*Korean J. Chem. Eng.*, **18**(4), 463-467 (2001)

# Characteristics of Carbon Dioxide Hydrogenation in a Fluidized Bed Reactor

**Jun Sik Kim, Hak Ki Kim*, Sang Bong Lee*, Myoung Jae Choi*, Kyu Wan Lee* and Yong Kang†**

Dept. of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea
*Environment and Resource Team, KRICT, PO Box 107, Daejeon 305-600, Korea

(*Received 13 March 2001 • accepted 24 May 2001*)

**Abstract**−Characteristics of $CO_2$ hydrogenation were investigated in a fluidized bed reactor (0.052 m ID×1.5 m in height). Coprecipitated Fe-Cu-K-Al catalyst ($d_p$=75-90 μm) was used as a fluidized solid phase. It was found that the $CO_2$ conversion decreases but the CO selectivity increases, whereas the space-time-yield attains maximum values with increasing gas velocity. The $CO_2$ conversion has increased, but CO selectivity has decreased with increasing hydrogenation temperature, pressure or $H_2/CO_2$ ratio in the fluidized bed reactor. Also, the $CO_2$ conversion and olefin selectivity appeared to be higher in the fluidized bed reactor than those of the fixed bed reactor.

Key words: Carbon Dioxide, Hydrogenation, Fluidized Bed, Catalyst

## INTRODUCTION

There has been considerable interest in the utilization of carbon dioxide for the synthesis of valuable chemicals as a useful energy resource and environmental solution of global warming. One of the promising goals in carbon dioxide utilization is the selective synthesis of valuable chemicals by the chemical conversion through its hydrogenation [Choi et al., 1996; Nam et al., 1997]. There have been two kinds of methods for the hydrocarbon synthesis from $CO_2$ hydrogenation: the combination of methanol and hydrocarbon synthesis (MTG process), and the direct hydrocarbon synthesis using modified Fischer-Tropsch process. For the direct hydrogenation of carbon dioxide to hydrocarbons over various iron-based catalysts, K, V, Cr, Mn and Zn promoted iron catalysts have been prepared by precipitation or impregnation method. It has been reported that Fe-K catalyst gives relatively high $CO_2$ conversion as well as high selectivity of light olefins [Inui et al., 1997; Riedel et al., 1999; Yan et al., 1999].

It has been understood that the fluidized beds can be utilized efficiently for multiphase reactions such as the catalytic hydrogenation of carbon dioxide, because it can realize higher heat and mass transfer rate due to the effective contacting and mixing in comparison with any other contacting mode [Fan et al., 1989; Kang et al., 1996, 1999; Kim and Kang, 1997]. Moreover, the fluidized bed has been proposed as a excellent reactor in view of the conversion of syn-gas, selectivity of valuable products and economic feasibility in the multiphase reactions such as the Fischer-Tropsch process [Dry, 1996; Steyberg et al., 1999].

Thus, in the present study, a fluidized bed reactor has been employed for the effective hydrogenation of carbon dioxide by using Fe-Cu-K-Al catalyst as a fluidized solid phase. Effects of operating variables on the $CO_2$ conversion and product selectivity have been examined in the fluidized bed reactor. Also, the performance of fluidized bed compared with that of fixed bed has been discussed in terms of product selectivity and olefin/paraffin mole ratio as well as $CO_2$ conversion.

## EXPERIMENTAL

### 1. Preparation of Catalyst

Fe-Cu-K-Al catalyst was prepared by precipitation and incipient wetness method. 100Fe : 6.6Cu : 15.7Al (wt%) precursor was made by using coprecipitation method with ammonium hydroxide and homogeneous metal nitrate solution which was made of $Fe(NO_3)_3\cdot9H_2O$, $Cu(NO_3)_2\cdot3H_2O$ and $Al(NO_3)_3\cdot9H_2O$ at pH 6.8. It was dried in air at 110 °C for 24 hours. And later, potassium was added to the dried precursor by the solution of $K_2CO_3$ (Fe : K=100 : 6 wt%) by using the incipient wetness method. The catalyst was dried at 110 °C for 48 hours and calcined in air at 450 °C for 6 hours. The catalyst sustained its activity for 1,500 hours during the long run test in a lab scale fixed bed. The physical and chemical properties of catalyst are given in Table 1.

### 2. Reaction System

Experiments were carried out in a stainless steel column (0.052 m ID×1.5 m high) as shown in Fig. 1. The gases ($CO_2$, $H_2$, $N_2$) were taken from cylinders. Their flow rates were controlled by MFC (mass flow controller, Brooks Co.). Superficial velocity of mixed gas ranged from 0.07 to 0.20 m/s at STP; and $H_2/CO_2$ ratio ranged from 2 to 5. Catalyst particles ($d_p$=75-90 μm) were supported on a perforated plate containing 19 evenly spaced holes of 1.5 mm diameter, which served as a mixed gas distributor.

Three zone heaters that were controlled by temperature control system were installed at calming section, main column and freeboard region, respectively. Reaction temperature ranged from 250

**Table 1. Physical and chemical properties of Fe-Cu-K-Al catalyst**

| | BET surface area [$m^2/g$] | $CO_2$ chemisorption [μmol/g] | Density, ρ [$kg/m^3$] |
|---|---|---|---|
| After reduction | 160.25 | 265.12 | 3,250 |

---

†To whom correspondence should be addressed.
E-mail: kangyong@hanbat.chungnam.ac.kr
‡Presented at the Int'l Symp. on Chem. Eng. (Cheju, Feb. 8-10, 2001), dedicated to Prof. H. S. Chun on the occasion of his retirement from Korea University.

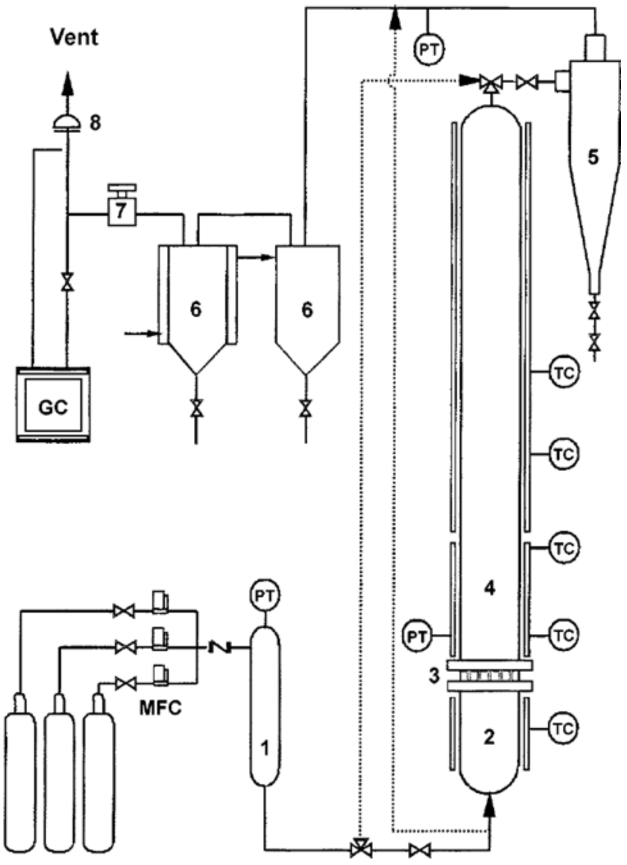

**Fig. 1. Experimental apparatus.**

| | |
|---|---|
| 1. Gas mixer | 5. Cyclone |
| 2. Wind box | 6. Cold separator |
| 3. Distributor | 7. Back pressure regulator |
| 4. Main column | 8. Digital flow meter |

to 350 °C. The temperatures at the heater surface as well as in the fluidized bed reactor were measured by iron-constantan thermocouples (K-type), which were mounted on the wall of the column at 20 cm intervals axially. Reaction pressure was maintained by BPR (back pressure regulator, Tescom Co.) and measured by pressure sensors in the range of 0.5-1.5 MPa. The pressure drop in the fluidized bed reactor was measured by differential pressure transducer. The products passing through a heat exchanger were condensed in the cold product separator (0 °C). A digital bubble flow meter was used to measure the exit gas flow rate. The compositions of the product gas phase and condensed liquid phase were analyzed by GC analyzer.

## RESULTS AND DISCUSSION

Fig. 2 shows the effects of gas velocity on the pressure drop in the bed, which is used to find a *minimum fluidization velocity* ($U_{mf}$). The pressure fluctuations were measured by differential pressure sensors from which the mean values of pressure drops were calculated. The pressure fluctuations can be seen in Fig. 2 as voltage signals at the fixed as well as fluidized states, respectively. The pressure drop increases with increasing gas velocity in the fixed beds and has a constant value with further increasing gas velocity in the expanded beds. From the intersection of increasing and constant lines of pressure drop, the $U_{mf}$ is determined at 0.012 m/s.

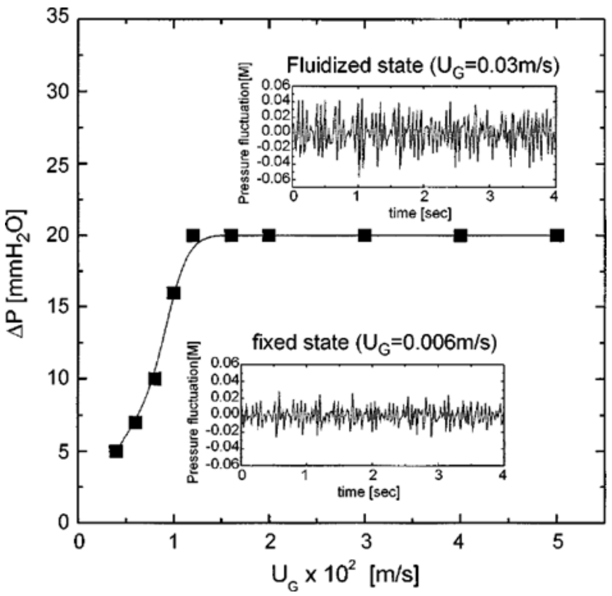

**Fig. 2. Mean value and fluctuations of pressure drop in the bed with the variation of gas velocity (T=300 °C, P=1 MPa).**

Since the mechanism of $CO_2$ hydrogenation is composed of the reverse water gas shift (RWGS) and Fischer-Tropsch (F-T) reactions, it can be expressed as

$$CO_2+H_2 \rightarrow CO+H_2O \text{ (RWGS)}$$

$$CO+2H_2 \rightarrow CH_2+H_2O \text{ (F-T)}$$

$$CO_2+3H_2 \rightarrow CH_2+2H_2O \text{ (overall)}$$

Thus, effects of the operating variables on the $CO_2$ hydrogenation have been well explained by the $CO_2$ conversion and CO selectivity. Also, The $CO_2$ conversion and CO selectivity were determined by Eqs. (1) and (2), respectively.

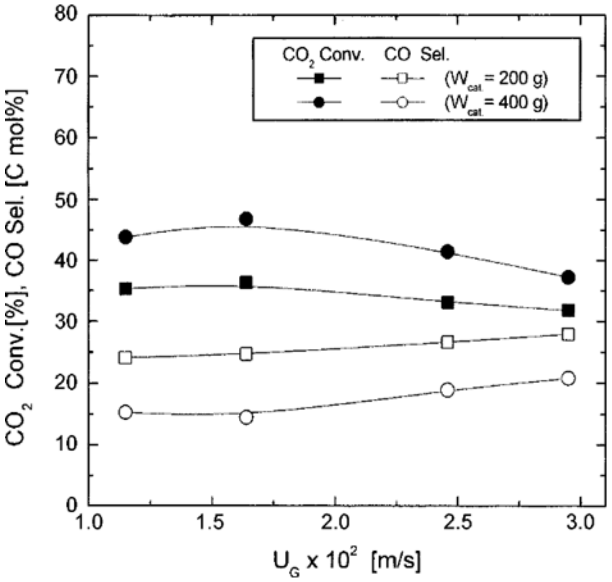

**Fig. 3. Effects of gas velocity on the $CO_2$ conversion and CO selectivity (T=300 °C, P=1 MPa, $H_2/CO_2$=3).**

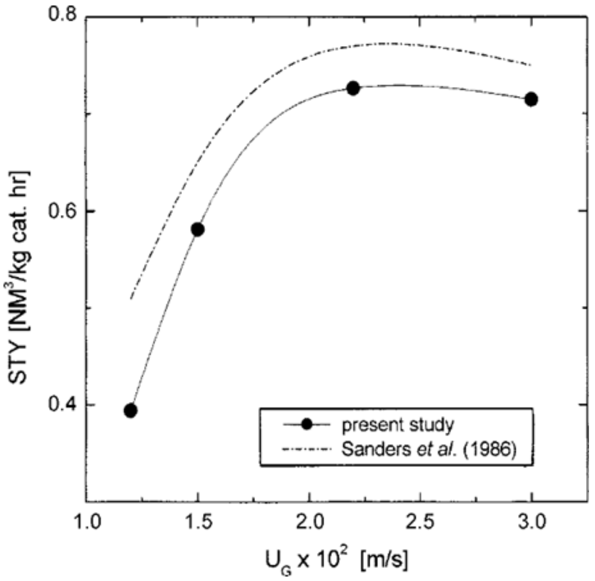

**Fig. 4. Effects of gas velocity on the space-time-yield (T=300 °C, P=1 MPa, $H_2/CO_2$=3, $W_{cat.}$=400 g).**

$$X_{CO_2} = \frac{\text{moles of } CO_2 \text{ reacted}}{\text{moles of } CO_2 \text{ fed}} \quad (1)$$

$$S_{CO} = \frac{\text{moles of CO formed}}{\text{moles of CO and hydrocarbons formed}} \quad (2)$$

Effects of gas velocity on the $CO_2$ conversion and CO selectivity can be seen in Fig. 3. In this figure, the $CO_2$ conversion decreases slightly, but the CO selectivity increases with increasing gas velocity. It can be understood that the residence time of gas phase in the reaction zone is decreased with increasing gas velocity, although the increase of gas velocity leads to the increase of intensity of contacting and mixing between gas reactant and catalyst. Moreover, $CO_2$ hydrogenation is the slow reaction, because the hydrocarbons are formed from carbon dioxide via carbon monoxide. Thus, the $CO_2$ conversion decreases with increasing the velocity of gas reactant. Also, the $CO_2$ conversion in the bed of 200 g catalyst loading is lower than that in the bed of 400 g catalyst loading, due to the effects of space velocity.

In Fig. 4, the space-time-yield (STY) has passed a maximum at $U_G$ range of 0.020-0.025 m/s. It is interesting to note that a similar trend can be also observed in bubble column slurry reactor using Fe-K catalyst for F-T synthesis [Sanders et al., 1986]. This can be explained by the flow regime transition from *homogeneous fluidization* to *heterogeneous fluidization* states. It has been pointed out that the unified approach relies on analogy in the hydrodynamic behavior between the gas-solid and gas-slurry systems using fine particles [Ellenberger et al., 1994; Krishna et al., 1996].

The value of space-time-yield (STY) has been defined by Eq. (3) [Deckwer et al., 1982].

$$STY = \frac{V_G X_{CO+H_2}}{W_{cat.}} \quad (3)$$

However, in the present study, space-time-yield has been defined as a parameter of reactor performance of $CO_2$ hydrogenation by Eq. (4). The fraction of CO is removed from the products of $CO_2$ hydrogenation, since CO is a byproduct.

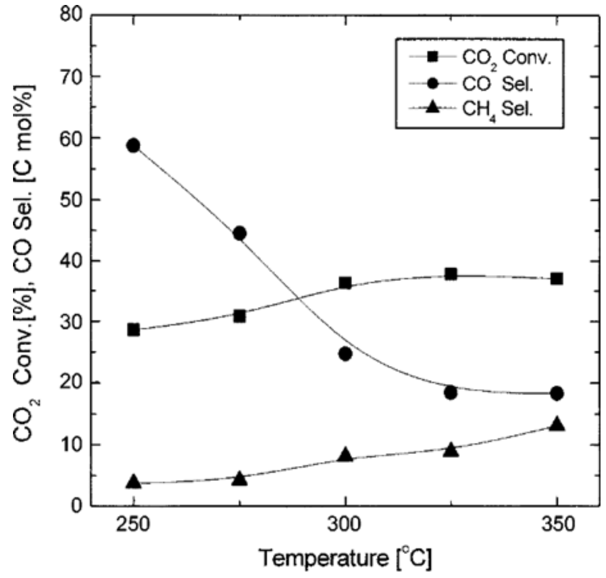

**Fig. 5. Effects of temperature on $CO_2$ conversion and CO, $CH_4$ selectivities (P=1 MPa, $U_G$=0.017 m/s, $H_2/CO_2$=3, $W_{cat}$=200 g).**

$$STY = \frac{V_G(X_{CO_2} - X_{CO_2}S_{CO})}{W_{cat}} \quad (4)$$

In Fig. 4, the STY values in $CO_2$ hydrogenation were lower than those in F-T synthesis, because a fraction of CO was removed from $CO_2$ conversion to consider hydrocarbon yield.

Effects of temperature on the $CO_2$ conversion, CO and $CH_4$ selectivity are shown in Fig. 5. In this figure, the $CO_2$ conversion increases but the CO selectivity decreases sharply, with increasing temperature. This figure also shows that the selectivity of CO is very high at 250 °C, but it decreases with increasing temperature until 325 °C and becomes stable with further increasing tempera-

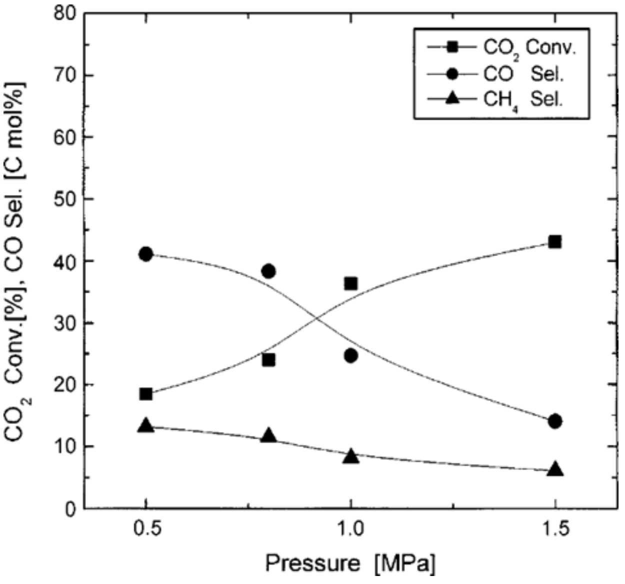

**Fig. 6. Effects of pressure on the $CO_2$ conversion and CO, $CH_4$ selectivity (T=300 °C, $U_G$=0.017 cm/s, $H_2/CO_2$=3, $W_{cat}$=200 g).**

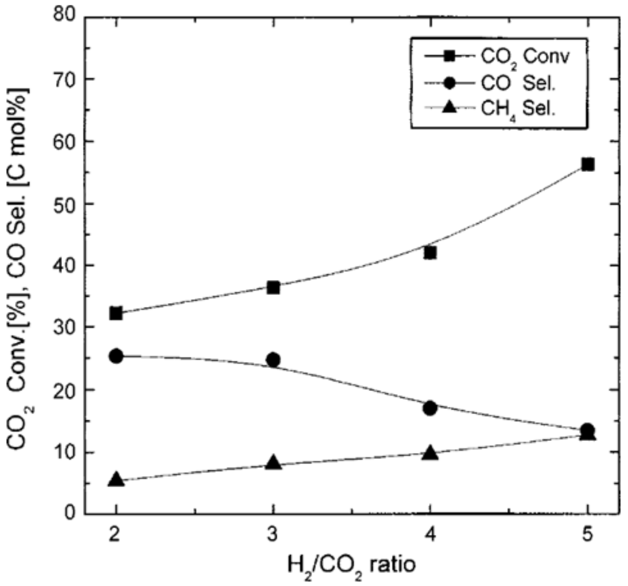

**Fig. 7. Effects of $H_2/CO_2$ ratio on the $CO_2$ conversion and CO, $CH_4$ selectivities (T=300 °C, P=1 MPa, $U_G$=0.017 m/s, $W_{cat.}$=200 g).**

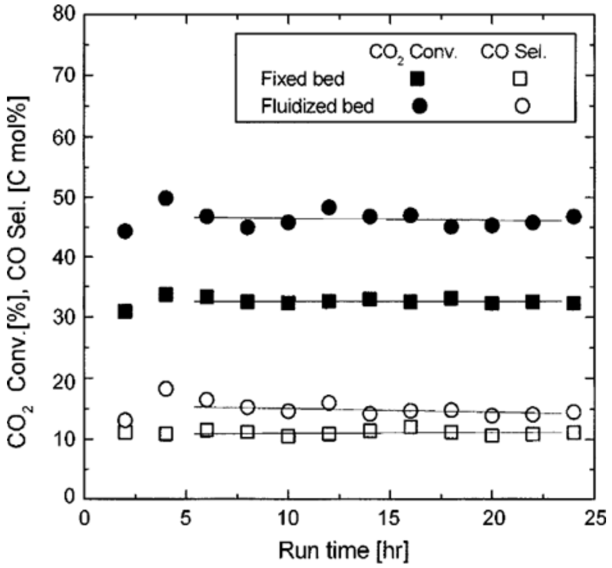

**Fig. 8. Comparison of reactor performance between fixed and fluidized bed (T=325 °C, P=1 MPa, $U_G$=0.025 m/s, $H_2/CO_2$= 3, $W_{cat.}$=400 g).**

ture. This is attributed to the fact that the water gas shift reaction occurs mainly at low temperature (250 °C), whereas the F-T reaction occurs above 300 °C. The $CH_4$ selectivity increases gradually with increasing temperature (Fig. 5). This can be due to the increase in the rate of hydrogenation of individual $CH_2$ unit to $CH_4$. It has been usually found that the $CH_4$ formation increases with temperature, irrespective of the catalyst type or the feed gas composition in F-T synthesis [Dry, 1996].

F-T reactors have been usually operated at a pressure range of 1-4 MPa to improve the reaction rate, due to pressure stability for the catalyst activity and for sufficient space-time to contact between gas phase and catalyst. The $CO_2$ conversion increases, but the CO selectivity decreases with increasing reaction pressure as can be seen in Fig. 6. It is noted in this figure that the effects of pressure become considerable at reaction conditions above 1 MPa. It has been found that the catalyst activity increases with increasing pressure in the lower range of pressure (up to 2 MPa). However, in the relative high pressure range (3-4 MPa), the catalyst activity exhibits a limiting pressure stability because of the deactivation of catalyst owing to the oxidation and carbon formation [Sanders et al., 1986].

Effects of $H_2/CO_2$ ratio on the $CO_2$ conversion and CO and $CH_4$ selectivities are shown in Fig. 7. In this figure, the $CO_2$ conversion increases but the CO selectivity decreases, with increasing the $H_2/CO_2$ ratio. Also, the $CH_4$ selectivity increases with increasing $H_2/CO_2$ ratio. Although the increase of $H_2/CO_2$ ratio leads to the high conversion of $CO_2$ and low selectivity of CO, the optimum value of $H_2/CO_2$ ratio would exist around $H_2/CO_2$=3, because the selectivities of by-products such as methane or paraffin increase with increasing $H_2/CO_2$ ratio.

Fig. 8 shows the $CO_2$ conversion and CO selectivity during 24 hour test run, to compare the performance of a fluidized bed reactor with that of a fixed bed. In the fixed bed, the direction of gas phase flow was downward by using 3-Way valves. In Fig. 8, the values of $CO_2$ conversion and CO selectivity are relatively high in the fluidized bed reactor compared with those in the fixed bed reactor, respectively, at the same operating conditions. The $CO_2$ conversion and products selectivity are shown in Table 2. The product selectivities of $CO_2$ hydrogenation are similar to those of F-T synthesis in fixed bed as well as fluidized bed reactors, respectively. It seems that in the fluidized bed, light hydrocarbons are favorable, whereas relatively heavier hydrocarbons are converted in a fixed bed reactor. The olefin/paraffin (O/P) mole ratio is found to be much higher in the fluidized bed than that in the fixed bed at the same condition, as can be seen in Fig. 9. It is noted that the O/P ratio of $CO_2$ hydrogenation products has been quite high compared to that of F-T synthesis [Satterfield et al., 1985]. The effects of reactor type on olefin/paraffin ratio can be due to the more homogeneous contacting and mixing between the feed gas phase and the solid catalyst particles in slurry or fluidized bed reactors.

## CONCLUSIONS

The hydrogenation of $CO_2$ has been investigated in a fluidized

**Table 2. Carbon dioxide conversion and product selectivity (300 °C, 1 MPa, $W_{cat.}$=400 g)**

| Reactor type | $CO_2$ conv. [C-mol%] | CO sel. [C-mol%] | Hydrocarbon distribution [C-mol%] | | | | | | | | O/P ratio [C-mol%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $C_1$ Sel. | $C_2^=$ Sel. | $C_2$ Sel. | $C_3^=$ Sel. | $C_3$ Sel. | $C_4^=$ Sel. | $C_4$ Sel. | $>C_5$ Sel. | |
| Fixed bed | 32.3 | 11.0 | 8.5 | 5.1 | 1.9 | 9.4 | 3.4 | 8.0 | 3.6 | 49.0 | 2.5 |
| Fluidized bed | 46.8 | 14.5 | 9.2 | 6.2 | 2.2 | 10.0 | 1.2 | 6.7 | 1.1 | 36.7 | 5.1 |

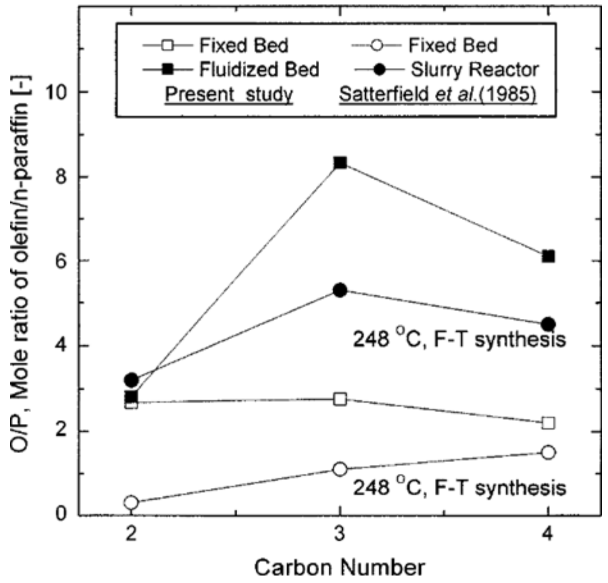

**Fig. 9. Olefin/Paraffin ratio variation in the $C_2$-$C_4$ hydrocarbon products (T=325 °C, P=1 MPa, $U_G$=0.025 m/s, $H_2/CO_2$=3, $W_{cat.}$=400 g).**

bed reactor by using Fe-Cu-K-Al catalyst as a fluidized solid phase. The $CO_2$ conversion decreases but the CO selectively increases, whereas the space-time-yield has attained maximum values with increasing gas velocity. The $CO_2$ conversion has increased but the CO selectivity has decreased, with increasing reaction temperature, pressure and $H_2/CO_2$ ratio in the reactor. The $CO_2$ conversion and olefin selectivity have exhibited higher values in the fluidized bed reactors than those in the fixed bed reactors. However, the CO selectivity has attained somewhat lower values in the fixed bed reactor.

## NOMENCLATURE

$d_p$ : particle size [mm]
STY : space time yield [$m^3/kg_{cat.}$ hr]
$S_{CO}$ : CO selectivity
T : temperature [°C]
$V_G$ : feed gas flow rate [$m^3$/hr]
$U_G$ : superficial velocity of gas phase [m/s]
$W_{cat.}$ : catalyst weight [kg]
$X_{CO+H_2}$ : CO and $H_2$ conversion
$X_{CO_2}$ : $CO_2$ conversion

## REFERENCES

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," *Catalysis Letters*, **40**, 115 (1996).

Deckwer, W.-D., Serpemen, Y., Ralex, M. and Schmidt, B., "Modeling the Fischer-Tropsch Synthesis in the Slurry Phase," *Ind. Eng. Chem. Proc. Des. Dev.*, **36**, 231 (1982).

Dry, M. E., "Practical and Theoretical Aspect of the Catalytic Fischer-Tropsch Process," *Applied Catalysis A*, **138**, 319 (1996).

Ellenberger, J. and Krishna, R., "A Unified Approach to the Scale-Up of Gas-Solid Fluidized Bed and Gas-Liquid Bubble Column Reactors," *Chem. Eng. Sci.*, **49**, 5391 (1994).

Fan, L. S., "Gas-Liquid-Solid Fluidization Engineering," Butterworths, Stoneham, MA (1989).

Inui, I., Hara, H., Takeguchi, T. Ichino, K., Kim, J. B., Iwamoto, S. and Pu, S. B., "Highly Effective Gasoline Synthesis from Carbon Dioxide," *Energy Convers. Mgmt.*, **38**, 385 (1997).

Kang, Y., Shim, J. S., Ko, M. H. and Kim, S. D., "Fractal Analysis of Pressure Fluctuations in a Three-Phase Bubble Column Reactor Operating at Low Pressure," *Korean J. Chem. Eng.*, **13**, 261 (1996).

Kang, Y., Woo, K. J., Ko, M. H., Cho, Y. J. and Kim, S. D., "Particle Flow Behavior in the Three-Phase Fluidized Beds," *Korean J. Chem. Eng.*, **16**, 784 (1999).

Kim, S. D. and Kang, Y., "Heat and Mass Transfer in Three Phase Fluidized Bed Reactors - an Overview," *Chem. Eng. Sci.*, **52**, 3639 (1997).

Krishna, R., Ellenberger, J. and Sie, S. T., "Reactor Development for Conversion of Natural Gas to Liquid Fuels: a Scale-Up Strategy Relying on Hydrodynamic Analogies," *Chem. Eng. Sci.*, **51**, 2041 (1996).

Nam, S. S., Lee, S. J., Kim, H., Jun, K. W., Choi, M. J. and Lee, K. W., "Catalytic Conversion of Carbon Dioxide into Hydrocarbons over Zinc Promoted Iron Catalysts," *Energy Convers. Mgmt.*, **38**, 397 (1997).

Riedel, T., Claeys, M., Schulz, H., Schaub, G., Nam, S. S., Jun, K. W., Choi, M. J., Kishan, G. and Lee, K. W., "Comparative Study of Fischer-Tropsch Synthesis with $H_2$/CO and Syngas using Fe- and Co-Based Catalysts," *Applied Catalysis A*, **186**, 201 (1999).

Sanders, E., Ledakowicz, S. and Deckwer, W. D., "Fischer-Tropsch Synthesis in Bubble Column Slurry Reactors on Fe/K-Catalyst," *Can. J. Chem. Eng.*, **64**, 133 (1986).

Satterfield, C. N., Huff, Jr. G. A., Stenger, H. G., Carter, J. L. and Madon, R. J., "A Comparison of Fischer-Tropsch Synthesis in a Fixed Bed Reactor and in a Slurry Reactor," *Ind. Eng. Chem. Fundam.*, **24**, 450 (1985).

Steynberg, A. P., Espinoza, R. L., Jager, B. and Vosloo, A. C., "High Temperature Fischer-Tropsch Synthesis in Commercial Practice," *Applied Catalysis A*, **186**, 41 (1999).

Yan, S. R., Jun, K. W., Hong, J. S., Lee, S. B., Choi, M. J. and Lee, K. W., "Slurry-Phase $CO_2$ the Hydrogenation over a Precipitated Fe-Cu-Al/K Catalyst: Investigation of Reaction Conditions," *Korean J. Chem. Eng.*, **16**, 357 (1999).