mgmt*, **36**(6-9), 573 (1995).
- Park, Y. K., Park, K. C., Jeong, K. E., Ihm, S. K. and Lee, D. K., "A Study on the Synthesis of Hydrocarbons through Carbon Dioxide Hydrogenation," *Kongop Hwahak*, **8**(1), 140 (1997).
- Paushkin, Ya. M., Zhorov, Yu. M., Lapidus, A. L. and Gorlov, E. G., "Hydrocarbons from Carbon Dioxide and Hydrogen," *Dokl. Akad. Nauk. SSSR*, **298**(2), 374 (1988).
- Shroff, M. D., Kalakkad, D. S., Coulter, K. E., Köhler, S. D., Harrington, M. S., Jackson, N. B., Sault, A. G. and Datye, A. K., "Activation of Precipitated Iron Fischer-Tropsch Synthesis Catalysts," *J. Catal.*, **156**, 185 (1995).
- Souma, Y., Ando, H., Fujiwara, M. and Kieffer, R., "Catalytic Hydrogenation of Carbon Dioxide to Hydrocarbons," *Energy Convers. Manage.*, **36**(6-9), 593 (1995).
- Trovarelli, A., Matteazzi, P., Dolcetti, G., Lutman, A. and Miani, F., "Nanophase Iron Carbides as Catalysts for Carbon Dioxide Hydrogenation," *Appl. Catal. A : General*, **95**, L9 (1993).
- Weatherbee, G. D. and Bartholomew, C. H., "Hydrogenation of CO<sub>2</sub> on Group VIII Metals IV Specific Activities and Selectivities of Silica-Supported Co, Fe, and Ru," *J. Catal.*, **87**, 352 (1984).