

Promotion of CO₂ Hydrogenation to Hydrocarbons in Three-Phase Catalytic (Fe-Cu-K-Al) Slurry Reactors

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Abstract—A three-phase slurry reactor has been employed to increase the CO₂ conversion and decrease the selectivity of CO in the direct hydrogenation of CO₂ to hydrocarbons, as it is beneficial for removal of the heat generated due to highly exothermic nature of the reaction. Experiments were conducted over iron-based catalysts (Fe-Cu-K-Al, $d_p=45-75\ \mu\text{m}$) in a slurry reactor. It was found that the slurry reactor is preferable to the fixed bed reactor. The productivity and selectivity of hydrocarbons in the slurry reactor appeared to be better than that in the fixed bed reactor for the hydrogenation of CO₂. The CO₂ conversion was increased with increasing reaction temperature (275-300 °C), pressure (1-2.5 MPa) or H₂/CO₂ ratio (2-5) in the three-phase slurry reactor. The CO₂ conversion was increased with increasing the amount of CO₂ fed.

Key words: Carbon Dioxide, Catalyst, Hydrogenation, Three-Phase Slurry Reactor

INTRODUCTION

The increase of environmental impact due to high concentration of CO₂ in the atmosphere has been of acute concern to the global community. To control and reduce this emission, various countermeasures such as capture, storage and utilization have been proposed. One of the advanced concepts for mitigating CO₂ is the catalytic conversion of CO₂ into valuable chemical feedstock, as it can be developed to commercial process by treating the large amount of CO₂ rapidly, although it has not been accepted as an effective mitigation way [Halman, 1993; Xiaoding and Moulijn, 1996; Aresta, 1997].

The catalyst system for the hydrogenation of CO₂ has been developed to obtain more valuable chemical feedstock such as light olefins and long chain hydrocarbons. For the direct hydrogenation of carbon dioxide to hydrocarbons over various kinds of Fe-based catalysts like K, Cr, Mn and Zn promoted iron catalysts have been prepared by precipitation or impregnation method [Barraut et al., 1981; Lee et al., 1989; Ando et al., 1998; Xu et al., 1998; Tan et al., 1999]. Our previous studies reported that Fe-K based catalyst gave relatively high CO₂ conversion as well as the high selectivity of long chain hydrocarbons and olefins in the fixed bed reactors [Choi et al., 1996, 2001; Nam et al., 1997; Yan et al., 1999, 2000; Hong et al., 2001; Riedel et al., 2001]. However, the conversion of CO₂ was not substantial (<20%) in a three-phase slurry reactor [Yan et al., 1999, 2000].

Recently, Fischer-Tropsch synthesis in slurry reactors [Jager and Espinoza, 1995; Raje and Davis, 1997; Buker and Lang, 1999] has been extensively investigated because of its numerous advantages such as effective heat removal generated from the exothermic reac-

tion and high productivity of hydrocarbons due to effective contact among the reacting phases with higher heat and mass transfer rate and ease of continuous operation mode compared to other contacting modes [Kim and Kang, 1997; Kang et al., 1999]. It can be anticipated that a three-phase slurry reactor can be an effective system for the hydrogenation of CO₂, since the reaction is highly exothermic. However, there is little available information on the characteristics of a three-phase slurry reactor.

In the present study, thus, a three-phase slurry reactor has been employed to increase the productivity of hydrocarbon with aim to decrease the selectivity of CO in conducting the direct hydrogenation of CO₂ to hydrocarbons. Effects of operating variables such as gas velocity, reaction temperature, and pressure and mol ratio of hydrogen to CO₂ on the CO₂ conversion and hydrocarbon selectivity in the slurry reactor are investigated.

EXPERIMENTAL

1. Preparation of Catalyst

Fe-Cu-K-Al catalyst was prepared by precipitation and incipient wetness method [Yan et al., 1999]. The precursor of 100Fe : 6.6Cu : 15.7Al (wt%) was made by using coprecipitation with ammonium hydroxide and homogeneous metal nitrate solution which was made of Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O and Al(NO₃)₃·9H₂O at pH 6.8. The precipitates were washed with distilled water, and dried in air at 110 °C for 24 hours. The potassium was added to the dried precursor by the solution of K₂CO₃ (Fe : K=100 : 6 wt%) by using the incipient wetness method. The catalyst was dried at 110 °C for 48

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

	BET surface area [m ² /g]	CO ₂ uptake [μmol/g]	Density, ρ [kg/m ³]
After reduction	160.25	265.12	3,250

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[‡]This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

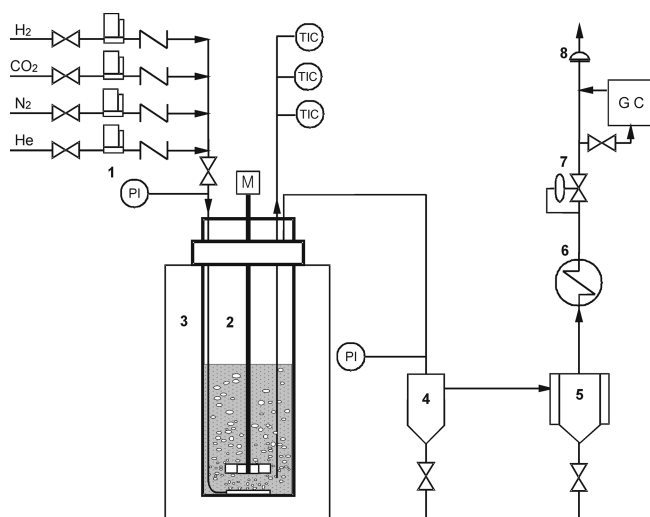


Fig. 1. Experimental apparatus.

- | | |
|-------------------------|----------------------------|
| 1. Mass flow controller | 5. Condenser |
| 2. Slurry reactor | 6. Heat exchanger |
| 3. Electric heater | 7. Back pressure regulator |
| 4. G/L separator | 8. Digital flow meter |

hours and calcined in air at 450 °C for 6 hours. The physical and chemical properties of catalyst are given in Table 1.

2. Reaction System

A three-phase slurry reactor (0.05 m ID×0.15 m high) with a stirrer was used for the hydrogenation of CO₂ (Fig. 1). 20–50 g of catalyst and 200 g of squalane as a slurry medium were loaded into the slurry reactor. Flow rates of gases (CO₂, H₂, N₂) were controlled by MFC (mass flow controller, Brooks Co.). Superficial velocity of mixed gas ranged from 0.2 to 1.5 cm/s with H₂/CO₂ ratio from 2 to 5. A perforated plate containing 7 evenly spaced holes of 1 mm diameter served as a gas distributor. Reaction temperature was controlled in the range of 230–300 °C with an electric heater and temperature control system. The temperatures at the heater surface as well as in the slurry medium were measured by iron-constantan thermocouples. Reaction pressure was regulated by BPR (back pressure regulator, Tescom Co.) in the range of 1.0–2.5 MPa and measured by pressure sensors. Oil products were passed through a heat exchanger, condensed in the cold product separator (0 °C) and were weighed and analyzed by GC equipped with FID (SPB-1 column). Uncondensed gases and light hydrocarbons (CO₂, CO and C₁–C₆) were analyzed by GC-TCD (Carbosphere column) and FID (Poraplot-Q column). The exit gas was measured by digital bubble flow meter. From the GC-TCD data using N₂ as internal standard gas, the CO₂ conversion (X_{CO_2}), and CO selectivity (S_{CO}) were determined by Eqs. (1) and (2), respectively.

$$X_{CO_2} = \frac{\text{moles of CO}_2 \text{ reacted}}{\text{moles of CO}_2 \text{ fed}} \quad (1)$$

$$S_{CO} = \frac{\text{moles of CO formed}}{\text{moles of CO}_2 \text{ converted}} = \frac{\text{moles of CO formed}}{\text{moles of CO and hydrocarbons formed}} \quad (2)$$

RESULTS AND DISCUSSION

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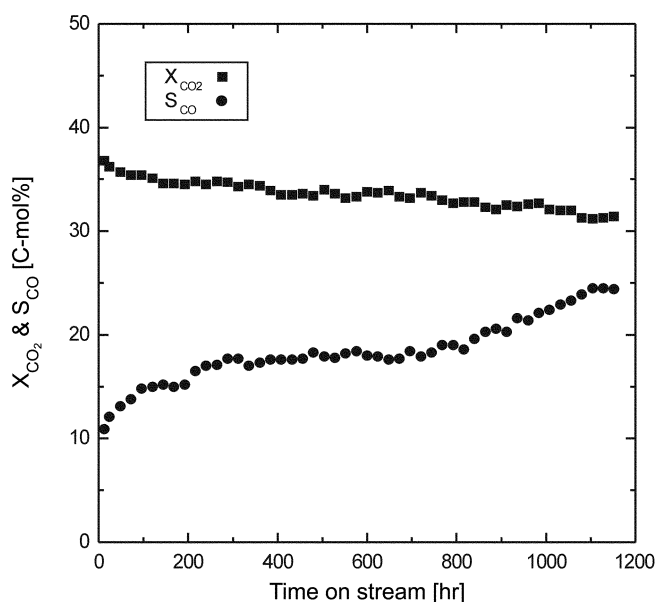


Fig. 2. Activity and time-on-stream test of Fe-Cu-K-Al catalyst in a fixed bed micro reactor (SV=2,000 ml/g_{cat}.hr, T=300 °C, P=1 MPa, H₂/CO₂=3).

Lifetime tests of Fe-Cu based catalysts were conducted in order to confirm the activity of the prepared catalyst for the CO₂ hydrogenation as shown in Fig. 2. The CO₂ conversion (X_{CO_2}) and CO selectivity (S_{CO}) were 35 % and 15%, respectively. The catalyst was tested for more than 1,000 hours to maintain the CO₂ conversion level up to 30 mol% in the fixed bed micro-reactor although deactivation of the catalyst slowly occurred indicated by increase of S_{CO} (Fig. 2).

Effects of stirrer speed on the values of X_{CO_2} and S_{CO} in three-phase slurry reactor are shown in Fig. 3. The values of X_{CO_2} increased

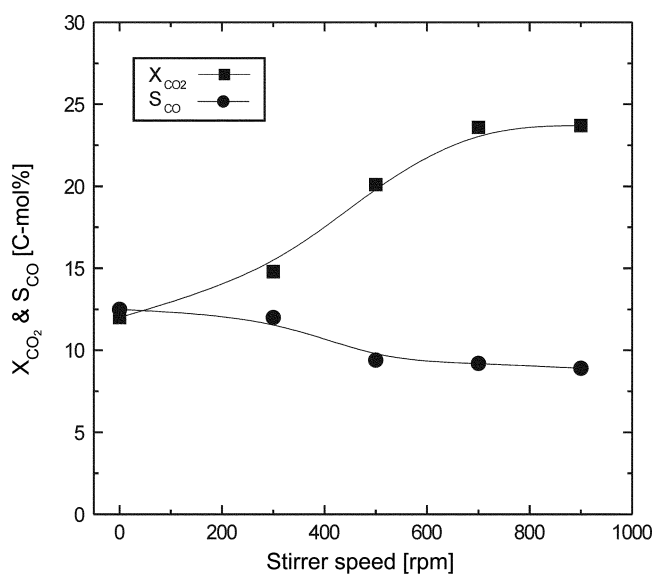


Fig. 3. Effects of stirrer speed on the CO₂ conversion and CO selectivity (SV=4,000 ml/g_{cat}.hr, U_G=0.37 cm/s, T=275 °C, P=2 MPa, H₂/CO₂=3).

gradually with increasing stirrer speed until 700 rpm, but did not change considerably with a further increase in the stirrer speed. It can be understood that the effect of external transport limitations on catalyst activity is considerable when the stirring speed is <700 rpm [Raje and Davis, 1997]. Therefore, all experiments were carried out in the reactor at stirring speed of 700 rpm. Fig. 3 depicts that the value of CO selectivity decreases with increasing stirrer speed.

Effects of gas velocity (U_G) on the X_{CO_2} and S_{CO} are shown in Fig. 4. The value of X_{CO_2} exhibits a local maximum, but that of S_{CO}

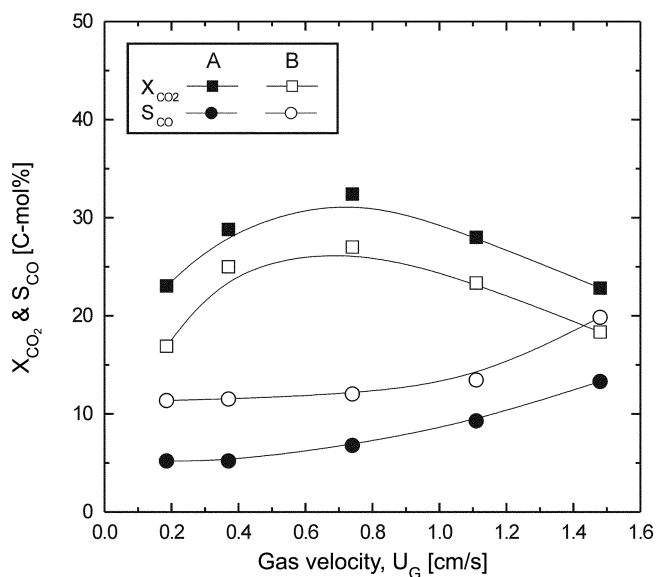


Fig. 4. Effects of gas velocity on the CO₂ conversion and CO selectivity ($T=275^\circ\text{C}$, $P=1\text{ MPa}$, $H_2/CO_2=3$).

$W_{cat.}$ [g]: A B
 40 20

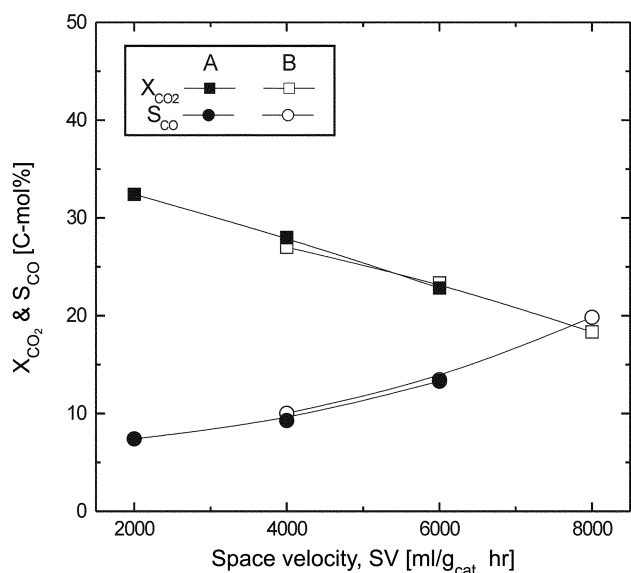


Fig. 5. Effects of gas velocity on the CO₂ conversion and CO selectivity ($T=275^\circ\text{C}$, $P=1\text{ MPa}$, $H_2/CO_2=3$).

$W_{cat.}$ [g]: A B
 40 20

increases with increasing gas velocity. It can be understood that the increase of gas velocity leads to the increase of intensity of contacting and mixing between the gas reactant and the catalyst. Owing to this increase of contacting intensity, the conversion of CO₂ would increase, although the gas phase residence time in the reaction zone decreases with increasing gas velocity. Note that the CO₂ conversion of 40 g catalyst charge was higher than that of 20 g; this can be due to the influence of space velocity. The U_G effects can be explained more clearly as a function of space velocity as shown in Fig. 5. The value of X_{CO_2} decreases while that of S_{CO} increases almost linearly with increasing space velocity.

It has been reported that the hydrogenation of CO₂ proceeds via a two-step mechanism [Lee et al., 1989; Riedel et al., 2001] as follows:



In the reverse water gas shift (RWGS) reaction [Eq. (3)], CO₂ converted to CO, which is an intermediate product in a consecutive reaction, and the CO is hydrogenated to the organic products in the F-T reaction [Eq. (4)].

Also, the productivity of reactor can be explained by space-time-yield (STY). The value of space-time-yield (STY1) has been defined by Eq. (5). However, in the present study, space-time-yield (STY2) has been defined as a parameter of reactor performance of CO₂ hydrogenation by Eq. (6). STY2 is based on the generated amount of hydrocarbons; the fraction intermediate (CO) is not considered as final product.

$$STY1 = \frac{V_G X_{CO_2}}{W_{cat.}} \quad (5)$$

$$STY2 = \frac{V_G (X_{CO_2} - X_{CO_2} S_{CO})}{W_{cat.}} = \frac{V_G Y_{HC}}{W_{cat.}} \quad (6)$$

Effects of U_G on the space-time-yield (STY) are shown in Fig. 6.

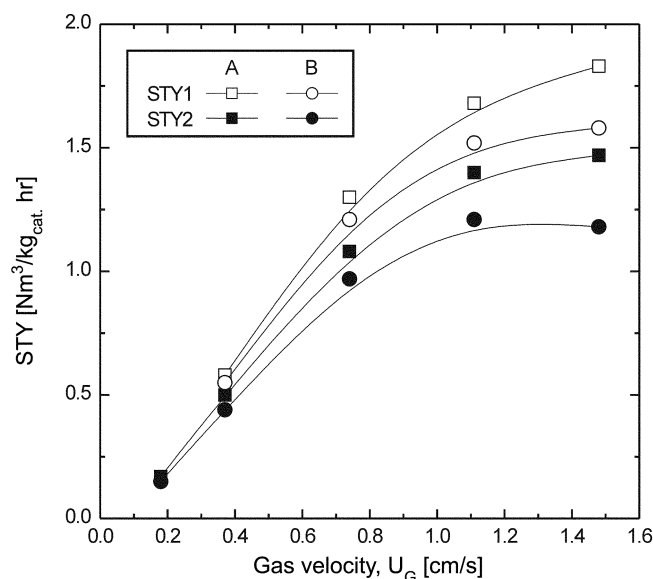


Fig. 6. Effects of gas velocity on the space time yield ($T=275^\circ\text{C}$, $P=1\text{ MPa}$, $H_2/CO_2=3$).

$W_{cat.}$ [g]: A B
 40 20

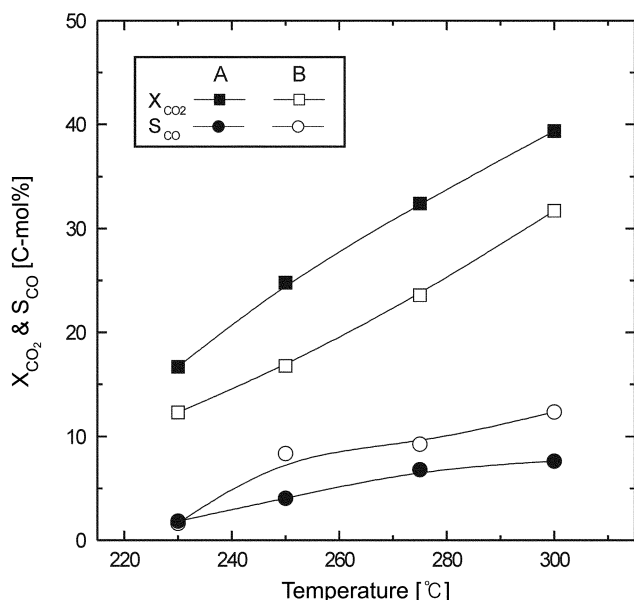


Fig. 7. Effects of temperature on the CO₂ conversion and CO selectivity (H₂/CO₂=3).

	A	B
U _G [cm/s]	0.74	0.37
SV [ml/g _{cat.} ·hr]	2000	4000
P [MPa]	1	2

The STY increased with increasing U_G. In slurry bubble reactors, this influence of gas velocity has been explained by the flow regime transition from homogeneous fluidization to heterogeneous fluidization states [Sanders et al., 1986]. In this study, regime transition was not observed in the gas velocity range of 0.2–1.5 cm/s. This range is considered as a homogeneous fluidization regime because of relatively low gas velocity and high stirrer speed. The STY1 values were higher than those of STY2, because the fraction of CO was removed from CO₂ conversion considering hydrocarbon yield only.

Effects of temperature on the values of the X_{CO₂} and S_{CO} are shown in Fig. 7. In this figure, the X_{CO₂} increases greatly, while the S_{CO} increases slightly, with increasing reaction temperature in the slurry reactor. It can be explained that the CO₂ hydrogenation (RWGS and F-T reaction) occurs well at high temperature. However, there are temperature limitations in slurry reactors because liquid medium volatilizes out of the reactor over high temperature of 300 °C.

In Fig. 8, the results of CO₂ hydrogenation over Fe-based catalysts are shown in terms of the STY. The values of STY1 increase with increasing reaction temperature. The difference between the values of STY1 and STY2 is, however, getting higher due to relatively higher CO₂ hydrogenation as the reaction temperature increases. Moreover, the differences were higher in fixed bed reactors [Barrault et al., 1981; Ando et al., 1998; Xu et al., 1998; Tan et al., 1999] than those in the slurry reactor. These results might demonstrate that the performance of low-temperature slurry reactor for the CO₂ hydrogenation is relatively higher than that of high-temperature fixed bed reactors.

Effects of reaction pressure on the values of X_{CO₂} and S_{CO} are shown in Fig. 9. In this figure, the values of X_{CO₂} increase, but the values of S_{CO} decrease with increasing pressure in the range of W_{cat.}

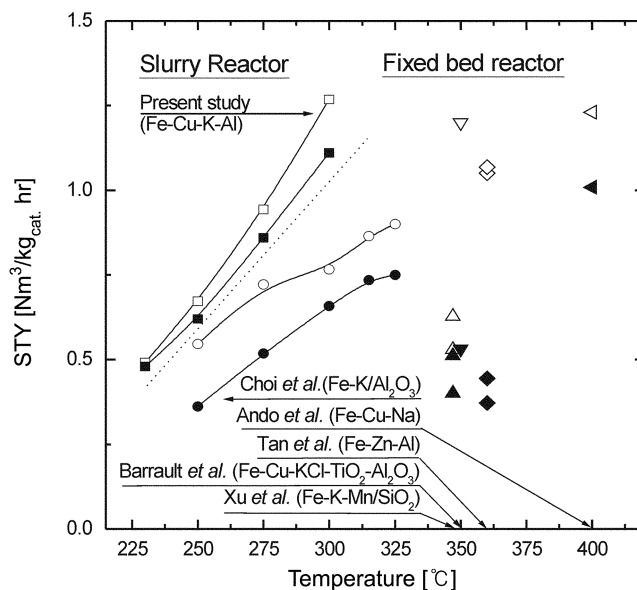


Fig. 8. Effects of temperature on the space time yield over Fe-based catalysts.

	STY1	STY2	P [MPa]	SV [ml/g _{cat.} ·hr]	H ₂ /CO ₂ [-]
Present	□	■	2	4000	3
Choi et al.	○	●	1	2000	3
Xu et al.	△	▲	2	1200	3
Barrault et al.	▽	▼	1.5	6000	1
Tan et al.	◇	◆	5	6000	3
Ando et al.	◁	◓	5	3000	3

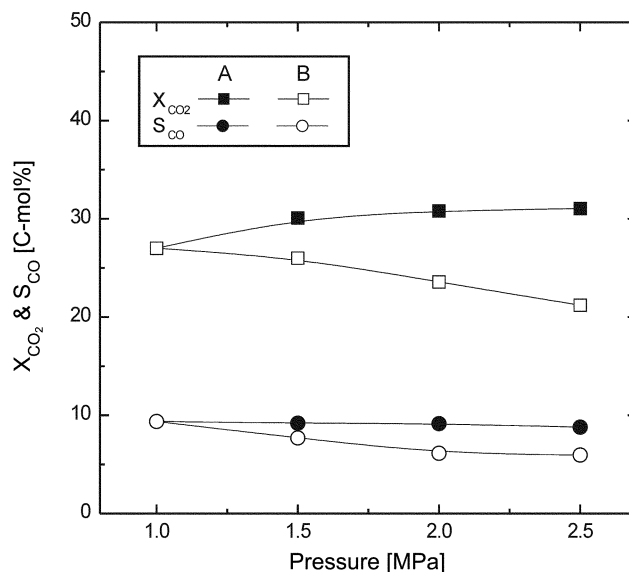


Fig. 9. Effects of pressure on the CO₂ conversion and CO selectivity in the slurry reactor (SV=4,000 ml/g_{cat.}·hr, T=275 °C, H₂/CO₂=3).

	A	B
U _G [cm/s]	0.74	0.30–0.74
W _{cat.} [wt%]	20–50	20

20–50 g (condition A). It can be explained that equilibrium conversion of CO₂ hydrogenation increases substantially with increasing operating pressure, since the overall reaction involves a decrease in

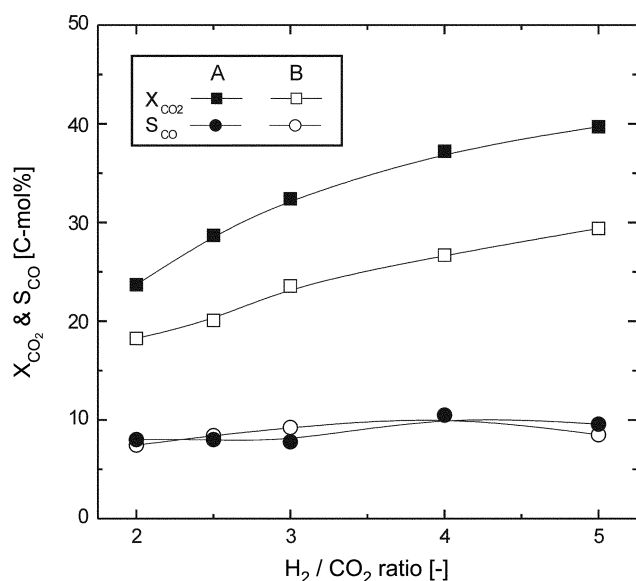


Fig. 10. Effects of H₂/CO₂ molar ratio on the CO₂ conversion and CO selectivity in the slurry reactor (T=275 °C).

	A	B
U _G [cm/s]	0.74	0.37
SV [ml/g _{cat} .hr]	2000	4000
P [MPa]	1	2

number of moles although the RWGS reaction has equal stoichiometric coefficients in the reaction equation. In contrast with constant gas velocity, it is noted in this figure that the effects of pressure decrease with increasing pressure in the W_{cat} of 20 g (condition B), because the increase of reaction pressure leads to the decrease of U_G in the slurry reactor. This might be attributed to condensed and accumulated long chain hydrocarbons and water in the slurry reactor, respectively, which cause inhibitions and reverse reaction due to high pressure and low U_G. Compared with CO hydrogenation (F-T reaction) [Dry, 1982; Sanders et al., 1986], the pressure effect on the CO₂ hydrogenation was less sensitive in the range of 1-2.5 MPa.

Effects of H₂/CO₂ ratio on the X_{CO₂} and S_{CO} are shown in Fig. 10. As expected, the values of X_{CO₂} increase with increasing the ratio of H₂/CO₂ due to excess H₂ which can promote the hydrogenation reaction. It has been reported that the partial pressure of H₂ strongly affects the reaction rate as well in F-T reaction [Dry, 1982; Sanders et al., 1986].

Note that more than twice the CO₂ gas has been converted to hydrocarbons with reasonable level of conversion efficiency in this three-phase slurry reactor, compared to that of a fixed bed reactor.

In addition, the selectivity of CO has been considerably reduced with production of long chain hydrocarbons in the slurry reactor (Table 2).

CONCLUSIONS

The level of CO₂ conversion (X_{CO₂}) increases with increasing reaction temperature, pressure, and molar ratio of hydrogen to CO₂ in the slurry reactor. The CO₂ conversion exhibits its maximum value of 39.4% at U_G=0.74 cm/s. It has been found that the production of hydrocarbon in the low-temperature slurry reactor in the CO₂ hydrogenation is relatively higher than that in the high-temperature fixed bed reactors. The selectivity of CO has been considerably reduced in the slurry reactor.

ACKNOWLEDGMENT

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NOMENCLATURE

d _p	: particle size [mm]
S _{CO}	: CO selectivity
STY	: space time yield [Nm ³ /kg _{cat} .hr]
T	: temperature [°C]
U _G	: superficial velocity of gas phase [m/s]
V _G	: volumetric flow rate of gas phase [m ³ /hr]
W _{cat}	: catalyst weight [g]
X _{CO₂}	: CO ₂ conversion
Y _{HC}	: total hydrocarbon yield

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Table 2. Carbon dioxide conversion and product selectivity (P=1 MPa, H₂/CO₂=3, W_{cat}=40 g)

Reactor type	SV [ml/g _{cat} .hr]	T [°C]	X _{CO₂} [%]	S _{CO} [%]	Hydrocarbon distribution [C-mol%]								O/O+P [%]
					C ₁	C ₂ ⁻	C ₂	C ₃ ⁻	C ₃	C ₄ ⁻	C ₄	≥C ₅	
Slurry reactor	4000	275	27.0	9.2	7.8	4.1	2.1	6.2	1.8	3.4	2.1	63.3	69.5
Slurry reactor	2000	275	32.4	7.4	5.4	3.2	1.9	5.2	1.5	3.1	1.9	70.4	68.5
Slurry reactor	2000	300	39.4	7.6	7.7	3.4	1.6	5.8	1.4	3.4	1.8	67.3	72.4
Fixed bed	2000	300	35.0	15.0	8.5	5.1	1.9	9.4	3.4	8.0	3.6	45.0	71.7

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