Hydrogenation of carbon dioxide over alumina supported Fe–K catalysts

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The hydrogenation of CO_2 has been studied over Fe/alumina and Fe–K/alumina catalysts. The addition of potassium increases the chemisorption ability of CO_2 but decreases that of H_2. The catalytic activity test at high pressure (20 atm) reveals that remarkably high activity and selectivity toward light olefins and C_{2+} hydrocarbons can be achieved with Fe–K/alumina catalysts containing high concentration of K (K/Fe molar ratio = 0.5, 1.0). In the reaction at atmospheric pressure, the highly K-promoted catalysts give much higher CO formation rate than the unpromoted catalyst. It is deduced that the remarkable catalytic properties in the presence of K are attributable to the increase in the ability of CO_2 chemisorption and the enhanced activity for CO formation, which is the preceding step of C_{2+} hydrocarbon formation.

Keywords: carbon dioxide hydrogenation; iron–potassium catalyst; hydrocarbons

1. Introduction

Recently, there has been considerable interest in the reutilization of carbon dioxide as a useful carbon source for the synthesis of valuable chemicals [1–10]. One of the promising goals in carbon dioxide utilization is the selective synthesis of olefins or liquid hydrocarbons by the hydrogenation of carbon dioxide with hydrogen.

However, relatively little attention has been paid so far to the catalytic hydrogenation of carbon dioxide while carbon monoxide hydrogenation has been extensively investigated with the purpose of utilization of coal as a carbon source. In previous studies [11–16], iron-based catalysts, which were originally used in the Fischer–Tropsch (FT) reaction, have been applied to the hydrogenation of carbon dioxide to hydrocarbons. According to the results, however, it seems that those catalysts are not satisfactory because they give an only small yield of C_{2+} hydrocarbons with significant production of carbon monoxide and methane. Therefore, more systematic work is needed in order to develop suitable catalysts for the production of light olefins or liquid hydrocarbons from carbon dioxide hydrogenation.

Lee and co-workers [16] reported that a potassium-promoted iron catalyst is superior to an unpromoted one in the formation of olefins and long-chain hydrocarbons from CO_2 hydrogenation. However, the potassium-promoted catalyst they examined contained only 3 at% potassium. Fe–K catalysts with low content of potassium are usual in the FT reaction [17,18]. In the present work, hydrogenation of CO_2 was carried out on alumina-supported Fe–K catalysts with varying potassium content and it was found that catalysts with higher K content (K/Fe atomic ratio = 0.5–1.0) give considerably high conversion and selectivity to C_{2+} hydrocarbons and light olefins.

2. Experimental

Supported iron oxide catalyst with an iron loading of 20% (w/w) was prepared by impregnating γ-alumina (Strem, 157 m^2/g) with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. To prepare iron–potassium catalysts with different ratios (K/Fe molar ratio = 0–1.0), an adequate amount of K_2CO_3 was added into the aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ before impregnation. After the impregnation, the catalyst samples were dried at 383 K for 24 h and calcined in air at 773 K overnight. BET surface areas of the catalysts are listed in table 1. An increase in the potassium content in the catalyst resulted in a decrease in the surface area, indicating a large portion of alumina micropores was covered by potassium.

Chemisorption measurements of carbon dioxide and hydrogen were performed at 298 K using a chemisorption apparatus (Micromeritics ASAP 2000). The samples (1.0–1.2 g) used in the chemisorption studies were reduced for 12 h at 723 K in a flow of hydrogen, evacuated at the reduction temperature and then cooled to the adsorption temperature. The difference between the

Table 1
BET surface areas of catalyst samples

	K/Fe molar ratio					
	0	0.05	0.1	0.2	0.5	1.0
surface area (m^2/g)	128	128	121	113	92	39

adsorption isotherms obtained by repeated use of a gas dosing and degassing system gives the amount of chemisorbed gas on the catalysts. The sequential chemisorptions were also carried out by evacuation of weakly adsorbed gas from the first adsorption followed by exposure of the catalyst to another gas.

The temperature programmed decarburization was performed with the catalysts treated with a mixture gas of carbon dioxide and hydrogen at 573 K and 1 atm for 30 min followed by cooling down to room temperature with purging helium. The gas was changed to hydrogen and the temperature of the catalyst bed was increased to 923 K with a ramp of 8 K/min. The evolved product was mainly methane and it was continuously detected by a flame ionization detector, which gave the temperature programmed decarburization profile.

The catalytic hydrogenation of carbon dioxide was performed in a continuous fixed bed reactor. The catalyst was reduced in a flow of hydrogen at 723 K for 20–24 h. After the reduction, the catalyst was brought to the reaction temperature and then the feed changed to the mixture of carbon dioxide and hydrogen. The space velocity was 1900 ml/(g-cat h). The products were analyzed by a gas chromatograph (Chrompack CP 9001) equipped with thermal conductivity and flame ionization detectors. Carbon monoxide, carbon dioxide and water were analyzed on a Porapak Q column and the hydrocarbons on a Poraplot Q capillary column. The experimental data were taken after 24 h of reaction.

3. Results and discussion

3.1. Chemisorption of CO_2 and H_2

Table 2 shows the H_2 and CO_2 chemisorption capacities of the iron–potassium catalysts. The CO_2 chemisorption capacity is enhanced remarkably whereas that of H_2 chemisorption is diminished by the addition of potassium into the Fe/Al_2O_3 catalyst. These results can be explained in terms of increase in surface basicity by the addition of potassium to the catalysts. Carbon dioxide, which has an acidic character, tends to adsorb favorably on the alkali promoted catalysts. In the blank experiment with K on alumina in the absence of Fe, H_2 was not chemisorbed on the K/alumina samples, but almost a same amount of CO_2 was chemisorbed on the sample in the absence of Fe as compared with the sample in the presence of Fe. From these results, it is apparent that H_2 is adsorbed on only Fe but CO_2 adsorbed on both Fe and K. Table 1 also exhibits the influence of pre-chemisorbed hydrogen on subsequent CO_2 chemisorption and vice versa in the iron–potassium catalysts. From the results of sequential adsorption, it is apparent that pre-chemisorption of H_2 could not reduce the chemisorption of CO_2 in the second adsorption and vice versa. This suggests that the active site for one gas is different from that for the other gas. It is most likely that CO_2 is adsorbed on the K mainly and that K blocks the Fe sites.

Table 2
The chemisorbed amounts of H_2 and CO_2 on Fe/alumina and K–Fe/alumina catalysts

K/Fe atomic ratio	$H_2 \rightarrow CO_2$ [a]		$CO_2 \rightarrow H_2$ [b]	
	H_2 uptake (μmol/g)	CO_2 uptake (μmol/g)	CO_2 uptake (μmol/g)	H_2 uptake (μmol/g)
0.0	31.0	169	167	34.8
0.2	26.4	305	290 (307) [c]	30.2
0.5	20.1	533	514 (509)	25.6
1.0	8.5	398	376 (379)	5.3

[a] The order of sequential adsorption was H_2 and CO_2.
[b] The order of sequential adsorption was CO_2 and H_2.
[c] Numbers in the parentheses indicate the results with K/alumina samples which contain the same amounts of K as K–Fe/alumina samples.

3.2. Decarburization of surface carbon

The surface carbides are investigated by temperature programmed decarburization, which shows the relative amount and stability of surface carbon species formed during the reaction. Fig. 1 shows the decarburization profile of the iron–potassium catalysts after treatment under the reaction conditions for 30 min. Potassium increases the stability of surface carbides on the catalyst as revealed by the high temperature shift of the decarburization profiles on the potassium containing catalysts. The decarburization profile of the Fe/alumina catalyst shows a single peak with a maximum peak temperature of 722 K. In contrast, complicated profiles appear on the Fe–K/alumina (K/Fe = 0.2, 0.5) catalysts, which repre-

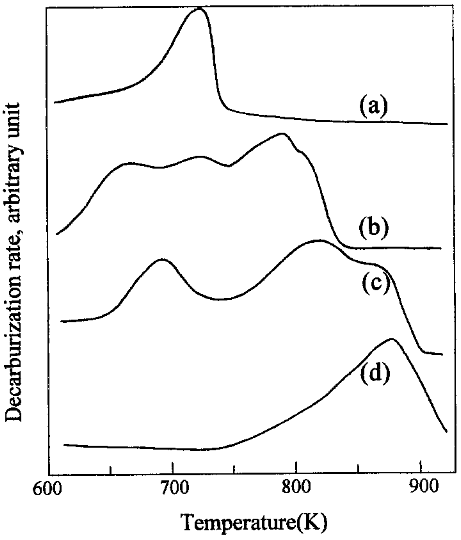

Fig. 1. Temperature programmed decarburization of carbides on the catalyst surface. (a) Fe/Al_2O_3, (b) Fe–K/Al_2O_3 (K/Fe = 0.2), (c) Fe–K/Al_2O_3 (K/Fe = 0.5), (d) Fe–K/Al_2O_3 (K/Fe = 1.0).

sents the presence of various carbides with different stability. However, at high potassium content (K/Fe = 1.0) a single broad peak is observed at the high temperature of 877 K. It seems that the carburization on the catalyst during the reaction is enhanced by K-promotion.

3.3. Catalytic activity and selectivity

Fig. 2 illustrates the catalytic activity for CO_2 hydrogenation as a function of potassium content at 573 K and 20 atm. The CO_2 conversion and yield of hydrocarbons increase with the potassium content of the catalyst increasing to K/Fe = 0.5 and then decrease slightly. Further, selectivities toward C_{2+} hydrocarbons and light olefins increase with increasing potassium content. It is noteworthy that highly potassium-promoted catalysts (K/Fe = 0.5, 1.0) give big changes in selectivities toward C_{2+} hydrocarbons and light olefins, in comparison with the unpromoted catalyst.

It is known that the formation of hydrocarbons from CO_2 takes place via the two-step mechanism of the reverse water–gas shift (RWGS) reaction and the FT reaction [12,16,19]. Since low reaction pressure favors the desorption of carbon monoxide as the intermediate toward hydrocarbons, information about the RWGS reaction on the catalysts would be obtained by carbon dioxide hydrogenation at atmospheric pressure. Table 3 shows the results of CO_2 hydrogenation on Fe/alumina and Fe–K/alumina catalysts at 573 K and atmospheric pressure. Indeed, the atmospheric reactions show higher selectivity toward carbon monoxide as compared to the reactions at 20 atm. From this table, it is evident that Fe–K/alumina catalysts have much higher activity for CO formation than Fe/alumina. In a previous study of CO_2 hydrogenation [20], CO formation was found to be the essential step of producing C_{2+} hydrocarbons with high conversion and selectivity. The higher activity of Fe–K/alumina catalysts for the RWGS reaction would surely contribute to the increase in the C_{2+} hydrocarbon formation from carbon dioxide at the elevated pressure.

Table 3
The results of CO_2 hydrogenation at 1 atm and 573 K

	K/Fe molar ratio			
	0	0.2	0.5	1.0
yield of CO	0.8	21.7	29.6	32.2
yield of hydrocarbons	0	11.7	0.9	0.7

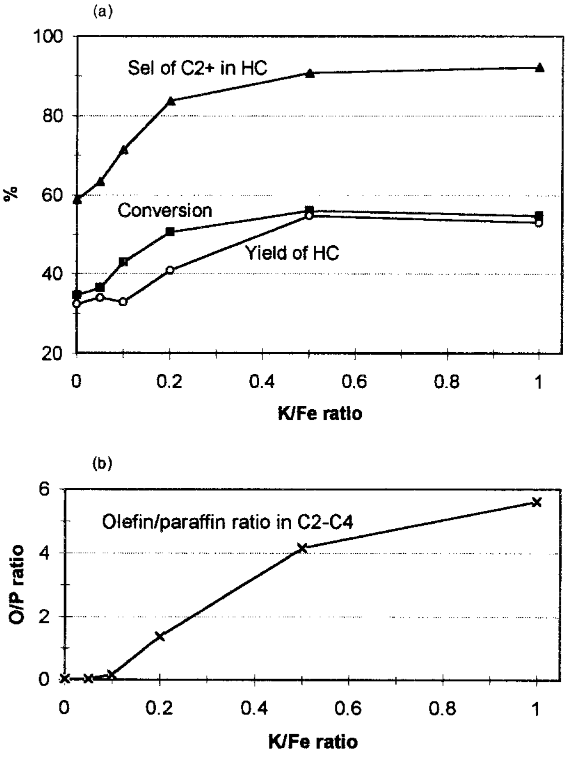

Fig. 2. Catalytic performance of Fe–K/alumina with varying K/Fe ratio (573 K and 20 atm).

Detailed reaction data at 673 K and 20 atm are listed in table 4. The distribution of hydrocarbons strongly depends on the potassium content of the catalyst. The selectivity to methane in hydrocarbons decreases largely as potassium is added to the catalyst. The chain growth probability, α, which is obtained for C_3–C_5 hydrocarbons is also shown in table 4. As the concentration of potassium in the catalysts increases, the chain growth probability α increases and then the increase becomes blunted over K/Fe = 0.5. This can be attributed to the increased ability of CO_2 chemisorption on highly K-containing catalysts as evidenced by the chemisorption study: that is, the preference for CO_2 rather than H_2 increases the probability of C–C bond formation. In contrast, the relatively low ratio of carbon dioxide to

Table 4
Data of CO_2 hydrogenation at 673 K and 20 atm

	K/Fe molar ratio			
	0	0.2	0.5	1.0
CO_2 conversion	48.9	67.3	69.6	68.4
selectivity (Cmol%)				
CO	12.4	6.0	3.9	4.5
hydrocarbons	87.6	94.0	96.1	95.5
hydrocarbon distribution (Cmol%)				
C_1	48.4	18.3	16.7	18.2
C_2 olefin	0.3	7.8	10.2	11.5
C_2 paraffin	20.2	6.1	2.1	2.1
C_3 olefin	1.2	19.9	17.2	18.7
C_3 paraffin	16.2	2.8	1.8	1.8
C_4 olefin	1.5	11.2	13.7	13.9
C_4 paraffin	7.4	5.7	2.6	0.5
C_5	3.8	13.7	16.3	16.1
C_{6+}	0.9	14.5	19.5	17.2
STY (Cmol/(kg h)) hydrocarbons	9.0	13.3	14.1	13.7
chain growth probability α[a]	0.39	0.60	0.72	0.69

[a] The chain growth probability used in Anderson–Schulz–Flory statistics.

hydrogen on the surface would probably favor methane formation.

It is reported that olefins are formed as a primary product over paraffins and undergo hydrogenation in the secondary steps [21]. The low surface concentration of hydrogen on highly K-containing catalysts would be also a favorable condition of olefin formation. This tendency appeared in the results that highly K-containing catalysts give a much improved selectivity toward olefins in C_2–C_4 hydrocarbons.

The higher product selectivity in the presence of a high concentration of potassium might be correlated with the results of decarburization which show that carburization on the catalyst during the reaction is enhanced by K-promotion. It is reported that iron carbides are responsible for the formation of olefins and long-chain hydrocarbons in CO_2 hydrogenation [16].

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