Slurry-Phase CO₂ Hydrogenation to Hydrocarbons over a Precipitated Fe-Cu-Al/K Catalyst: Investigation of Reaction Conditions

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Abstract–The hydrogenation of CO_2 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_2/CO_2 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_2 hydrogenation performance at a relatively low temperature (533 K). With the increase of reaction temperature CO_2 conversion and olefin to paraffin (O/P) ratio in C_2-C_4 hydrocarbons as well as the selectivity to C_2-C_4 fraction increased, while CO and CH_4 selectivity showed a reverse trend. With the increase in reaction pressure, CO_2 conversion and the selectivity to hydrocarbons increased, while the CO selectivity and O/P ratio of C_2-C_4 hydrocarbons decreased. The investigation of H_2/CO_2 ratio revealed that CO_2 conversion and CH_4 selectivity increased while CO selectivity and O/P ratio of C_2-C_4 decreased with increasing H_2/CO_2 ratio.

Key words : CO_2 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_2 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_2 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_2 hydrogenation to hydrocarbons have been published, which can be categorized into two groups according to the catalyst and reaction route. One is the CO_2 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_2 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_2 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_2 to hydrocarbons over iron-based catalysts via two consecutive steps [Lee et al., 1989, 1992]. CO_2 first reacts with H_2 to form CO and H_2O, the socalled 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_2 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_2 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 bass)	100Fe : 8.7Cu : 15.7Al : 8 K
BET surface area (m²/g)	134.3
Pore volume (cc/g)	0.19
Mean pore diameter (•)	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-cm³ 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-

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	

alyst was reduced in-situ with N₂/H₂ (10 % of H₂) 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 N₂/H₂ mixture was used as the reference gas for detecting H₂ consumption with a thermal conductivity detector (TCD). For the reactions, the flow rates of the reactant gases (H₂ and CO₂) 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-cm³ 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.
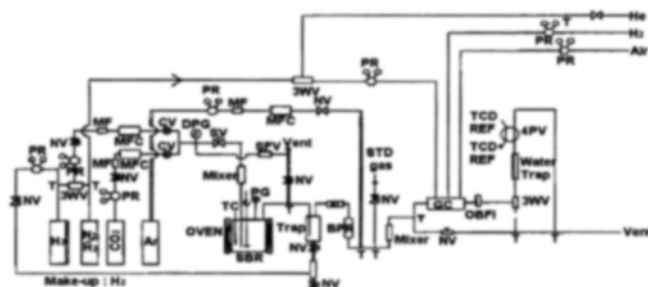
The feed-gas and non-condensable products were analyzed on-line with a DS 6200 GC : Ar, CO₂, CO and CH₄ were analyzed with a 6-feet carbosphere column and a TCD, while light hydrocarbons (C₁-C₈) were analyzed with a 30-meter GS-Q capillary column and a flame ionization detector (FID). Liquid hydrocarbons 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, CO₂ conversion could be calculated directly by comparison of differences in the CO₂/Ar peak ratio in the feed and during the reaction. CO and CH₄ 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 CH₄ 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 Fe₂O₃ : Fe₂O₃→Fe₃O₄→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 N₂/H₂ mixture (10 mole % of H₂)
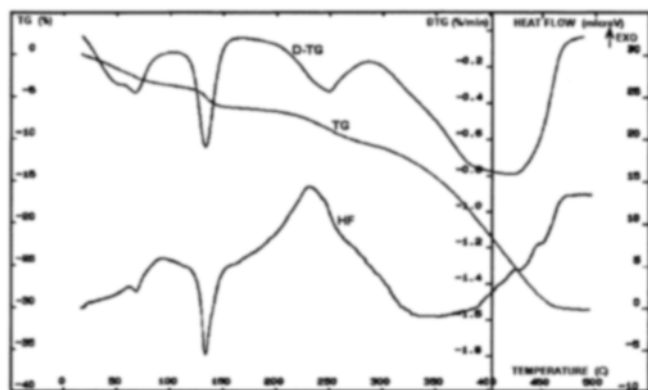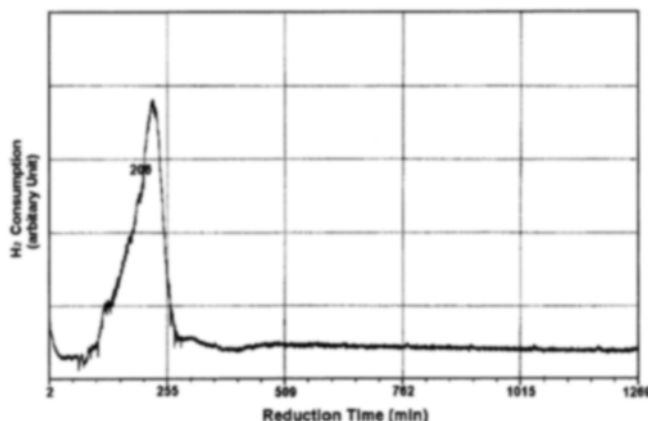
Fig. 2. TPR profiles of the catalyst.

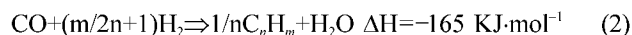**Fig. 3. Reduction curve of the catalyst.**
(reduction conditions : T=533 K, P=81 psig, W/F=15 g-cat.h/mol N₂+H₂)

was conducted in a slurry-bed reactor at 533 K and 81 psig. The consumption of H₂ 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 CO₂ hydrogenation over the Fe-Cu-Al/K catalyst at different temperatures in terms of CO₂ conversion, CO selectivity, hydrocarbon (HC) distribution and olefin/paraffin (O/P) ratio are shown in Table 2. It is obvious that CO₂ conversion and O/P ratio increased with the increase in reaction temperature, but CO and CH₄ selectivity showed a reverse trend. As for the hydrocarbon distribution, C₂-C₄ fraction showed a positive response to temperature, while C₅₊ decreased with increasing reaction temperature.

As mentioned in the introduction, CO₂ hydrogenation over iron-based catalysts proceeds via two sequential steps :

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \quad \Delta H = 41 \ KJ \cdot mol^{-1} \quad (1)$$

$$CO + (m/2n+1)H_2 \Rightarrow 1/nC_nH_m + H_2O \quad \Delta H = -165 \ KJ \cdot mol^{-1} \quad (2)$$

The first step is a reverse water gas shift reaction (RWGS) which converts CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ hydrogenation resulting from increasing temperature would consume more adsorbed H species than C species on the catalyst surface stoichiomet-rically, 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 CH₄ selectivity were observed. With regards to the hydrocarbon distribution, it is easily understood that selectivity toward C₂-C₄ fraction increased while selectivity to C₅₊ 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 CO₂ conversion and the product selectivity, in which it is seen that with the increase in reaction pressure CO₂ conversion as well as the selectivity to hydrocarbon products increased, while CO selectivity and O/P ratio of C₂-C₄ 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 CO₂ hydrogenation performance*

Temp. (K)	CO₂ conv. (%)	CO sel. (%)	CH₄ sel. (%)	Hydrocarbon distribution (C-atom %)					O/P ratio (molar)		
				C₁	C₂	C₃	C₄	C₅₊	C₂⁼/C₂°	C₃⁼/C₃°	C₄⁼/C₄°
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, H₂/CO₂=3/1, reductant gas : pure H₂.

Table 3. Effect of reaction pressure*

Pressure (Psig)	CO₂ conv. (%)	CO sel. (%)	CH₄ sel. (%)	Hydrocarbon distribution (C-atom %)					O/P ratio (molar)		
				C_1	C_2	C_3	C_4	C_{5+}	$C_2^=/C_2^0$	$C_3^=/C_3^0$	$C_4^=/C_4^0$
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 (CO₂+H₂), H₂/CO₂=3, reduction gas : H₂/N₂ mixture.

Table 4. Effect of H₂ to CO₂ feed ratio*

H₂/CO₂ (%)	CO₂ conv. (%)	CO sel. (%)	CH₄ sel. (%)	Hydrocarbon distribution (C-atom %)					O/P ratio (molar)		
				C_1	C_2	C_3	C_4	C_{5+}	$C_2^=/C_2^0$	$C_3^=/C_3^0$	$C_4^=/C_4^0$
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 (CO₂+H₂), reduction gas : H₂/N₂ mixture.

as that on the product side. Hence, pressure has no effect on CO_2 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_2 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_2 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_2 conversion.

3. Effect of H₂/CO₂ Ratio

The effect of H_2/CO_2 feed ratio on CO_2 conversion and product distribution is illustrated in Table 4, where it can be seen that CO_2 conversion and CH_4 selectivity increased while CO selectivity and O/P ratio of C_2-C_4 decreased with the increase of H_2/CO_2 ratio. It can be visualized easily that with the increase in H_2/CO_2 feed ratio, adsorbed H_2/CO_2 ratio on catalyst surface also increased. As a result, hydrogenation reactions for CO_2 and CO as well as for the secondary hydrogenation of olefin were promoted. Therefore, an increase in CO_2 conversion and CH_4 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_2 conversion, selectivity toward C_2-C_4 hydrocarbons and O/P ratio increased, but CO selectivity decreased.

3. In the cases studied, CO_2 conversion and the selectivity to hydrocarbon products increased, while the CO selectivity and O/P ratio decreased with increasing reaction pressure.

4. H_2/CO_2 feed ratio can influence both CO_2 conversion and product selectivity. In the cases studied, CO_2 conversion and CH_4 selectivity increased with H_2/CO_2 feed ratio while CO selectivity and O/P ratio showed the reverse trend.

Based on the above conclusions, the CO_2 hydrogenation reaction should be conducted at different conditions depending on the aim-product. In order to enhance the selectivity to olefins the CO_2 hydrogenation reaction should be carried out at higher temperature, medium pressure and lower H_2/CO_2 ratio.

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