Hydrogenation of Carbon Dioxide on Unpromoted and Potassium-Promoted Iron Catalysts

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(Received October 7, 1988)

Synopsis. The promotional effect of potassium was studied on catalytic behavior of iron in CO_2 hydrogenation. A higher product selectivity toward light olefins and long-chain hydrocarbons was obtained on promoted catalyst than on unpromoted catalyst. This can be attributed to the enhancement of carburization on iron catalyst by potassium, as evidenced by Mössbauer spectroscopy and temperature-programmed decarburization.

The catalytic hydrogenation of CO has been extensively studied because it is an important step in utilization of coal as a carbon source. However, the hydrogenation of CO_2 has gained considerably less attention.[1-5] Previous studies indicated that the hydrogenation of CO_2 to hydrocarbons (HC) is proceeded via two elementary steps in series.[5-7] CO_2 first reacts with H_2 to form CO and H_2O, so-called reverse water-gas shift (RWGS) reaction, followed by Fischer-Tropsch (F-T) reaction in which CO is further hydrogenated to HC. Since iron-based catalysts are widely used in the industrial shift reaction as well as F-T reaction,[8,9] iron should be a potential catalyst for the hydrogenation of CO_2 to HC. On the other hand, potassium has long been known as an effective promoter of iron-based catalysts for the production of olefins and long-chain hydrocarbons in F-T reaction with enhanced water-gas-shift activity.[10] Accordingly, it is expected that potassium will also exhibit remarkable promotional effect in CO_2 hydrogenation.

In the present work, hydrogenation of CO_2 was carried out on the unpromoted and potassium-promoted iron catalysts. The bulk phase changes of catalysts during reaction were characterized by Mössbauer spectroscopy. Comparison between the relative stabilities of carbon deposits on used catalysts was accomplished by temperature-programmed decarburization. All the experimental evidences are helpful to elucidate the promotional effect of potassium on iron catalyst in CO_2 hydrogenation.

Experimental

Iron oxide was prepared by slowly adding ammonium hydroxide into an aqueous iron(III) nitrate solution until pH of 8.5 was reached. The precipitate was vacuum dried overnight at 393 K and calcined at 773 K for 24 h. To prepare potassium-promoted catalyst (with potassium loading of 3 atom%), calcined iron oxide was impregnated with an aqueous solution of potassium carbonate to incipient wetness followed by further calcination at 773 K for 3 h. Two catalyst samples are designated as Fe and K/Fe, respectively.

Prior to reaction tests, the calcined samples were reduced in situ in flowing hydrogen at 773 K for 15 h. The reactions were carried out in a tubular flow reactor at 593 K under 101 kPa or 1013 kPa, using a H_2/CO_2 (4/1 mole ratio) mixture of 600 cm^3(NTP) $h^{-1}g^{-1}$ (based on unreduced catalysts) as feed gas. Effluent gas from the reactor was analyzed by a gas chromatograph equipped with Porapak Q columns and both thermal conductivity detector (TCD) and flame ionization detector (FID).

In each of the temperature-programmed decarburization (TPDC) runs, the catalyst of 0.1 g was subjected to a H_2/CO_2 feed gas of 10 $cm^3 min^{-1}$ under 101 kPa. After a certain period, the catalyst bed was purged with helium for 2 min followed by quickly cooling down to room temperature. The gas stream was then switched to hydrogen and temperature increased to 773 K at 5 K min^{-1} to evolve carbon deposits on the catalyst. Continuous detection of any H_2-evolved carbon by FID gives a TPDC profile.

All ^{57}Fe-Mössbauer spectra were recorded at room temperature with a ^{57}Co(Rh) source oscillating in constant acceleration mode. The hyperfine spectrum of a natural iron foil was used to calibrate the velocity scale. After computer folding, each spectrum consisted of 512 points and was fitted with Lorentzian lines using a nonlinear regression program.[11]

Results and Discussion

The Mössbauer spectra show a single sextet with a hyperfine field of 330 kOe for both freshly reduced Fe

Table 1. Conversion and Product Selectivity in CO_2 Hydrogenation[a)]

Catalyst	Reaction pressure	CO_2 conv.	Yield of CO	Yield of HC	HC distribution/carbon %					Olefin/ paraffin ratio in C_2—C_4
	kPa	%	%	%	CH_4	C_2	C_3	C_4	C_{5+}	
Fe	101	21.6	17.1	4.5	66.5	18.3	9.2	3.3	2.7	0.90
Fe	1013	32.0	7.5	24.5	33.1	15.6	15.2	9.9	26.2	0.21
K/Fe	101	19.2	18.7	0.5	59.4	15.8	11.4	5.8	7.6	6.4
K/Fe	1013	34.7	6.3	28.4	19.7	12.6	16.9	14.5	36.3	5.3

a) Reaction conditions: temp=593 K, H_2/CO_2=4/1 (mole ratio), GHSV=600 $cm^3 h^{-1} g^{-1}$. Data were taken after 24 h reaction (101 kPa) and 48 h reaction (1013 kPa).

and K/Fe catalysts, indicating that all iron atoms exist in the form of α-Fe before reaction. The BET surface areas of these two catalysts are nearly the same (14±2 $m^2\ g^{-1}$). However, CO uptake at 195 K by K/Fe catalyst (0.8 $\mu mol\ g^{-1}$) is far less than that by Fe catalyst (4.5 $\mu mol\ g^{-1}$), consistent with the picture in which a large portion of iron surface is covered by potassium.[12]

The conversion and product selectivity of CO_2 hydrogenation on both catalysts are listed in Table 1 for comparison. The promotional effect of potassium was reflected in the higher selectivity toward light olefins and long-chain hydrocarbons on K/Fe catalyst. This catalytic result can be satisfactorily explained from the viewpoint that the carburization (in contrast to hydrogenation) on iron catalyst was enhanced by potassium during CO_2 hydrogenation.

Figure 1 shows the Mössbauer spectra of used catalysts after CO_2/H_2 reactions. During computer fitting, seven sextets attached to four components (α-Fe, Fe_3O_4, θ-Fe_3C, and χ-Fe_5C_2) are taken into consideration. Based on the assumption that the recoil-free fraction of ^{57}Fe nuclei in γ-ray resonance absorption is the same for all components, the percentages of spectral peak areas (see Table 2) represent directly the distribution of iron atoms in individual components.

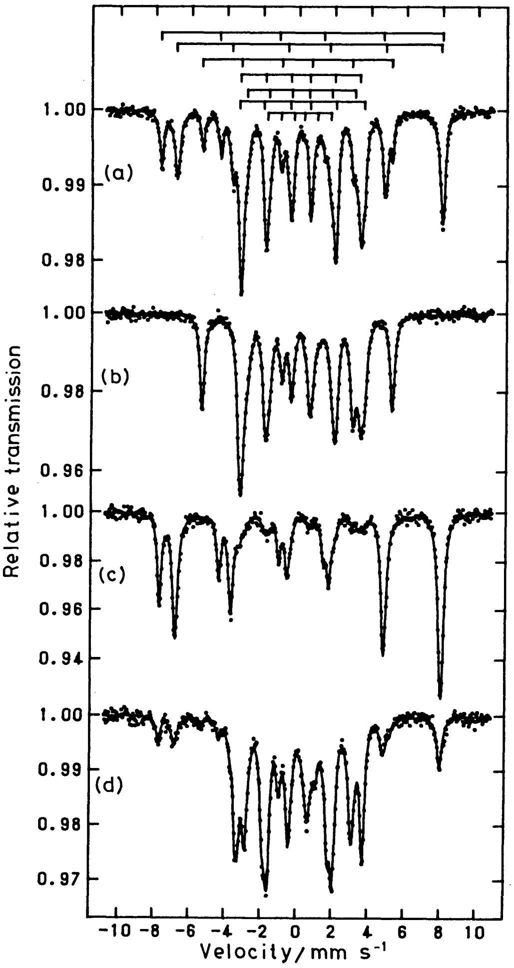

Fig. 1. Mössbauer spectra of (a) Fe and (b) K/Fe catalysts after CO_2/H_2 reaction under 101 kPa for 24 h, and (c) Fe and (d) K/Fe catalysts after CO_2/H_2 reaction under 1013 kPa for 48 h. The seven identifications shown for the (a) spectrum represent, from top down respectively, the tetrahedral and octahedral sites in Fe_3O_4, α-Fe, θ-Fe_3C, and I, II, and III sites in χ-Fe_5C_2.

Metallic iron catalysts will be oxidized (to Fe_3O_4) as well as carburized (to χ-Fe_5C_2 or θ-Fe_3C) during CO_2 hydrogenation. For a given catalyst, high reaction pressure favors the formation of Fe_3O_4. Since H_2O is the common product in both elementary steps (RWGS and F-T reactions) of overall CO_2 hydrogenation, high conversion of CO_2 especially with increased HC yield leads to abundant H_2O production. Therefore, it is believed that the preference for Fe_3O_4 formation under elevated pressure is due to the oxidation of metallic iron by H_2O.

The bulk carburization of iron catalyst is enhanced in the presence of potassium promoter. Not only carbide phases are more preferable on K/Fe catalyst than on Fe catalyst for given reaction conditions, but the relative dominance of carbide phases shifts from θ-Fe_3C to χ-Fe_5C_2. The χ-Fe_5C_2 phase is known to be less stable than θ-Fe_3C phase,[13,14] and its formation requires a lower H_2/CO feed ratio in CO hydrogenation. However, CO is an intermediate product instead of reactant in CO_2 hydrogenation. This in turn leads to a high ratio of H_2/CO on the catalyst surface, which is a favorable condition for θ-Fe_3C formation.

Table 2. Peak Area Percentages of Spectral Contributions Shown in Fig. 1

Spectrum	α-Fe	Fe_3O_4	θ-Fe_3C	χ-Fe_5C_2
(a)	7.4	33.9	33.2	25.5
(b)	28.8	—	25.9	45.3
(c)	—	86.8	6.7	6.5
(d)	2.3	14.1	—	83.6

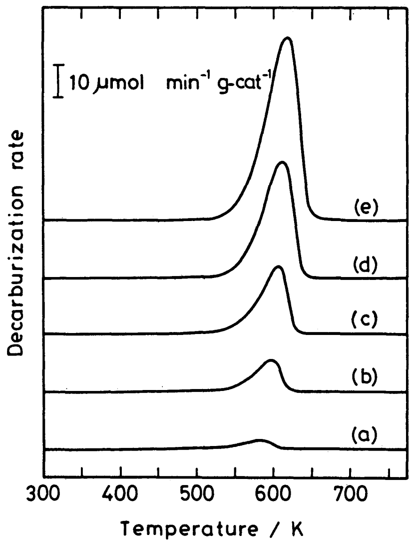

Fig. 2. Temperature-programmed decarburization profiles (with a heating rate of 5 K min^{-1}) of Fe catalyst after CO_2/H_2 reaction for (a) 2, (b) 5, (c) 10, (d) 20, and (e) 40 min.

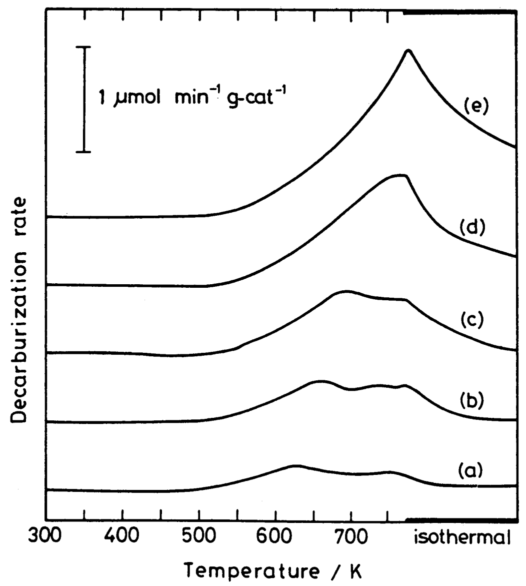

Fig. 3. Temperature-programmed decarburization profiles (with a heating rate of 5 K min^{-1}) of K/Fe catalyst after CO_2/H_2 reaction for (a) 2, (b) 5, (c) 10, (d) 20, and (e) 40 min.

The enhancement of carburization on K/Fe catalyst destroys this condition to some extent, and hence χ-Fe_5C_2 is more likely to form.

The relative stabilities of carbon deposits on used catalysts are also reflected by the peak temperatures of TPDC profiles. The higher peak temperature implies the more stable carbon deposits, and vice versa. Figures 2 and 3 show the TPDC profiles of Fe and K/Fe catalysts, respectively, after subjecting to CO_2/H_2 reaction for various times between 2 and 40 min.

All TPDC profiles for Fe catalyst show a single peak with peak temperature shifting from 587 K to 621 K when reaction time increases from 2 to 40 min. As shown in Fig. 2, most carbon deposits are evolved in the temperature range between 500 K and 650 K. In contrast, multiple peaks can be observed on the TPDC profiles of K/Fe catalyst if reaction time is shorter than 10 min, indicating that more than one forms of carbon deposits exist with different reactivities toward hydrogen. The distribution of carbon deposits with various stabilities makes the TPDC peaks of K/Fe catalyst much broader, regardless of the take-off temperature of TPDC peaks close to that of Fe catalyst. As the reaction time further increases, overlapping between unresolved TPDC peaks tends to combine in a single but even broader peak with peak temperature higher than 770 K. Since the temperature rise was stopped at 773 K in TPDC experiments and then held isothermally at that temperature, the decarburization rate turns to drop due to the decrease of driving force.

In summary, it is no doubt that carbon deposits on K/Fe catalyst are more stable than on Fe catalyst upon comparing the corresponding TPDC peak temperatures. The existence of more stable carbon deposits provides another evidence for the enhancement of carburization on iron catalyst by potassium promoter. This promotional effect of potassium also leads to the preference for bulk phase changes of K/Fe catalyst to carbides rather than oxides, as observed in Mössbauer spectroscopy, and bears the responsibility for the higher product selectivity of light olefins and long-chain hydrocarbons in CO_2 hydrogenation.

The authors wish to thank Dr. Teng-Yuan Dong (Institute of Chemistry, Academia Sinica) for his generosity of providing the Mössbauer spectrometer and assistance in the spectroscopic experiments. Financial support of this work by National Science Council (grant NSC77-0402-E002-05) is gratefully acknowledged.

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