

Characteristics of Carbon Dioxide Hydrogenation in a Fluidized Bed Reactor

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(Received 13 March 2001 • accepted 24 May 2001)

Abstract—Characteristics of CO₂ hydrogenation were investigated in a fluidized bed reactor (0.052 m ID×1.5 m in height). Coprecipitated Fe-Cu-K-Al catalyst ($d_p=75-90\ \mu\text{m}$) was used as a fluidized solid phase. It was found that the CO₂ conversion decreases but the CO selectivity increases, whereas the space-time-yield attains maximum values with increasing gas velocity. The CO₂ conversion has increased, but CO selectivity has decreased with increasing hydrogenation temperature, pressure or H₂/CO₂ ratio in the fluidized bed reactor. Also, the CO₂ 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 CO₂ 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 CO₂ 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 an 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 CO₂ 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 CO₂ 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(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O and Al(NO₃)₃·9H₂O 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 K₂CO₃ (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 (CO₂, H₂, N₂) 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 H₂/CO₂ ratio ranged from 2 to 5. Catalyst particles ($d_p=75-90\ \mu\text{m}$) 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 free-board region, respectively. Reaction temperature ranged from 250

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‡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.

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

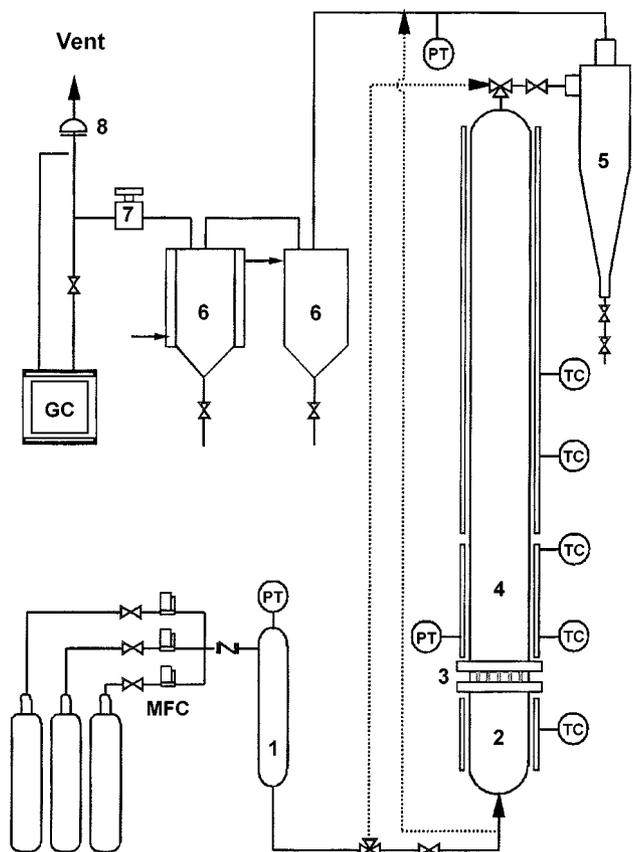


Fig. 1. Experimental apparatus.

- | | |
|----------------|----------------------------|
| 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

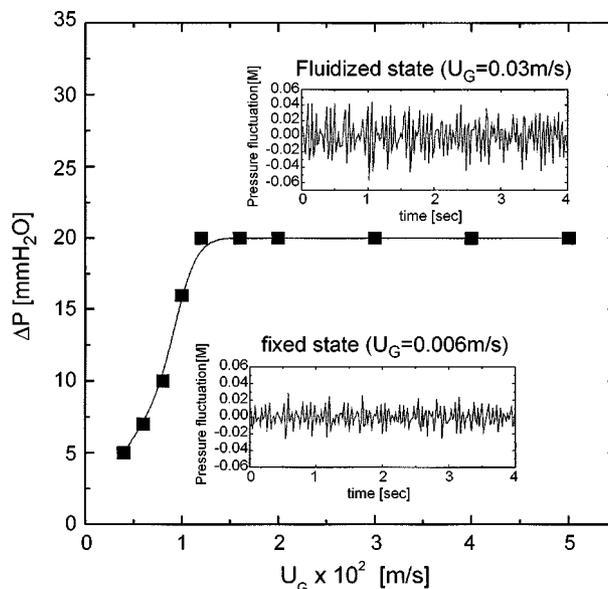
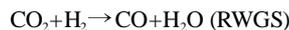


Fig. 2. Mean value and fluctuations of pressure drop in the bed with the variation of gas velocity ($T=300$ °C, $P=1$ MPa).

lines of pressure drop, the U_{mf} is determined at 0.012 m/s.

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



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.

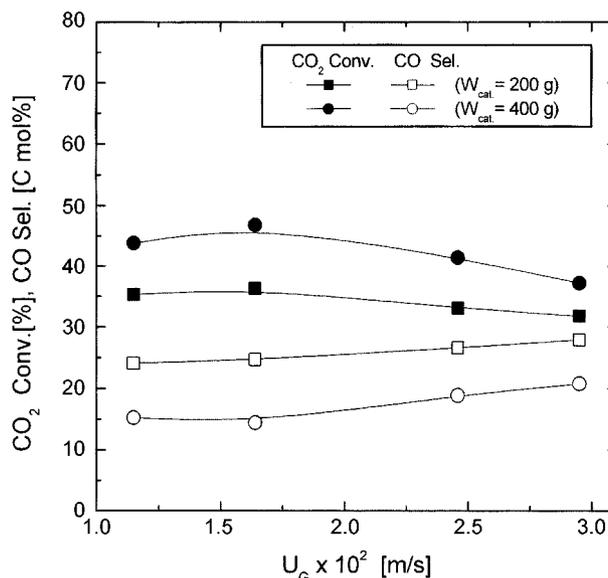


Fig. 3. Effects of gas velocity on the CO_2 conversion and CO selectivity ($T=300$ °C, $P=1$ MPa, $\text{H}_2/\text{CO}_2=3$).

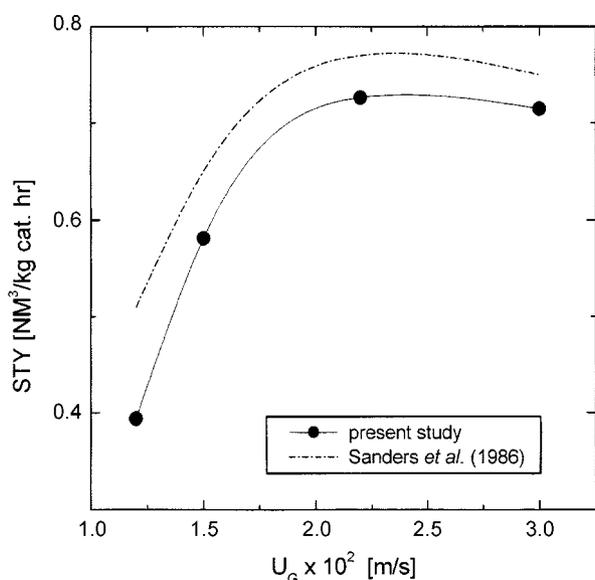


Fig. 4. Effects of gas velocity on the space-time-yield ($T=300^{\circ}\text{C}$, $P=1\text{ MPa}$, $\text{H}_2/\text{CO}_2=3$, $W_{\text{cat.}}=400\text{ g}$).

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

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

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].

$$\text{STY} = \frac{V_G X_{\text{CO}+\text{H}_2}}{W_{\text{cat.}}} \quad (3)$$

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

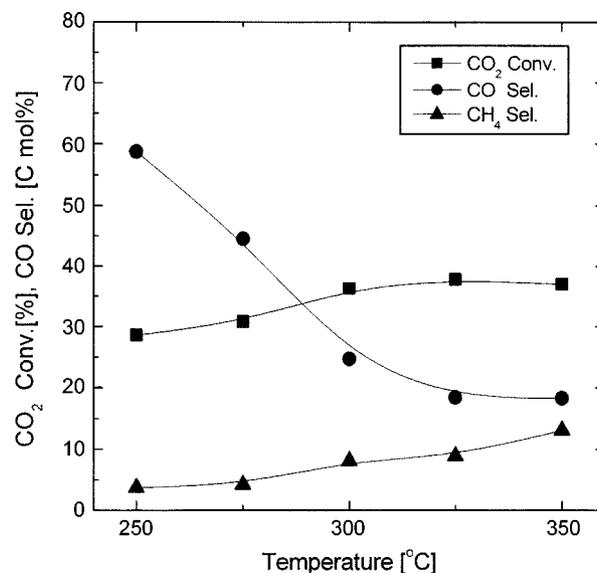


Fig. 5. Effects of temperature on CO_2 conversion and CO, CH_4 selectivities ($P=1\text{ MPa}$, $U_G=0.017\text{ m/s}$, $\text{H}_2/\text{CO}_2=3$, $W_{\text{cat.}}=200\text{ g}$).

hydrogenation, since CO is a byproduct.

$$\text{STY} = \frac{V_G(X_{\text{CO}_2} - X_{\text{CO}_2} S_{\text{CO}})}{W_{\text{cat.}}} \quad (4)$$

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-

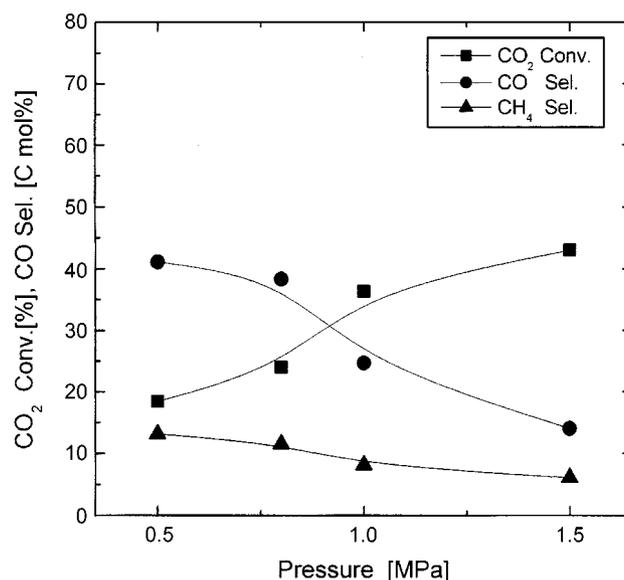


Fig. 6. Effects of pressure on the CO_2 conversion and CO, CH_4 selectivity ($T=300^{\circ}\text{C}$, $U_G=0.017\text{ cm/s}$, $\text{H}_2/\text{CO}_2=3$, $W_{\text{cat.}}=200\text{ g}$).

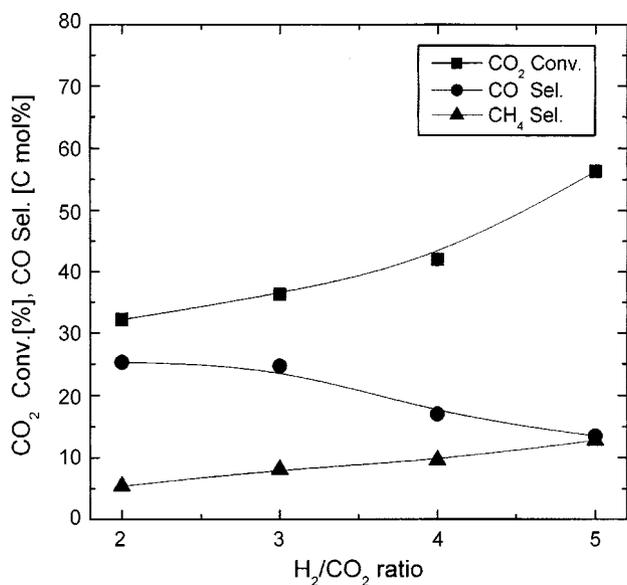


Fig. 7. Effects of H₂/CO₂ ratio on the CO₂ conversion and CO, CH₄ selectivities (T=300 °C, P=1 MPa, U_G=0.017 m/s, W_{cat}=200 g).

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 CH₄ selectivity increases gradually with increasing temperature (Fig. 5). This can be due to the increase in the rate of hydrogenation of individual CH₂ unit to CH₄. It has been usually found that the CH₄ 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 CO₂ 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 H₂/CO₂ ratio on the CO₂ conversion and CO and CH₄ selectivities are shown in Fig. 7. In this figure, the CO₂ conversion increases but the CO selectivity decreases, with increasing the H₂/CO₂ ratio. Also, the CH₄ selectivity increases with increasing H₂/CO₂ ratio. Although the increase of H₂/CO₂ ratio leads to the high conversion of CO₂ and low selectivity of CO, the optimum value of H₂/CO₂ ratio would exist around H₂/CO₂=3, because the selec-

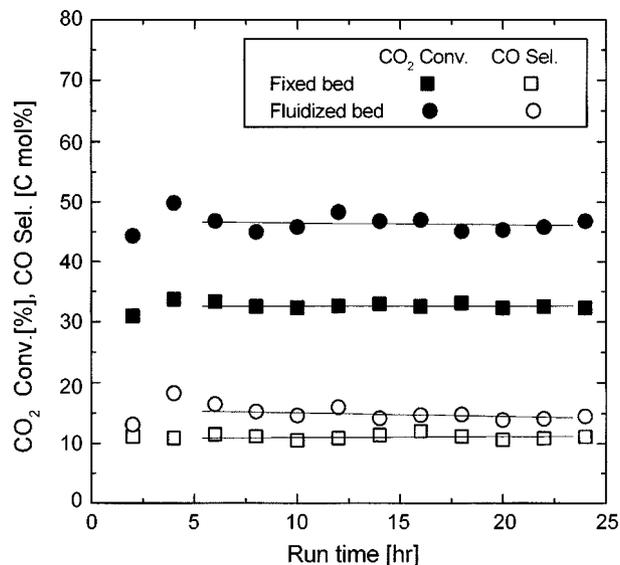


Fig. 8. Comparison of reactor performance between fixed and fluidized bed (T=325 °C, P=1 MPa, U_G=0.025 m/s, H₂/CO₂=3, W_{cat}=400 g).

tivities of by-products such as methane or paraffin increase with increasing H₂/CO₂ ratio.

Fig. 8 shows the CO₂ 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 CO₂ 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 CO₂ conversion and products selectivity are shown in Table 2. The product selectivities of CO₂ 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 CO₂ 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 CO₂ 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

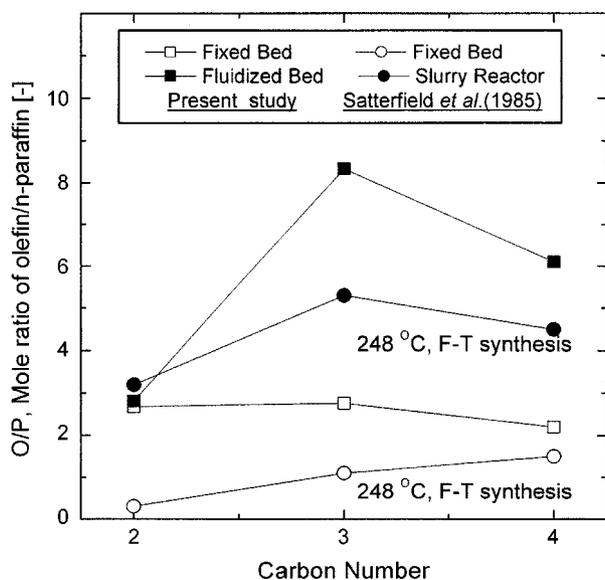


Fig. 9. Olefin/Paraffin ratio variation in the C₂-C₄ hydrocarbon products (T=325 °C, P=1 MPa, U_G=0.025 m/s, H₂/CO₂=3, W_{cat.}=400 g).

bed reactor by using Fe-Cu-K-Al catalyst as a fluidized solid phase. The CO₂ conversion decreases but the CO selectively increases, whereas the space-time-yield has attained maximum values with increasing gas velocity. The CO₂ conversion has increased but the CO selectivity has decreased, with increasing reaction temperature, pressure and H₂/CO₂ ratio in the reactor. The CO₂ 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

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