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Kinetic and Mechanistic Studies on the Kölbel-Engelhardt Reaction over an Iron Oxide Catalyst

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The yield and selectivity to hydrocarbons in the Kölbel-Engelhardt (KE) reaction over a Fe_2O_3 catalyst at 548—593 K under atmospheric pressure were as low as 0.6—2.2% and 2.0—3.8%, respectively, but the observed four characteristic features of the reaction, *i.e.*, the distribution of produced hydrocarbons following the Schulz-Flory plot, the decrease in propagation probability with increasing reaction temperature, nearly the same value of propagation probability irrespective of a great change in contact time of the reaction, and the remarkable decrease in the yield ratio of olefins to paraffins with increasing contact time of the reaction agreed with the common features of the synthesis of hydrocarbons by the Fischer-Tropsch reaction. The catalyst was composed of Fe_3O_4 with a low concentration of χ-type carbide (Fe_5C_2) during the KE reaction, and the results of the effect of contact time on the reaction revealed that formation of hydrocarbons took place following the water-gas shift (WGS) reaction. Furthermore, both the rates of formation of hydrocarbons in the reactions of carbided iron catalyst (Fe_5C_2) with H_2O and with H_2 at 573 K were smaller by a factor of >5 than the rate of formation of hydrocarbons in the KE reaction at a steady state at 573 K. Thus, it is concluded that a much greater portion of hydrocarbons produced in the KE reaction was *via* a sequential reaction pathway involving the WGS reaction followed by the Fischer-Tropsch reaction, not *via* the decomposition of carbided iron catalyst with H_2O and its reduction with H_2. Based on the observed increase in the catalytic activity of Fe_2O_3 upon addition of a small amount of such metal oxides as Cu, Pt, Co, Ni, and Rh oxides, the mechanical mixture of a WGS reaction catalyst and a Fischer-Tropsch reaction catalyst is proposed to be an effective catalyst for the production of hydrocarbons and one illustration of this view is presented.

The catalytic reaction of CO with H_2O to produce hydrocarbons and CO_2 is known as the Kölbel-Engelhardt (KE) reaction.[1] Recently, the KE reaction has received a great deal of attention as a process for the production of hydrocarbons from CO-rich synthesis gas, and the catalytic activity of Fe and Fe-based catalysts,[2-4] a RuY-zeolite catalyst[5] and supported Rh catalysts[6] has been investigated. However, the mechanism of the KE reaction has not been firmly established. There are two possible pathways by which the reaction may proceed. The first pathway involves the coupling of a WGS reaction and a Fischer-Tropsch reaction. The second possibility involves a reaction of H_2O with metal carbide or surface carbons to form hydrocarbons. Gustafson and Lunsford[5] indicated that the KE reaction over a RuY-zeolite catalyst by which only CH_4, CO_2, and H_2 were produced proceeds *via* a sequential reaction pathway involving the WGS reaction followed by the methanation reaction. While the first pathway is thus generally acceptable there are reports[7,8] which suggest that H_2O may react with metal carbide to form hydrocarbons in the KE reaction over Fe-based catalysts.

In the present work, we have mechanistically investigated the KE reaction over a Fe_2O_3 catalyst and have then discussed the promotional effects of Cu, Pt, Co, Ni, Cr, Rh, Ru, and Pd oxides on the catalytic activity of Fe_2O_3 in relation to the mechanism of the KE reaction.

Experimental

Reaction and Analysis The catalytic reaction of CO with H_2O was carried out at 548—593 K with a conventional flow fixed-bed reactor at atmospheric pressure. The reactor system comprised a 18-mm-i.d. Pyrex tube, 350 mm long, and a concentric thermowell. The reactor was heated with a cylindrical electric furnace. The catalyst was of powder-type, and Rasching rings (3×3 mm) were added above and below the catalyst bed. Research grade CO–Ar mixed gas (CO 90.2 vol%, Japan Oxygen Company, Ltd.) was used. It was fed into the reactor after bubbling through a H_2O-saturator held at a controlled temperature. The standard feed rate of the CO–Ar gas was 20 NTP cm^3 min^{-1} and the feed molar ratio of CO to H_2O was always 3. Purchased He and H_2 of greater than 99.99% purity were used without further purification. All reaction products were analyzed by gas chromatography. Two columns in series, 2.0 m of Porapak Q(383 K) and 1.5 m of Molecular sieve 5A(308 K), and hydrogen as the carrier gas were used for the analysis of CO, CO_2, Ar, and H_2O. Hydrogen, CH_4, and CO were analyzed by means of 2.0 m of Molecular Sieve 5A (323 K) with Ar as the carrier gas, and hydrocarbons were analyzed with a temperature-programmed FID system (Shimadzu GC-MINI 2, 333→473 K, Chromosorb 102 3.0 m).

Catalyst. A Fe_2O_3 catalyst was prepared following the method reported[9]: the $Fe(OH)_3$ cake obtained was dried at *ca.* 380 K in an electric oven for 24 h and was then calcined at 673 K in air for 6 h. X-Ray powder diffraction analysis revealed that Fe_2O_3 thus prepared was of α-type (hematite).[10] Its surface area determined by the conventional B.E.T. method was 28 m^2 g^{-1}. We also prepared metal oxide-promoted Fe_2O_3 catalysts and SiO_2-and Al_2O_3-supported metal oxide catalysts using an impregnation method. Metal oxide-promoted Fe_2O_3 catalysts were prepared by use of the Fe_2O_3 catalyst prepared above. Al_2O_3 employed as a carrier was JRC-ALO-4(60—80 mesh, 166—174 $m^2 g^{-1}$), one of the referenced Al_2O_3 catalysts in the Catalysis Society of Japan.[11] SiO_2(32—60 mesh) as a carrier had a B. E. T. surface area of 200 m^2 g^{-1}. Metal nitrates were used as a catalyst resource for Cu, Co, Ni, and Cr oxides whereas metal chlorides were used similarly for Ru, Rh, and Pd oxides. These impregnated catalysts were then calcined at 673 K in air for 3 h. Supported Pt oxide catalysts were similarly prepared by use of $H_2PtCl_6 \cdot 6H_2O$. A CuO-ZnO catalyst (24 m^2 g^{-1}), a commercial catalyst for the WGS reaction, was prepared following the method reported.[12)]

Results

KE Reaction over Fe_2O_3. The characteristic feature of the KE reaction over Fe_2O_3 was first investigated. Non-pretreated Fe_2O_3 catalyst (15.0 g) was packed in the reactor and was heated to the reaction temperature after complete purging of air from the reactor with He at room temperature. Table 1 summarizes the steady-state catalytic activities of Fe_2O_3 in the KE reaction at 548, 573, and 593 K. These catalytic activities were obtained after a preliminary period of 4—5 h and the conversion of H_2O was always nearly 100% at these three reaction temperatures. The main products in the reaction were CO_2 and H_2, as reported previously.[2—4)] The conversion of CO and the yield of hydrocarbons were 30.5 and 0.6% at 548 K, and the conversion increased to 45.2 and 67.5% with increasing reaction temperature from 548 K to 573 and 593 K but the yield of hydrocarbons still remained to be as low as 1.7% (selectivity=3.8%) and 2.2% (3.2%) at 573 and 593 K, respectively (Table 1). The equilibrium conversion of CO due to the WGS reaction calculated on the basis of thermodynamic data[13)] is 32.7% at a (CO/H_2O) feed molar ratio of 3 at 600 K. Hence, the relatively great values of the conversion of CO, 45.2 and 67.5%, found at 573 and 593 K (Table 1) are probably caused by the occurrence of the Boudouard reaction($2CO \rightarrow CO_2+C$). On the other hand, the distribution of hydrocarbons produced by the KE reaction at these three reaction temperatures followed the Schulz-Flory plot[†] (Fig. 1, at 573 K). The values of propagation probability obtained are also summarized in Table 1. The propagation probability decreased with increasing reaction temperature (Table 1).

TABLE 1. SUMMARY OF THE STEADY-STATE CATALYTIC ACTIVITY OF Fe_2O_3 FOR THE KE REACTION[a)]

Reaction temp/K	548	573	593
Conversion of CO/%	30.5	45.2	67.5
Yield of H.C.[b)]/%	0.6	1.7	2.2
Selectivity to H.C.[b)]/%	2.0	3.8	3.2
Hydrocarbon	Distribution/carbon wt%		
C_1	15	24	35
C_2'	10	14	18
C_2	10	14	11
C_3'	19	22	18
C_3	1	3	2
C_4	13	8	6
C_5	12	7	4
C_6	9	4	3
C_7	9	2	1
C_{8+}[c)]	1	2	3
Propagation probability/—	0.66	0.48	0.38

a) Catalyst: Fe_2O_3 15.0 g, non-pretreated. Contact time: 311 g-catalyst·h·mol CO^{-1}. CO/H_2O feed molar ratio: 3. b) Hydrocarbons. C_2'=ethylene, C_2=ethane, C_3'=propylene, C_3=propane, $C_n (n \geq 4)$=hydrocarbons having *n* carbon atoms in a molecule. c) Hydrocarbons having eight and more than eight carbon atoms in a molecule.

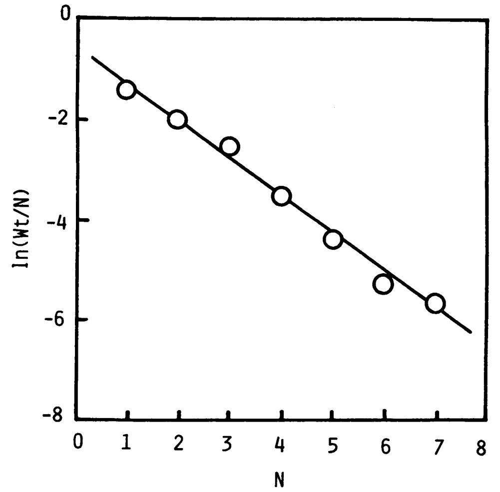

Fig. 1. Schulz-Flory plot for the hydrocarbons obtained at a steady state in the KE reaction at 573 K. Catalyst: Fe_2O_3 15.0 g, non-pretreated. Contact time: 311 g-catalyst·h·mol CO^{-1}. CO/H_2O feed molar ratio: 3.

The steady state of Fe_2O_3 during the KE reaction at a (CO/H_2O) feed molar ratio of 3 at 573 K was quenched by flushing the reactor with He. The result of X-ray powder diffraction analysis revealed that the quenched catalyst was composed of Fe_3O_4 (magnetite)[14)] and Fe_5C_2 (χ-type carbide)[15)] with a ratio of the strongest diffraction peak of 100:5.

Effect of Contact Time. Figure 2 shows the effect of contact time on the KE reaction over Fe_2O_3 at 573 K. At a contact time of 18.7 g-catalyst·h·mol CO^{-1} the yield of hydrocarbons was negligible although the conversion of CO was as high as 18.0%: both the yields of CO_2 and H_2 were nearly the same as the conversion of CO. However, formation of hydrocarbons was seen at 29.4 g-catalyst·h·mol CO^{-1} and the yield of hydrocarbons then increased with increasing contact time of the reaction to reach 2.8% at 562 g-catalyst·h·mol CO^{-1} (Fig. 2). The propagation probability calculated on the basis of the Schulz-Flory plot remained nearly constant at 0.47—0.49 at 573 K although the contact time changed greatly between 29.4 and 562 g-catalyst·h·mol CO^{-1}. In contrast, the ratio of the combined yield of $C_2H_4+C_3H_6$ to that of $C_2H_6+C_3H_8$ was 25.9, 9.4, and 0.5 at 29.4, 141, and 562 g-catalyst·h·mol CO^{-1}, respectively. Thus the ratio of the yield of olefins to that of paraffins decreased markedly with increasing contact time of the reaction.

Reaction of H_2O with Carbided Iron Catalyst. The reaction of H_2O with Fe_5C_2 was studied at 573 K. The

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[†] Schulz-Flory plot

$$\ln \frac{W_t}{N} = N \ln P + \ln \frac{(1-P)^2}{P},$$

where *N*, *P*, and W_t are number of carbon atom in hydrocarbon molecule produced, propagation probability, and distribution (carbon weight fraction) of hydrocarbon molecule having *N* carbon atoms, respectively.

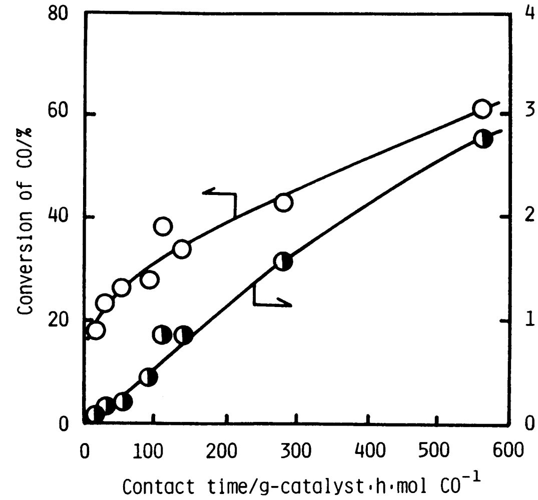

Fig. 2. Effect of contact time on the KE reaction at 573 K.
Catalyst: Fe_2O_3, non-pretreated. CO/H_2O feed molar ratio: 3.
○: Conversion of CO, ◑: Yield of hydrocarbons.

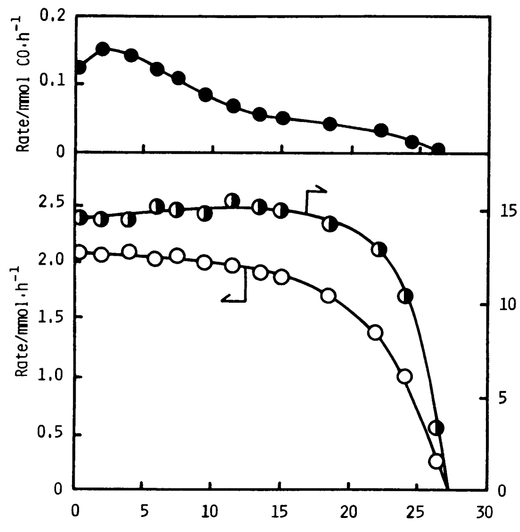

Fig. 3. Variation in the rates of H_2, CO_2, and hydrocarbon formations during the reaction of H_2O with carbided iron catalyst at 573 K.
Catalyst pretreatment: Fe_2O_3 (15.0 g) was carbided in a stream of CO-Ar(CO 90.2 vol%, 60 NTP cm^3 min^{-1}) at 573 K for 22 h.
Reaction with H_2O: Ar/H_2O feed molar ratio = 3, Ar 20 NTP cm^3 min^{-1}.
○: Rate of CO_2 formation, ◑: rate of H_2 formation, ●: rate of hydrocarbon formation.

Fe_2O_3 catalyst (15.0 g) had been carbided in a stream of CO-Ar (CO 90.2 vol%, 60 NTP cm^3 min^{-1}) at 573 K for 22 h. The result of X-ray powder diffraction analysis revealed that the Fe_2O_3 catalyst was completely carbided to Fe_5C_2[15] by the above pretreatment. Figure 3 shows variation in the rates of formation of H_2, CO_2, and hydrocarbons with time during the reaction of H_2O with the carbided iron catalyst at 573 K. The rate of formation of hydrocarbons showed the maximum value (0.15 mmol CO·h^{-1}) at 45 min, but it then decreased with time and reached negligible values within 27 h. The rates of formation of CO_2 and H_2 also showed a similar behavior (Fig. 3). Thus, the decomposition of Fe_5C_2 with H_2O at 573 K was completed within 27 h. It should be noted that the maximum rate of formation of hydrocarbons obtained in the reaction of H_2O with the carbided iron catalyst at 573 K was smaller by a factor of five than the rate of formation of hydrocarbons at a steady state in the KE reaction at 573 K (0.816 mmol CO·h^{-1}, Table 1). The hydrocarbons formed in the reaction had the distributions similar to those of hydrocarbons produced in the KE reaction (Table 1) although the distribution of CH_4 in the former reaction was fairly greater than that in the latter reaction and although the yield of higher hydrocarbons was negligible in the former reaction (*i.e.*, C_1 47 wt%, C_2' 12 wt%, C_2 9 wt%, C_3' 16 wt%, C_3 7 w%, and C_4 9 wt% at 18 h). The result of X-ray powder diffraction analysis revealed that the carbided iron catalyst completely changed to Fe_2O_3 after the reaction with H_2O at 573 K for 27 h.

TABLE 2. MATERIAL BALANCE FOR THE REACTION OF H_2O WITH CARBIDED IRON CATALYST AT 573 K FOR 27 h[a)]

Reactants and products	Amount/mol
H_2O fed	0.42
H_2O reacted	0.38
H_2 evolved	0.37
CO_2 evolved	0.061
Hydrocarbons formed	0.002[b)]
Carbon in carbided iron catalyst	0.075[c)]

a) Reaction conditions: see Fig. 3. b) Carbon atoms converted to hydrocarbons. c) Calculated as Fe_5C_2 in atom unit.

The material balance for the reaction of H_2O with the carbided iron catalyst at 573 K for 27 h (Fig. 3) is presented in Table 2. The amount of oxygen caught by the carbided iron catalyst was 0.38—0.061×2=0.26 atoms, which is nearly equal to the amount of oxygen contained in 15.0 g of Fe_2O_3 (0.28 atoms). Similarly, the amount of CO_2 evolved (0.061 mol) was nearly equal to that of carbon previously existed in the Fe_5C_2 (0.075 atoms), and the ratio of the amount of H_2 evolved to that of CO_2 evolved was 0.37/0.061=6.0. The total yield of hydrocarbons was as low as (0.002/0.075)×100 =3% (Table 2).

Reduction of Carbided Iron Catalyst with H_2. The Fe_2O_3 catalyst (15.0 g) had similarly been carbided in a stream of CO-Ar at 573 K for 22 h, and the carbided iron catalyst obtained was then reduced at 573 K in a stream of H_2-Ar (H_2 33.3 vol%, 30 NTP cm^{3}min^{-1}). The main product in the reaction was CH_4. Although formation of C_2H_4, C_2H_6, and C_3H_6 was seen at the initial stages of the reaction, the yield of these hydrocarbons was as low as 0.05, 0.5, and 0.6%, respectively, of the yield of CH_4. The rate of formation of hydrocarbons in the reduction experiment at 573 K was 0.22, 0.19, and 0.12 mmol CO·h^{-1} at 10, 30, and 60 min, respectively. These three values were much smaller than the rate of formation of hydrocarbons observed in the KE reaction at a steady state at 573 K (0.816 mmol CO·h^{-1}, Table 1).

Effect of Pretreatment of Catalyst. The effect of pretreatment of Fe_2O_3 on its catalytic activity for the KE reaction was studied. When the catalyst had been reduced at 573 K in a stream of CO–Ar (CO 90.2 vol%, 60 NTP cm^3 min^{-1}) for 23 h, the conversion of CO, the yield and selectivity to hydrocarbons were 64.4, 3.1, and 4.8%, respectively, at 30 min (Table 3). These values are clearly greater than those observed at a steady state in the KE reaction over the non-pretreated Fe_2O_3 catalyst (Table 1). The decrease in catalytic activity of the prereduced Fe_2O_3 with time (Table 3) was probably caused by the reoxidation of the catalyst with H_2O. Similarly, the catalytic activity of Fe_2O_3 was much more greatly enhanced by the pretreatment with CO and H_2 (Table 3). The X-ray diffraction pattern of the catalyst prereduced with CO and H_2 could not be measured because the reoxidation took place in atmosphere.

Promotional Effect of Metal Oxides. The activity of metal oxide-promoted Fe_2O_3 catalysts for the KE reaction was monitored at 573 K (Table 4). When the Fe_2O_3 catalyst had been promoted by oxides of Cu, Pt, Co, and Ni, the conversion of CO, the yield and selectivity to hydrocarbons fairly increased although the distribution of hydrocarbons formed remained nearly unchanged. In contrast, the catalytic activity of Fe_2O_3 rather decreased when it had been promoted by oxides of Cr, Rh, Ru, and Pd. Unlike Cr, Ru, and Pd oxides, however, Rh oxide was able to enhance the yield and selectivity to hydrocarbons markedly (Table 4). Since the Fe_2O_3 catalyst impregnated with HCl (0.7 wt%) showed a negligible activity for the KE reaction at 573 K (conversion of CO=1.6%, yield of hydrocarbons =0%), the extremely low catalytic activity of the Fe_2O_3 promoted by oxides of Rh, Ru, and Pd (Table 4) can be attributed to the presence of Cl^- in these catalysts (See preparation of catalyst).

The catalytic activity of SiO_2-supported Cu, Pt, Co, Ni, Cr, Rh, Ru, and Pd oxides for the KE reaction was similarly monitored at 573 K (Table 5). The catalysts had been reduced at 573 K in a stream of H_2 (20 NTP cm^3 min^{-1}) for 3 h because the metal oxide-promoted Fe_2O_3 catalysts were exposed to H_2 at 573 K formed via the WGS reaction during the KE reaction. The main products in the reaction were CO_2 and H_2, and with the exception of the catalytic results for the supported Co and Ni oxides both the yields of CO_2 and H_2 were nearly equal to the conversion of CO. Thus, only the supported Co and Ni oxide catalysts were able to produce hydrocarbons whereas the other supported metal oxide catalysts promoted

Table 3. Effect of various pretreatments on the catalytic activity of Fe_2O_3 in the KE reaction at 573 K[a)]

Pretreatment	CO[b)]		CO and H_2[c)]	
	At 30 min	At 10 h	At 30 min	At 10 h
Conversion of CO/%	64.4	43.7	96.1	43.6
Yield of H.C.[d)]/%	3.1	1.7	7.9	1.7
Selectivity to H.C.[d)]/%	4.8	3.9	8.3	3.9

a) Catalyst: Fe_2O_3 15.0 g. Contact time: 311 g-catalyst·h·mol CO^{-1}. CO/H_2O feed molar ratio: 3. b) The catalyst was previously reduced at 573 K in a steam of CO–Ar (CO 90.2 vol%, 60 NTP cm^3 min^{-1}) for 23 h. c) The catalyst was previously reduced at 573 K in a stream of CO–Ar (CO 90.2 vol%, 40 NTP cm^3 min^{-1}) for 30 h and was then reduced at 573 K in a stream of H_2 (20 NTP cm^3 min^{-1}) for 30 h. d) Hydrocarbons.

Table 4. Summary of the activity of metal oxide-promoted Fe_2O_3 catalysts in the KE reaction at 573 K[a)]

Metal	Conversion of CO/%	Yield of H.C.[b)]/%	Selectivity to H.C.[b)]/%	Distribution of hydrocarbons/carbon wt%									
				C_1	C_2'	C_2	C_3'	C_3	C_4	C_5	C_6	C_7	C_{8+}
None	45.2	1.7	3.8	24	14	14	22	3	8	7	4	2	3
Pt	47.3	1.9	4.1	22	9	18	19	5	12	7	4	2	2
Cu	57.4	2.9	5.0	23	8	18	20	5	12	6	4	2	2
Co	53.2	2.6	4.8	24	10	16	21	4	12	6	4	1	2
Ni	52.9	3.4	6.3	27	6	20	16	7	11	6	3	2	2
Cr	38.3	0.7	1.7	22	18	11	20	1	13	8	4	1	3
Rh	18.5	2.1	13.8	29	5	9	23	4	13	12	4	2	0
Ru	3.9	0.01	0.3	40	60	0	0	0	0	0	0	0	0
Pd	4.9	0	0	—	—	—	—	—	—	—	—	—	—

a) Catalyst: M_xO_y–Fe_2O_3 (M/Fe_2O_3=0.2 wt%) 15.0 g, non-pretreated. Contact time: 311 g-catalyst·h·mol CO^{-1}. CO/H_2O feed molar ratio: 3. The catalytic activity was determined after a preliminary period of 5 h. b) Hydrocarbons.

TABLE 5. SUMMARY OF THE CATALYTIC ACTIVITY OF SiO_2-SUPPORTED METAL OXIDES FOR THE KE REACTION AT 573 K[a)]

Catalyst	Conversion of CO/%	Yield of H.C.[b)]/%
0.4 wt% Pt	21.0	0
2.0 wt% Cu	33.0	0
2.0 wt% Co	23.1	1.2
2.0 wt% Ni	51.0	10.7
2.0 wt% Cr	1.7	0
0.4 wt% Rh	0.4	0
1.6 wt% Ru	3.8	0
0.4 wt% Pd	4.7	0

a) Catalyst: M_xO_y–SiO_2 15.0 g, previously reduced in a stream of H_2 (20 NTP cm^3 min^{-1}) at 573 K for 3 h. Contact time: 311 g-catalyst·h·mol CO^{-1}. CO/H_2O feed molar ratio: 3. The catalytic activity was determined after a preliminary period of 20 min. b) Hydrocarbons. The other products were CO_2 and H_2.

only the WGS reaction (Table 5). The observation of the relatively great catalytic activities of the supported Pt and Cu oxide catalysts for the WGS reaction agrees with the previous results reported.[16)] Hence, one could say that Pt and Cu oxides have a relatively great ability to catalyze the WGS reaction whereas Co and Ni oxides are able to catalyze both the WGS and the KE reactions. No formation of hydrocarbons over the SiO_2-supported Rh oxide catalyst is attributable to its fairly low catalytic activity for the WGS reaction as seen in the extremely low conversion of CO (Table 5).

Discussion

We first discuss the mechanism of the KE reaction over iron-based catalysts. Although the yield and selectivity to hydrocarbons in the KE reaction at 548—593 K were as low as 0.6—2.2% and 2.0—3.8%, respectively (Table 1), the observed four characteristic features of the reaction, *i.e.*, the distribution of produced hydrocarbons following the Schulz-Flory plot, the decrease in propagation probability with increasing reaction temperature, nearly the same value of propagation probability irrespective of the great change in contact time of the reaction, and the remarkable decrease in the yield ratio of olefins to paraffins with increasing contact time of the reaction (Table 1, Figs. 1 and 2) well agree with the common features of the synthesis of hydrocarbons by the Fischer-Tropsch reaction reported. The findings that only the WGS reaction took place at sufficiently small contact times of the KE reaction and that formation of hydrocarbons became to be observable at a relatively great contact time of the reaction (Fig. 2) suggest that the KE reaction over Fe_2O_3 proceeds *via* a sequential reaction pathway involving the WGS reaction followed by the hydrogenation of CO to hydrocarbons.

Formation of hydrocarbons by the reaction of carbided iron catalysts with H_2O was already found.[7,8)] Based on this finding the mechanism of the KE reaction over iron oxide catalysts was proposed in which hydrocarbons are formed via a direct reaction of H_2O with iron carbide.[7)] However, the two findings made in the present work, *i.e.*, the low rate of formation of hydrocarbons in the reaction of H_2O with carbided iron catalyst at 573 K as compared with the rate of formation of hydrocarbons in the KE reaction over Fe_2O_3 at a steady state at 573 K (Fig. 3) and the very low concentration of Fe_5C_2 in the catalyst during the KE reaction at 573 K (See Results section) do not support the mechanism of the KE reaction reported.[7)] Since the ratio of the total yield of H_2 to that of CO_2 in the reaction of the carbided iron catalyst with H_2O at 573 K was 6.0 and since the total yield of hydrocarbons in the reaction was as low as 3% of the amount of carbon existed in the carbided iron catalyst (Table 2), we believe that the reaction of the carbided iron catalyst (Fe_5C_2) with H_2O proceeds preferentially in the following reaction scheme:

$$2Fe_5C_2 + 23H_2O \longrightarrow 5Fe_2O_3 + 23H_2 + 4CO_2. \qquad (1)$$

On the other hand, both the selective formation of CH_4 in the reduction of the carbided iron catalyst with H_2 at 573 K and the low rate of CH_4 formation as compared with the rate of formation of hydrocarbons observed in the KE reaction at a steady state at 573 K (See Results section) do not support the view that the C_2 and higher hydrocarbons obtained in the KE reaction were produced *via* a reduction of the carbided iron catalyst with H_2 formed by the WGS reaction. Although a very little portion of hydrocarbons produced in the KE reaction was caused by the decomposition of Fe_5C_2 by H_2O and by the hydrogenation of Fe_5C_2 and/or carbons[6,17)] deposited on the catalyst surface, we may conclude that a much greater portion of hydrocarbons produced in the KE reaction was via a sequential reaction pathway involving the WGS reaction followed by the Fischer-Tropsch reaction. This mechanism of the KE reaction over Fe_2O_3 agrees with that reported for a RuY-zeolite catalyst.[5)] The observed increase in the yield of hydrocarbons with increasing the degree of reduction of Fe_2O_3 (*Table 3*) suggests the role as the active sites played by the zero-valent iron atoms and/or metallic irons for the catalytic hydrogenation of CO to hydrocarbons. Based on these findings made in the present work, we propose the following catalytic cycle during the course of the KE reaction over Fe_2O_3.

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2 \qquad (2)$$

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2 \qquad (3)$$

$$5Fe + 4CO \longrightarrow Fe_5C_2 + 2CO_2 \qquad (4)$$

$$3F_5C_2 + 32H_2O \longrightarrow 5Fe_3O_4 + 6CO_2 + 32H_2 \qquad (5)$$

$$nCO + 2nH_2 \xrightarrow{Fe} \text{-}(CH_2)_n\text{-} + nH_2O \qquad (6)$$

We now discuss the promotional effect of metal oxides on the catalytic activity of Fe_2O_3 in the KE reaction. The observed increase in the yield and selectivity to hydrocarbons upon addition of Cu and Pt oxides to Fe_2O_3 which were able to catalyze the WGS reaction (Tables 4 and 5) supports the mechanism of the KE reaction over Fe_2O_3 proposed in the present work. Since the cat-

Table 6. Summary of the catalytic results for the KE reaction over mechanically admixed catalysts at 573 K[a)]

Catalyst	CuO-ZnO(3.0 g) +5 wt% Ni-Al_2O_3(7.0 g)	CuO-ZnO(3.0 g) +5 wt% Co-SiO_2(7.0 g)
Conversion of CO/%	59.2	40.9
Yield of H.C.[b)]/%	13.8	3.2
Selectivity to H.C.[b)]/%	24.1	8.1
Hydrocarbon	Distribution/carbon wt%	
C_1	77	31
C_2'	0.2	13
C_2	10	5
C_3'	2	23
C_3	6	0
C_4	3	12
C_5	1	7
C_6	0.4	4
C_7	0.1	4
C_{8+}	0	1

a) Catalyst: non-pretreated. Contact time: 207 g-catalyst·h·mol CO^{-1}. CO/H_2O feed molar ratio: 3. The catalytic activity was determined after a preliminary period of 30 min. b) Hydrocarbons.

alytic activity and selectivity of Fe_2O_3 for the KE reaction were also enhanced by the addition of Co, Ni, and Rh oxides which were able to catalyze the hydrogenation of CO to hydrocarbons (Tables 4 and 5), one could say that the mechanical mixture of two catalysts one of which has an ability to promote the WGS reaction and the another has an ability to promote the hydrogenation of CO to hydrocarbons is an effective catalyst for the production of hydrocarbons by the KE reaction. One illustration of this view is presented in Table 6. Here, CuO-ZnO was used as a catalyst for the WGS reaction whereas Al_2O_3-supported Ni (5 wt%) and SiO_2-supported Co (5 wt%) were used as catalysts for the hydrogenation of CO to hydrocarbons. In the case of CuO-ZnO+Ni-Al_2O_3 catalyst, the yield and selectivity to hydrocarbons at 573 K, 13.8 and 24.1%, are much greater than those observed over Fe_2O_3 at 573 K (Table 1) although the distribution of CH_4 in the hydrocarbons produced was as high as 77 wt% and that of C_2H_4 was only 0.2 wt%. A similar increase in the yield and selectivity to hydrocarbons was also seen in the case of CuO-ZnO+Co-SiO_2 catalyst (Table 6).

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