Hydrogenation of CO$_2$ over Fe-K Based Catalysts in a Fixed Bed Reactor at Elevated Pressure

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Abstract–Catalytic hydrogenation of CO$_2$ to produce hydrocarbons was conducted in a fixed bed reactor (1.6 cm-ID×60 cm-High). Fe-K based catalysts (KRICAT-A, B) were used for more than 850 hours to maintain CO$_2$ conversion level up to 30 C-mol% in the fixed bed micro-reactor. Effects of operating variables on the CO$_2$ conversion, hydrocarbon yield and its selectivity were investigated. The CO$_2$ conversion and total hydrocarbon yield increased with increasing reaction temperature (250-325 °C), pressure (0.5-2.5 MPa) and H$_2$/CO$_2$ mol ratio (2-5); however, they decreased with increasing space velocity (1,000-4,000 ml/g$_{cat}$hr) in the reactor. The selectivities of liquid products increased with increasing reaction pressure; however, they decreased with increasing temperature, space velocity and H$_2$/CO$_2$ ratio. From the results of an experimental study, optimum operating conditions for the maximum yield of olefinic liquid products were found as T=315 °C, P=1.5 MPa, SV=2,000 ml/g$_{cat}$hr and H$_2$/CO$_2$ ratio=3 in the fixed bed reactor within these experimental conditions.

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

INTRODUCTION

The environmental impact of high concentration of CO$_2$ into the atmosphere has been of acute concern to the global community. To control and reduce this emission, various countermeasures such as removal, recovery, storage disposal, and utilization have been proposed [Fujimoto et al., 1992; Lee et al., 1995; Inui et al., 1997; Park et al., 1998; Shen et al., 2000]. One of the efficient ways to mitigate this problem is to catalytically convert CO$_2$, at the generation point, into valuable industrially important feedstock such as petrochemicals. The catalytic hydrogenation of CO$_2$ has been recognized as the most possible technology because it can be developed to a commercial process and to treat rapidly large amount of CO$_2$. Recently, the catalytic hydrogenation of CO$_2$ has gained special attention as a potential way for producing liquid fuels and petrochemicals as well as F-T synthesis. There has been some progress for the hydrogenation of CO$_2$ in a catalyst system to obtain more valuable chemicals; the most promising properties have been exhibited over Fe-K based catalysts using Al$_2$O$_3$ as the structural support and potassium as the chemical promoter in a fixed bed micro-reactor [Choi et al., 1996; Nam et al., 1997, 2000; Yan et al., 1999, 2000; Eisenacher et al., 2000]. However, there has been little available information about the effects of operating variables in a fixed bed reactor. In this study, effects of operating variables on the CO$_2$ conversion, hydrocarbon yield and its selectivity for the maximum yield of olefinic liquid products were investigated in the fix bed reactor.

The results of this study can be utilized to determine the optimum operating conditions as well as to design and scale up a fixed bed reactor for CO$_2$ hydrogenation.

EXPERIMENTAL

The Fe-K based catalysts (KRICAT-A, B) were prepared by impregnating the supports (γ-alumina, La-alumina) with Fe(NO$_3$)$_3$· 9H$_2$O and K$_2$CO$_3$ solutions. The catalyst was dried (110 °C, 24 hr), calcined (500 °C, 12 hr) and crushed (d$_p$=350-850 μm). The catalysts were reduced at 450 °C and atmospheric pressure in a hydrogen flow (300 ml/min) for 24 h. The composition and properties of the catalysts are given in Table 1.

CO$_2$ hydrogenation was carried out in a bench scale fixed bed reactor (1.6 cm-ID×60 cm-High). A schematic diagram of the fixed bed reactor system used for CO$_2$ hydrogenation is shown in Fig. 1. The reaction and internal standard gases (CO$_2$, H$_2$, N$_2$, He) were taken from cylinders and their flow rates were controlled by MFC (mass flow controller, Brooks co.), respectively. Reaction temperature was controlled in the range of 250-325 °C by temperature control system and reaction pressure was maintained in the range of 0.5-2.5 MPa by BPR (back pressure regulator, Tescom co.). 21 g of catalysts were filled out and the total gas flow rates of reaction gases were changed in the range of 350-1,400 ml/min; the space velocity of the mixed gas was controlled ranging from 1,000 to 4,000 ml/g$_{cat}$hr at STP. And H$_2$/CO$_2$ mol ratio was ranged from 2 to 5. The liquid products were separated from gas products in the gas-liquid separator and condenser. The exit gas flow rate was measured by the digital bubble flow meter to evaluate the reaction conversion.

The gaseous products were analyzed by two kinds of on-line GC-TCD using internal standard gases, N$_2$ and He, to know the consumption of CO$_2$ and H$_2$, respectively. With the data obtained from
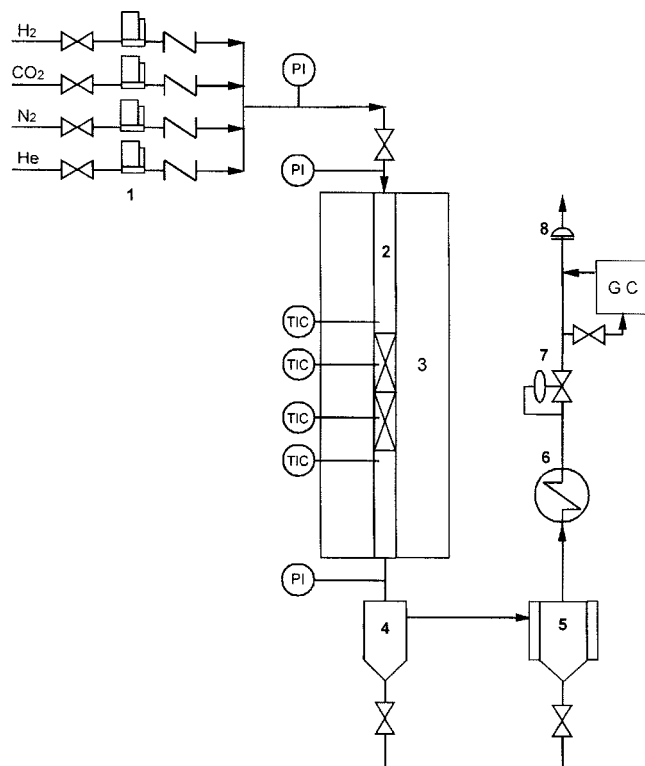
[†]To whom correspondence should be addressed.
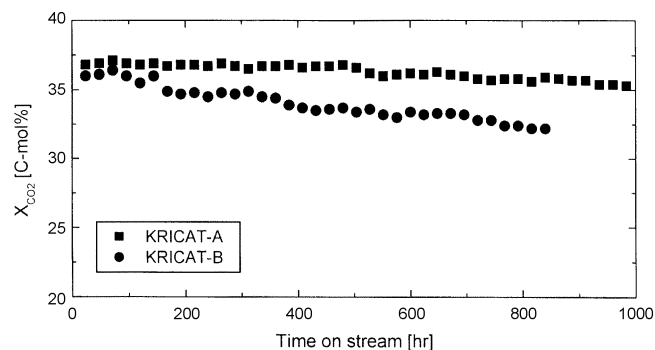E-mail: mjchoi@pado.krict.re.kr

Table 1. Composition and properties of Fe-K based catalysts

Catalyst	Composition [wt%]	BET surface area [m²/g]	CO_2 chemisorption [μmol/g]	H_2 uptake [μmol/g]
KRICAT-A	Fe-K/Al$_2$O$_3$ (20 : 7 : 100)	92	514	20
KRICAT-B	Fe-K/La-Al$_2$O$_3$ (20 : 7 : 4 : 100)	106	399	0.34

Fig. 1. Experimental apparatus.
1. Mass flow controller 5. Condenser
2. Fixed bed reactor 6. Heat exchanger
3. Electric heater 7. Back pressure regulator
4. Gas-liquid separator 8. Digital flow meter

the GC-TCD analysis, the conversion of CO_2 and the yield of CO and CH_4 were calculated. Also the peak area of organic products were referred to the peak area of CH_4 (GC-TCD); the organic product selectivities and yields were calculated and determined from

Fig. 2. Activity and lifetime test of KRICAT catalyst in a lab scale fixed bed reactor (T=300 °C, P=1 MPa, SV=2,000 ml/g$_{cat.}$ hr, H$_2$/CO$_2$=3).

the GC-FID analysis.

RESULTS AND DISCUSSION

A lifetime test of Fe-K based catalysts (KRICAT A and B) was conducted on the CO_2 hydrogenation with 1 g catalyst in the fixed bed micro-reactor, because these catalysts have shown high activity in CO_2 hydrogenation and selectivity of α-olefin among the KRICAT series. As shown in Fig. 2, the catalysts were used more than 850 hours to maintain the CO_2 conversion level up to 30 C-mol% in the fixed bed micro-reactor. Therefore, these catalysts could be used for CO_2 hydrogenation to find an optimum operating condition in a fixed bed reactor.
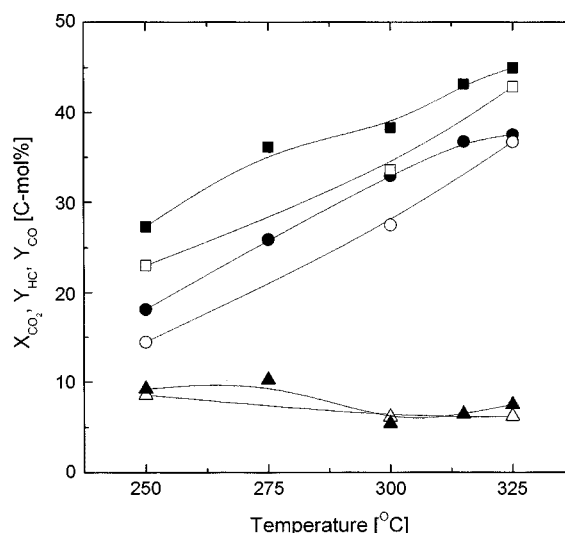
For the CO_2 hydrogenation, the CO_2 conversion (X_{CO_2}) and the CO yield (Y_{CO}) and total hydrocarbon yield (Y_{HC}) were determined by Eqs. (1), (2) and (3), respectively.

$$X_{CO_2} = \frac{\text{moles of } CO_2 \text{ reacted}}{\text{moles of } CO_2 \text{ fed}} \tag{1}$$

$$Y_{CO} = \frac{X_{CO_2} \times \text{moles of CO formed}}{\text{moles of CO and hydrocarbons formed}} \tag{2}$$

$$Y_{HC} = \frac{X_{CO_2} \times \text{moles of hydrocarbons formed}}{\text{moles of CO and hydrocarbons formed}} \tag{3}$$

Effects of temperature on the CO_2 conversion (X_{CO_2}) and the CO yield (Y_{CO}) and total hydrocarbon yield (Y_{HC}) are shown in Fig. 3. In this figure, the total hydrocarbon yield increased as well as the

Fig. 3. Effects of temperature on the CO_2 conversion and the CO and total hydrocarbon yield (P=1 MPa, SV=2,000 ml/g$_{cat.}$hr, H$_2$/CO$_2$=3).

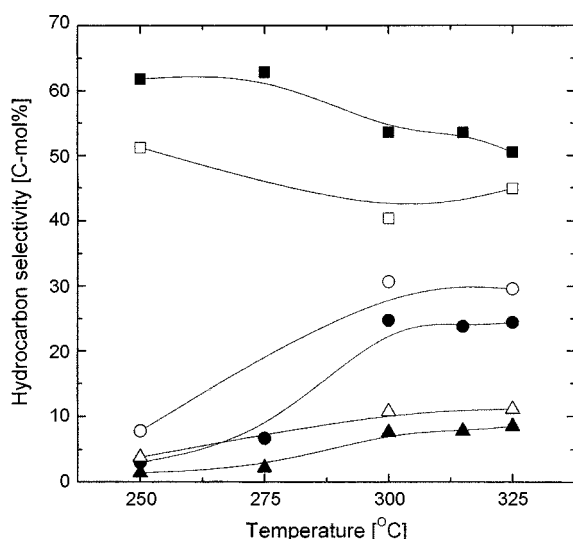|	X_{CO_2}	Y_{HC}	Y_{CO}
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

Fig. 4. Effects of temperature on the hydrocarbon selectivities of liquid, gas and CH$_4$ (P=1 MPa, SV=2000 ml/g$_{cat}$hr, H$_2$/CO$_2$= 3).

	Liquid (>C$_5$)	Gas (C$_2$-C$_4$)	CH$_4$
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

CO$_2$ conversion but the CO yield decreased, with increasing temperature. It can be explained that the F-T reaction occurred at a much higher temperature than that of the reverse water gas shift reaction [Dry, 1996]. Hydrogenation of CO$_2$ proceeds via a two-step reaction mechanism [Nam et al., 1997; Yan et al., 1999; Riedel et al., 2001]. In the reverse water gas shift reaction (Eq. 4), CO$_2$ converted to CO, which is an intermediate product in a consecutive reaction and the CO is hydrogenated organic products in the F-T reaction (Eq. (5)).

$$CO_2+H_2 \rightarrow CO+H_2O \tag{4}$$

$$CO+2H_2 \rightarrow -(CH_2)-+H_2O \tag{5}$$

Hydrocarbon selectivity is related to the moles of hydrocarbons per moles of CO and hydrocarbons. The selectivity of liquid products (>C$_5$) decreased but the gas products (C$_2$-C$_5$) increased with increasing temperature until 300 °C and became stable with further increasing temperature (Fig. 4). This figure shows that gas products are favorable at relatively high temperature; however, these have an equilibrium value above 300 °C in the fixed bed reactor. The most undesirable product, methane (CH$_4$), also increased slightly with increasing temperature in the CO$_2$ hydrogenation.

Effects of space velocity (SV) on X$_{CO_2}$, Y$_{CO}$ and Y$_{HC}$ are shown in Fig. 5. The space velocity was determined by Eq. (6).

$$SV = \frac{\text{volumetric flow rate of feed gas}}{\text{amounts of catalyst}} \tag{6}$$

X$_{CO_2}$ and Y$_{HC}$ decreased, but Y$_{CO}$ increased with increasing space velocity. It can be explained typically that the residence time of gas phase in the reaction zone is decreased with increasing space velocity. At relatively higher space velocity (3,000 ml/g$_{cat}$hr), the increase of Y$_{CO}$ is considered as an evidence of two-step reaction mechanism for the formation of hydrocarbons from CO$_2$. Also, the hy-
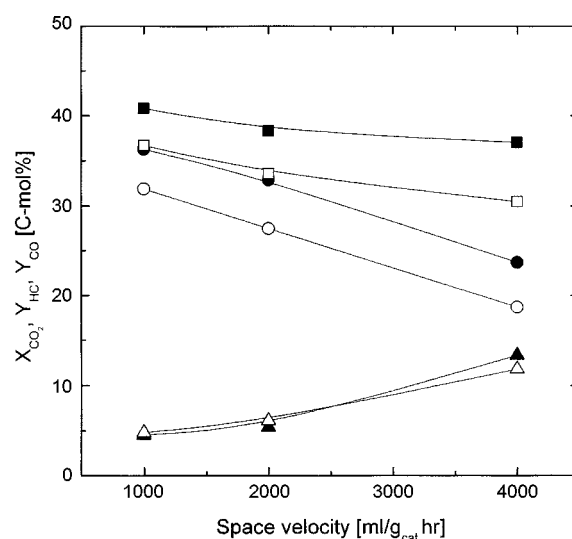
Fig. 5. Effects of space velocity on the CO$_2$ conversion and the CO and total hydrocarbon yield (T=300 °C, P=1 MPa, H$_2$/CO$_2$= 3).

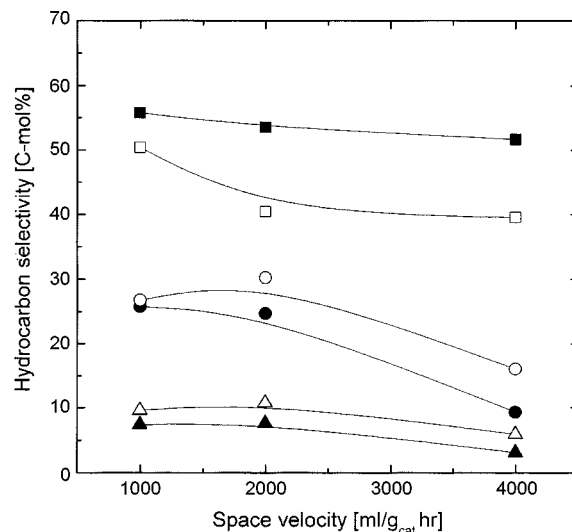|	X$_{CO_2}$	Y$_{HC}$	Y$_{CO}$
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

Fig. 6. Effects of space velocity on the hydrocarbon selectivities of liquid, gas and CH$_4$ (T=300 °C, P=1 MPa, H$_2$/CO$_2$=3).

	Liquid (>C$_5$)	Gas (C$_2$-C$_4$)	CH$_4$
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

drocarbon selectivity decreased as well as Y$_{HC}$, with increasing space velocity (Fig. 6). It is interesting to note that the increase of space velocity had a low selectivity of gas product due to low conversion rate, although gas products are favored at the high space velocity (high gas velocity and low catalyst concentration). It can be understood that the influence of conversion rate is more considerable than that of space velocity on the product distribution (selectivities of gas and liquid product).

Effects of reaction pressure on X$_{CO_2}$, Y$_{CO}$ and Y$_{HC}$ are shown in Fig. 7. X$_{CO_2}$ and Y$_{HC}$ increased, but Y$_{CO}$ decreased with increasing
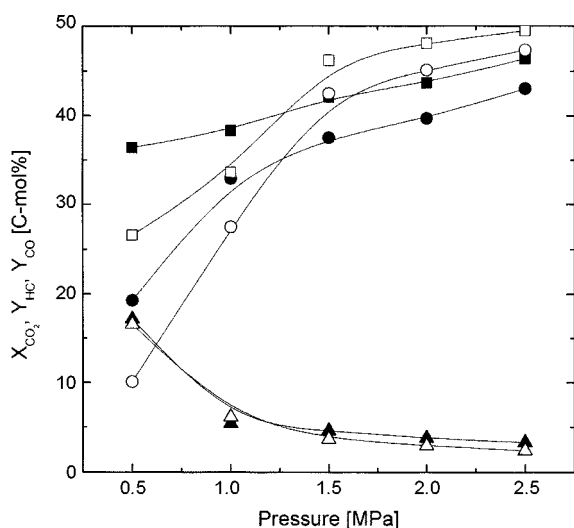
Fig. 7. Effects of pressure on the CO₂ conversion and the CO and total hydrocarbon yield (T=300 °C, SV=2,000 ml/g$_{cat.}$hr, H₂/CO₂=3).

	X$_{CO_2}$	Y$_{HC}$	Y$_{CO}$
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

pressure. It can be explained that equilibrium conversion increases substantially with increasing operating pressure because the hydrogenation of CO₂ involves a decrease in number of moles. And, the elevated pressure enables, to the catalysts, sufficient activity and effective contacting between gas phase and catalyst due to the increase of residence time. It is noted in this figure that the effects of pressure become considerable at reaction conditions above 1.5 MPa. It has been found that the catalyst activity increases with increasing pressure in the lower range of pressure up to 2 MPa [Dry, 1996; Steynberg et al., 1999]. Also, different pressure stability of the cat-
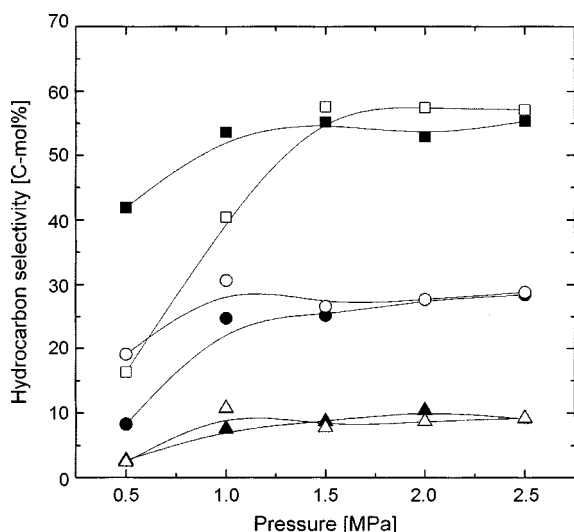

Fig. 8. Effects of pressure on the hydrocarbon selectivities of liquid, gas and CH₄ (T=300 °C, SV=2,000 ml/g$_{cat.}$hr, H₂/CO₂=3).

	Liquid (>C₅)	Gas (C₂-C₄)	CH₄
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

alysts was observed between the catalysts. KRICAT-B (Fe-K/La-Al₂O₃) was relatively high activity in terms of X$_{CO_2}$ at high pressure. Generally, the addition of a lanthanum oxide to Al₂O₃ improved the total activity and increased the selectivity to alkenes and higher hydrocarbons [Nam et al., 2000]. However, effect of lanthanum was not exhibited at relatively low pressure below 1 MPa. This phenomenon may be attributed to the physical properties of catalysts such as pore size and surface area.

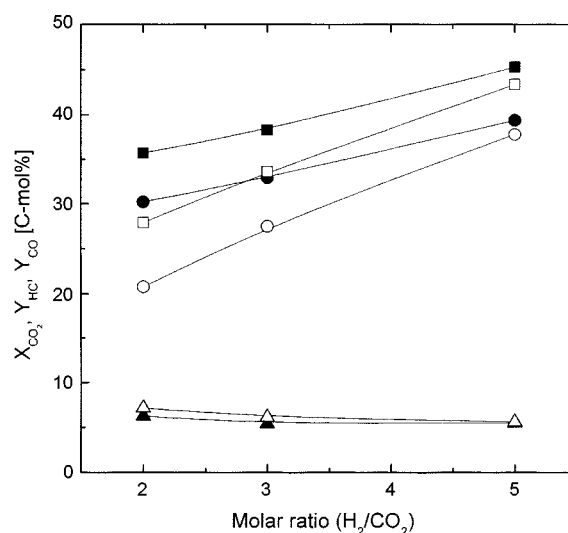The gas and liquid hydrocarbon selectivities increased with in-

Fig. 9. Effects of H₂/CO₂ ratio on the CO₂ conversion and the CO and total hydrocarbon yield (T=300 °C, P=1 MPa, SV= 2,000 ml/g$_{cat.}$).

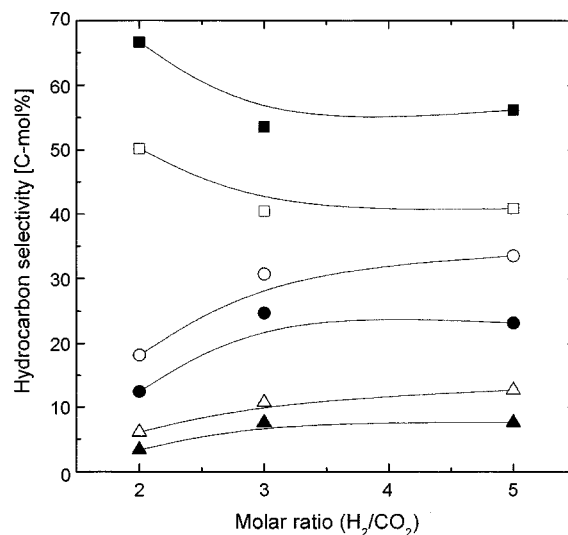|	X$_{CO_2}$	Y$_{HC}$	Y$_{CO}$
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

Fig. 10. Effects of H₂/CO₂ ratio on the hydrocarbon selectivities of liquid, gas and CH₄ (T=300 °C, P=1 MPa, SV=2,000 ml/ g$_{cat.}$).

	Liquid (>C₅)	Gas (C₂-C₄)	CH₄
KRICAT-A :	■	●	▲
KRICAT-B :	□	○	△

Table 2. Carbon dioxide conversion and product selectivity (T=315 °C, P=1.5 MPa, SV=2,000 ml/g$_{cat.}$hr, H$_2$/CO$_2$=3)

Catalyst	CO$_2$ conv. [C-mol%]	CO sel. [C-mol%]	Hydrocarbon distribution [C-mol%]								O/O+P ratio C$_2$-C$_4$ [%]
			C$_1$ Sel.	C$_2^=$ Sel.	C$_2$ Sel.	C$_3^=$ Sel.	C$_3$ Sel.	C$_4^=$ Sel.	C$_4$ Sel.	>C$_5$ Sel.	
KRICAT-A	51.7	8.0	7.8	6.2	1.1	9.3	1.2	6.0	0.9	59.5	87.0
KRICAT-B	45.8	8.8	9.6	5.3	0.9	7.5	1.0	5.4	0.9	60.6	85.1
Dry [1982]^a	-	-	2.0	0.1	1.8	2.7	1.7	3.1	1.9	84.0	52.2

^{a}Sasol I; F-T synthesis - fixed bed, 220 °C, 2.5 MPa.

creasing pressure until 1.5 MPa and had a stable value with further increasing pressure in the liquid, gas and methane product (Fig. 8). The influence of pressure exhibited more selectively on the liquid products than that of gas products and methane.

Since it has been observed that the partial pressure of H$_2$ strongly affected the reaction rate in the F-T synthesis, effects of H$_2$/CO$_2$ ratio on X$_{CO_2}$, Y$_{CO}$ and Y$_{HC}$ are shown in Fig. 9. X$_{CO_2}$ and Y$_{HC}$ increased, but Y$_{CO}$ decreased slightly with increasing H$_2$/CO$_2$ ratio. It can be understood that the excess of H$_2$ enables high X$_{CO_2}$ and Y$_{HC}$. In Fig. 10, the gas products and methane selectivities increased but the liquid products selectivity decreased, with increasing H$_2$/CO$_2$ ratio in the fixed bed reactor.

From a few experimental results, effects of operating variables over KRICAT-A and B have exhibited the same trends on CO$_2$ conversion and hydrocarbon selectivity. The optimum operating conditions were found (temperature: 315 °C, pressure: 1.5 MPa, space velocity: 2,000 ml/g$_{cat.}$hr, H$_2$/CO$_2$: 3) and the CO$_2$ conversion in the fixed bed reactor was increased up to 45-50% by controlling the reaction conditions. At optimum operating conditions, the CO$_2$ conversion and product selectivities are shown in Table 2. The product selectivities of CO$_2$ hydrogenation are similar to those of F-T fixed bed reactor in terms of carbon number, whereas olefin/olefin and paraffin (O/O+P, %) is found to be much higher in the CO$_2$ hydrogenation than that in commercial F-T synthesis (Table 2). The formation of olefins was favored by high temperature, high space velocity, low pressure and high H$_2$/CO$_2$ as well as a conventional F-T reaction [Dry, 1982; Riedel et al., 1999, 2001]; however, O/O+P were varied only in the range of 85-90% of all experiments in the present study.

CONCLUSIONS

The CO$_2$ conversion and total hydrocarbon yield increased with increasing temperature, pressure and H$_2$/CO$_2$ ratio; however, they decreased with increasing space velocity in the fixed bed reactor. The selectivities of liquid products increased with increasing reaction pressure; however, they decreased with increasing temperature, space velocity and H$_2$/CO$_2$ ratio. It was found that the olefin/olefin and paraffin ratio (O/O+P, C-mol%) exhibited very high level up to 85-90% in the experimental conditions. The optimum operating conditions for the maximum yield of olefinic liquid products in the fixed bed reactor were found to be as follows: T=315 °C, P= 1.5 MPa, SV=2,000 ml/g$_{cat.}$hr, H$_2$/CO$_2$ ratio=3.

NOMENCLATURE

d$_p$: particle size [μm]

P : pressure [MPa]
SV : space velocity [ml/g$_{cat.}$hr]
T : temperature [°C]
X$_{CO_2}$: CO$_2$ conversion
Y$_{CO}$: CO yield
Y$_{HC}$: total hydrocarbon yield

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