

CO HYDROGENATION OVER POTASSIUM-PROMOTED Fe/CARBON CATALYSTS

Ki June Yoon[†] and Eun Jin Kim*

Department of Chemical Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea

(Received 23 November 1994 • accepted 13 January 1995)

Abstract—The effects of potassium on the catalytic behavior in CO hydrogenation over K-promoted Fe/carbon catalysts having low K/Fe ratios were investigated. Even though the doses of potassium were low the promotional effects were pronounced, especially on the olefin-to-paraffin ratio, and the C₂ to C₄ olefin selectivities of the K-promoted catalysts were as high as 51 to 66 mol%. Over the catalysts having no or low potassium content the olefin-to-paraffin ratio and the ratio of the CO₂ formation rate to the rate of CO conversion to hydrocarbons remained roughly the same regardless of temperature, while over the K-promoted catalysts having higher potassium content they increased with temperature. Formation of significant amounts of filamentous carbon was observed in the K-promoted catalysts; however, the carbon deposition did not appear to affect the inherent activity and selectivity of the K-promoted catalysts.

Key words: CO Hydrogenation, Carbon Support, Iron, Potassium-promoted, Low Potassium

INTRODUCTION

Although CO hydrogenation by the Fischer-Tropsch process has received much attention in the past, the ability to selectively produce short-chain olefins still remains a challenging task [Venter et al., 1989a]. Many catalyst systems have been investigated to try to overcome this limitation, and one of the systems of interest is the carbon-supported iron catalyst system [Venter et al., 1987]. Small iron particles dispersed on various oxides exhibit strong interactions with many oxide surfaces, and this prevents the complete reduction of all the iron [Vannice, 1975, 1977, 1982]. It has recently been shown that high-surface-area carbon has several attractive features as a support of iron for the Fischer-Tropsch synthesis. The use of high-surface-area carbon as a support can not only prevent the reducibility problem but also can stabilize highly dispersed iron particles. It is also of interest because small unpromoted iron particles on carbon have exhibited higher selectivities to olefins than bulk iron catalysts under comparable conditions [Jung et al., 1982; Kaminsky et al., 1985; Chen et al., 1987, 1989; Venter et al., 1987, 1989a, 1989b; Martín-Martínez and Vannice, 1991].

Potassium has long been known to enhance the formation of both longer chains and olefinic hydrocarbons in CO hydrogenation over bulk iron catalysts [Storch et al., 1951; Anderson, 1956; Dry, 1981]. However, the observed influence of potassium on the synthesis performance of catalysts can usually be linked to its chemical interaction with other promoters or supports. The use of high-surface-area supports tends to reduce direct potassium-iron contact, thus resulting in reduction of the promotional effects of potassium. Especially in the case that the supports are acidic oxides such as SiO₂ and Al₂O₃, the added potassium has a tendency to preferentially interact chemically with the support, and high doses of potassium are required to see the effects [Stork and Pott, 1974;

Dry, 1981]. For example, McVicker and Vannice [1980] reported that the catalysts containing high doses of potassium, which were prepared by impregnating SiO₂ and Al₂O₃ with K-Fe carbonyl complexes, exhibited noticeable promotional effects in CO hydrogenation. On the other hand, the influence of increasing the potassium content is not always consistent and it depends on the type of catalyst and on the reaction conditions under which it is being tested. For example, over a series of fused catalysts the activity increased, decreased or passed through a maximum depending on the reaction temperature as the potassium content increased [Anderson, 1956; Dry, 1981].

Although the promotional effects of potassium have been demonstrated for supported iron catalysts, studies of K-promoted Fe/carbon catalysts are relatively few. Venter et al. [1987, 1989b] showed that K-Fe/carbon and K-Fe-Mn/carbon catalysts prepared from the corresponding metal carbonyl complexes gave very high C₂-C₄ olefin selectivities. These catalysts had high K/Fe ratios ranging from 0.233 to 0.70 by weight, but most of the potassium was found to be contained in the areas of carbon vacated by the metal. Nevertheless it was almost certain that some potassium remained on the surface of the metal particles because the olefin selectivity was much higher than that of an Fe-Mn/carbon catalyst [Chen et al., 1989]. As carbon is known to be neutral and to have little interactions with iron or potassium compared to the acidic oxides, relatively small amounts of potassium may be expected to exhibit noticeable promotional effects; however, few studies on K-Fe/carbon catalysts with low potassium content have been reported. The purpose of this study is focused on the effects of potassium in K-promoted Fe/carbon catalysts which have K/Fe weight ratios no higher than 1/10. The catalysts in this study were prepared by the conventional coimpregnation of a high-surface-area carbon with potassium and iron nitrate salts. Catalytic behavior of the catalysts was investigated in terms of activity, selectivity and activity maintenance behavior employing the potassium content and the reaction temperature as the major variables, and the catalysts were characterized using CO chemisorp-

[†] Author to whom correspondence should be addressed.

*Present address: Yarn Sales Dept., Tongyang Nylon Co., Seoul 120-020

tion, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The K-promoted Fe/carbon catalysts having low K/Fe ratios exhibited pronounced promotional effects, and changes of the olefin-to-paraffin ratio with temperature depended on the potassium content.

EXPERIMENTAL

The carbon support used was Cabot Corporation's Black Pearls 2000 carbon black. As received, this carbon had 0.89 wt% sulfur as determined by following the procedure for analysis of sulfur content in coal, so the carbon was treated under flowing hydrogen at 1223K for 15 h to decrease the sulfur content [Jung et al., 1982; Kaminsky et al., 1985; Chen et al., 1987, 1989]. This desulfurized Black Pearls 2000 contained 0.21 wt% sulfur and had a N_2 BET surface area of 1400 m^2/g and a pore volume of 2.6 cm^3/g . The ash content of the desulfurized carbon after ignition at 973 K was 0.92 wt%. From the elemental analysis it was considered that most of the ash consisted of $CaSO_4$, and trace amounts of K, Mg and Si were detected. These analysis results are similar to those reported previously [Kaminsky et al., 1985; Chen et al., 1987; Venter et al., 1989a].

An Fe/carbon and three K-Fe/carbon catalyst samples were prepared by the incipient wetness method. The Fe/carbon sample was prepared by impregnating the desulfurized carbon with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Hayashi Pure Chemical). The K-Fe/carbon samples were prepared similarly with aqueous solutions of mixtures of $Fe(NO_3)_3 \cdot 9H_2O$ and KNO_3 (Duksan Pharmaceutical), and the K/Fe weight ratios were chosen to be 1/40, 1/20 and 1/10, respectively. The samples were then dried overnight at 373 K. All the final Fe loadings were 16 wt%, as determined by ashing in air at 1023 K. It was assumed that the K/Fe ratio was maintained as prepared, and the four samples were designated as F-16, KF-0.4-16, KF-0.8-16 and KF-1.6-16, respectively.

The kinetic data were obtained using a Pyrex, plug-flow micro-reactor system operating at a total pressure of 103 kPa (1 atm) under differential reactor conditions in most cases. The amounts of dried samples used were 0.2-0.5 g and the samples were pretreated under flowing H_2 (50 cm^3/min) at 723 K for 18 h prior to cooling to reaction temperature and admitting CO. These pretreatment conditions were chosen after preliminary kinetic studies; the F-16 catalyst which was treated at 723 K for 18 h exhibited higher activity, C_2 -selectivity and C_2 to C_4 olefin selectivity than that which was treated at 673 K for 3 h or for 18 h.

Each set of kinetic data, except that for the activity maintenance experiments, was obtained using a bracketing technique, which consisted of a 20-min exposure to the reactant gases following a 20- to 40-min exposure to pure H_2 [Vannice, 1975]. The H_2/CO ratio was fixed at 2 and the total flow rates of the reactant gases were 55-90 cm^3/min . The reaction temperature studied ranged from 573 to 673 K. The H_2 used was from Dong-A Gas (purity 99.99%) and it was further purified by passing through a packed bed of 1% Pd/ Al_2O_3 pellets and an Oxytrap to remove trace of oxygen and then a molecular sieve trap. The CO used was from Takachiho Chemical (purity 99.95%) and it was further purified by passing through an Oxytrap and a molecular sieve trap. The product analyses were performed by temperature-programmed gas chromatography using a Carbosieve S-II column from Supelco Inc. for analysis of CO, CO_2 and CH_4 , and a Chromosorb 102 column from Supelco Inc. for analysis of CO_2 , CH_4 and other hydro-

Table 1. CO chemisorption results for fresh, reduced catalysts

Catalyst	CO Chem. (195K) [$\mu mol/g-Fe$]	Fe_s	
		Fe_s	d^a [nm]
F-16	1750	0.195	3.8
KF-0.4-16	1175	0.131	-
KF-0.8-16	970	0.108	-
KF-1.6-16	440	0.049	-

^aBy assuming that iron particles are spherical.

carbons.

The CO chemisorption measurements were carried out in a conventional volumetric adsorption apparatus using a dual isotherm method [Emmett and Brunauer, 1937; Jung et al., 1982]. The sample was pretreated by the same procedure as used in the kinetic study to obtain reduced Fe particles, and then evacuated at 723 K for 1 h and cooled to 195 K (dry ice-acetone bath temperature) under dynamic vacuum. The first CO isotherm on the reduced samples was determined, and then the sample was evacuated at 195 K for 1 h and the second CO isotherm was determined. The difference between the two isotherms at 26.7 kPa gave the amount of CO irreversibly chemisorbed on the iron. Details of the procedure are given elsewhere [Jung et al., 1982]. XRD measurements were made on both the fresh, reduced catalysts and the used (after-reaction) catalysts. A Rigaku Rotaflex D/max-C diffractometer with nickel-filtered $CuK\alpha$ radiation was used over a 2θ range of 20-80°. TEM analyses of the samples were conducted with a Phillips CM20 microscope.

RESULTS AND DISCUSSION

1. CO Chemisorption on Fresh Catalysts

CO chemisorption results for the fresh catalysts are listed in Table 1. The fraction of iron exposed, defined as the ratio of surface iron atoms (Fe_s) to total iron atoms (Fe_t), was calculated assuming an adsorption stoichiometry of $CO/Fe_s=0.5$ [Emmett and Brunauer, 1937; Boudart et al., 1975; Jung et al., 1982; Venter et al., 1989b]. The amount of CO chemisorption decreased as the potassium content increased. This is considered to be due to the surface of iron particles being increasingly covered with the potassium, which in turn blocks chemisorption of CO. As will be discussed later with the TEM results, there is no evidence that the particle size is increased with the potassium content. The average iron particle size (d) of the Fe-only catalyst was estimated to be 3.8 nm from the equation $d=0.75/(Fe_s/Fe_t)$ by assuming the particles were spherical [Jung et al., 1982]. Average iron particle sizes of the K-promoted catalysts were not estimated because the surfaces were partly covered with potassium and thus the above equation could not be applied.

2. Activity Maintenance Behavior

Activity and selectivity changes with time on-stream were investigated under continuous flow of the reactant gases at 633 K. For the Fe-only catalyst the rate of CO conversion to hydrocarbons (HC), r_{HC} , was quite stable over a 24 h-period, as shown in Fig. 1. The rate of CH_4 formation, r_{CH_4} , was also shown in Fig. 1 as CH_4 is representative of the hydrocarbon products. As indicated by the fairly constant r_{CH_4}/r_{HC} ratio, the product selectivities remained practically unchanged with time on-stream.

For the KF-0.4-16 catalyst, both r_{HC} and r_{CH_4} increased slowly with time on-stream as shown in Fig. 2, but the product distribution, including CO_2 , was not changed. For the KF-0.8-16 and KF-

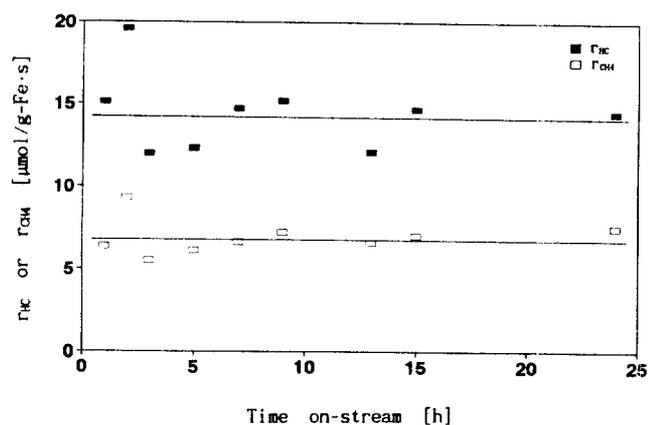


Fig. 1. Activity maintenance behavior of the F-16 catalyst at 633 K under 103 kPa with $H_2/CO=2$.

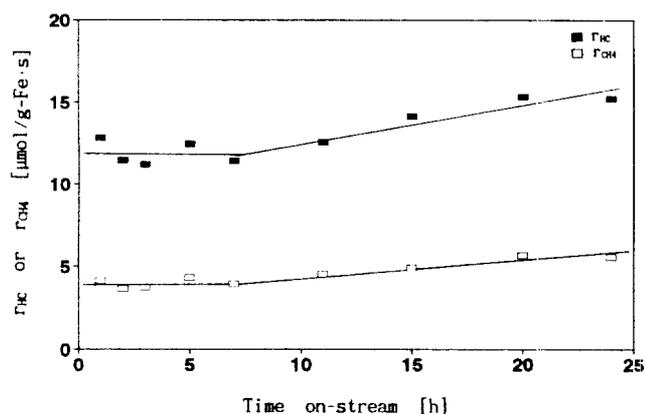


Fig. 2. Activity maintenance behavior of the KF-0.4-16 catalyst at 633 K under 103 kPa with $H_2/CO=2$.

1.6-16 catalysts increases of CO hydrogenation activity with time on-stream were faster than for the KF-0.4-16 catalyst. At the same time pronounced pressure build-up was observed in the beds of the KF-0.8-16 and KF-1.6-16 catalysts, and thus the experiments were stopped after about 6 h. During this period the activities increased by 20-30%, but the hydrocarbon product selectivities changed little while the CO_2 formation rate remained almost constant or decreased slightly. After reaction over the K-promoted catalysts it was found that the catalyst beds were expanded significantly. This apparent activity increase with time on-stream is considered not due to an inherent activity increase with time which has sometimes been observed in CO hydrogenation over iron during initial stages [Raupp and Delgass, 1979], but due to pressure build-up which was caused by the bed expansion. In CO hydrogenation over unpromoted and promoted iron catalysts, the reaction orders in most cases have been reported in the literature to be near or above 1 with respect to H_2 and to range from -0.5 to 0.4 with respect to CO, so the overall reaction order can be regarded to be positive [Vannice, 1976; Jung et al., 1982; Kaminsky et al., 1985; Venter et al., 1989b]. Therefore the activity increase observed in this study could be attributed to the pressure build-up. The reaction orders for CO_2 formation have been reported to be near zero with respect to both H_2 and CO [Kaminsky et al., 1985], and this is consistent with the observation in this study.

Table 2. Carbon deposition rates for K-promoted catalysts

Catalyst	Measured ^{a)}	Calculated ^{b)}
	[g-C/g-Fe·h]	[g-C/g-Fe·h]
KF-0.4-16	0.16	0.79
KF-0.8-16	0.71	0.93
KF-1.6-16	0.61	0.93

^{a)}Determined from weight increases of the catalysts during activity maintenance experiments.

^{b)}By assuming that CO_2 obtained in excess of r_{CO_2}/r_{HC} of 1 is produced by the CO disproportionation.

Table 3. Activity and product distribution with temperature over F-16

($H_2/CO=2$, $P=103$ kPa)

Temp. [K]	CO conv. to HC [%]	r_{HC} [$\mu\text{mol CO/g-Fe}\cdot\text{s}$]	TOF of CO to HC [$\text{s}^{-1}\times 10^3$]	r_{CO_2}/r_{HC}	
				r_{CO_2}	r_{HC}
573	2.1	6.2	1.8	0.8	
593	2.3	6.6	1.9	1.3	
613	3.9	11.2	3.2	1.2	
633	4.3	12.1	3.5	1.9	
653	7.3	20.5	5.9	1.5	
673	9.8	26.5	7.6	1.5	

Temp. [K]	Product distribution [mol%]					C_2 and C_3	
	C_1	C_2	C_3	C_4	C_5	C_2	C_3
573	30	22	16	13	3	8	1
593	31	18	12	18	3	12	1
613	32	18	11	18	5	10	3
633	36	20	12	20	2	7	2
653	40	19	12	19	2	6	1
673	44	19	10	17	3	5	1

The bed expansion was in turn found to be caused by carbon deposition; as shown later significant amounts of filamentous carbon were observed by the TEM on the catalysts after reaction. After the activity maintenance experiments the weight of each K-promoted catalyst was measured and the average rate of carbon deposition was determined. The results are shown in Table 2. Carbon deposition during CO hydrogenation, especially over K-promoted iron catalysts, has long been observed [Anderson, 1956; Dry, 1981; Venter et al., 1987; Venter et al., 1989b]. Assuming that H_2O is a primary product of CO hydrogenation and it is completely converted to CO_2 via the water gas shift reaction, the maximum ratio of the CO_2 formation rate to the rate of CO conversion to hydrocarbons, r_{CO_2}/r_{HC} , is 1 in the absence of carbon deposition and other reactions to produce CO_2 . Therefore, a r_{CO_2}/r_{HC} ratio greater than unity indicates carbon deposition via CO disproportionation [Dry, 1981; Venter et al., 1987]. For the K-promoted iron catalysts used in this study the ratios were greater than 2, and this ratio increased with the K content, as shown in Tables 3-6. The rates of carbon deposition were calculated from the r_{CO_2}/r_{HC} ratios with the above assumption, and the results are shown in Table 2 for the comparison purpose. The measured carbon deposition rate was consistently lower than that calculated from the r_{CO_2}/r_{HC} ratio and the difference was the greatest for the KF-0.4-16 catalyst. This suggests that a portion of CO_2 may be produced by some reaction(s) other than the water gas shift reaction and CO disproportionation, or that the deposited carbon may subsequently be removed by reacting with H_2 .

Table 4. Activity and product distribution with temperature over KF-0.4-16
(H₂/CO=2, P=103 kPa)

Temp. [K]	CO conv. to HC [%]	r _{HC} [μmol CO/g-Fe·s]	TOF of CO to HC [s ⁻¹ ×10 ³]	r _{CO₂} / r _{HC}
573	0.8	1.9	0.8	2.9
593	1.4	4.8	2.0	2.5
613	2.6	9.1	3.9	2.3
633	3.9	16.7	7.1	2.1
653	5.5	23.5	10.0	2.1
673	6.9	28.5	12.0	2.3

Temp. [K]	Product distribution [mol%]									C ₂ and C ₃ OPR
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	
57	27	30	4	26	1	10	2	-	-	10.2
593	30	27	4	24	1	9	2	4	-	10.5
613	30	26	5	25	1	10	1	3	-	8.7
633	34	27	4	23	1	8	2	2	-	10.1
653	37	26	5	23	1	5	3	1	-	8.7
673	39	27	5	21	1	3	3	1	-	8.2

Table 5. Activity and product distribution with temperature over KF-0.8-16
(H₂/CO=2, P=103 kPa)

Temp. [K]	CO conv. to HC [%]	r _{HC} [μmol CO/g-Fe·s]	TOF of CO to HC [s ⁻¹ ×10 ³]	r _{CO₂} / r _{HC}
573	1.1	2.8	1.4	2.5
593	1.6	5.8	3.0	2.1
613	2.4	8.6	4.4	2.5
633	3.9	16.6	8.6	2.3
653	4.1	19.5	10.1	3.1
673	5.1	24.5	12.6	3.2

Temp. [K]	Product distribution [mol%]									C ₂ and C ₃ OPR
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	
573	19	21	9	24	4	12	4	7	-	3.4
593	24	19	5	21	3	21	2	5	-	4.7
613	25	30	4	22	2	11	1	5	-	8.6
633	28	28	3	23	2	11	1	5	-	10.7
653	30	30	3	25	1	7	1	2	-	12.3
673	33	27	3	22	1	10	1	3	-	13.7

In summary, the activity of all the catalysts remained inherently quite stable and the hydrocarbon selectivity was practically not changed with time on-stream. Marked carbon deposition was observed especially for the K-promoted catalysts. The carbon deposition, however, did not affect the hydrocarbon product distribution.

3. Activity and Selectivity with Potassium Content and Temperature

Kinetic results obtained over the catalysts with varying potassium content and temperature are shown in Tables 3-6. Although there were some variations depending on the reaction temperature, the turnover frequency (TOF) for CO conversion to HC based on the CO chemisorption at 195 K tended to increase with the potassium content. However, the specific activity (activity per g-Fe) was roughly the same regardless of the potassium content. This is the consequence that the surface area of exposed iron decreases with the potassium content while the TOF increases.

With increasing temperature the hydrocarbon product distribu-

Table 6. Activity and product distribution with temperature over KF-1.6-16
(H₂/CO=2, P=103 kPa)

Temp. [K]	CO conv. to HC [%]	r _{HC} [μmol CO/g-Fe·s]	TOF of CO to HC [s ⁻¹ ×10 ³]	r _{CO₂} / r _{HC}
573	1.7	5.5	6.3	1.4
593	1.2	5.5	6.2	2.9
613	2.0	9.9	11.3	2.2
633	2.5	11.4	13.0	2.9
653	3.3	17.6	20.2	3.4
673	4.1	24.6	28.1	4.0

Temp. [K]	Product distribution [mol%]									C ₂ and C ₃ OPR
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	
573	16	29	11	23	4	8	4	4	-	3.6
593	27	27	8	21	2	10	-	5	-	4.5
613	29	22	5	21	2	15	1	5	-	6.3
633	28	29	4	24	1	9	1	4	-	10.0
653	29	31	3	24	1	9	1	3	-	15.3
673	34	28	2	21	1	9	2	4	-	18.1

tion shifted to shorter chains for all the catalysts, as expected [Dry, 1981]. As the carbon-number distribution and the olefin-to-paraffin ratio (OPR) depend on several reaction parameters such as the H₂/CO ratio, temperature, total pressure, conversion and pretreatment conditions besides the catalyst itself, comparison of the product distribution under the same basis with the results obtained by other investigators is not simple [Ott et al., 1980; Amelse et al., 1981; Anderson, 1984; Venter et al., 1987]. However, some representative results from other studies on Fe/carbon and K-Fe/carbon catalysts may be compared with those in this study, as summarized in Table 7. Selectivities to CH₄ and C₂ + C₃ (olefins) obtained from a Fe/carbon catalyst at 548 K under 103 kPa with a H₂/CO ratio of 1 were 33 and 40 mol%, respectively [Martín-Martínez and Vannice, 1991]. Selectivities to CH₄ and C₂ to C₄ olefins obtained from a K-Fe/carbon catalyst at 558 K under 103 kPa with a H₂/CO ratio of 3 were 41 and 55 mol%, respectively [Venter et al., 1987]. Although the temperature range employed in this study was rather higher compared to that in many other studies, the CH₄ selectivities obtained were quite low. The selectivities to C₂ to C₄ olefins in this study were 41-48 mol% for the Fe-only catalyst and 51-66 mol% for the K-promoted catalysts, and these are quite favorable values in the C₂ to C₄ olefin selectivity.

It was noticed that the effect of potassium on enhancement of the formation of higher hydrocarbons depended on the potassium content. Up to a certain K/Fe ratio (say, 1/20) the hydrocarbon product distribution shifted to higher hydrocarbons with the potassium content. However, further increase in the potassium content did not seem to enhance the formation of higher hydrocarbons, as observed by comparison of the results for the KF-1.6-16 catalyst with those for the KF-0.8-16 catalyst.

The promotional effect of potassium on the formation of olefins was remarkable. The OPR for the K-promoted catalysts was higher than that for the Fe-only catalyst at any temperature. An interesting feature observed about the OPR was that the variation of the OPR with temperature depended on the potassium content. One may expect from the thermodynamical point of view that the OPR would increase with temperature. However, for the F-16 and KF-0.4-16 catalysts no obvious trend of the OPR increase

Table 7. Comparison of selectivity with previous studies on Fe/carbon and K-Fe/carbon catalysts (P=103 kPa)

Catalyst	Operating parameters			Selectivity			Ref.
	Temp. [K]	H ₂ /CO Ratio	CO conv. to HC [%]	CH ₄ [mol%]	C ₂ to C ₄ Olef. [mol%]	C ₂ and C ₃ OPR	
F-16	573	2	2.1	30	43	1.9	*
4.00% Fe/carbon ^{a)}	548	1	3.7	33	40 ^{b)}	8.0	[e]
		3	10.9	46	24 ^{d)}	1.7	[e]
		3	2.0	42	27	0.5	[f]
3.78% Fe/carbon ^{a)}	498	3	2.0	56	8 ^{d)}	0.36	[g]
4.4% Fe/carbon ^{a)}	548	3	6.0	61	3 ^{d)}	0.09	[g]
5.0% Fe/carbon ^{b)}	548	3	3.1	27	66	10.2	*
KF-0.4-16	573	2	0.8	19	57	3.4	*
KF-0.8-16	573	2	1.1	16	60	3.6	*
KF-1.6-16	573	2	1.7	41	55	15.7	[f]
K-Fe/carbon ^{c)}	558	3	1.9	45	38	4.1	[h]
K-Fe/carbon ^{c)}	505	3	2.0				

^{a)}Prepared from Fe₃(CO)₁₂. ^{b)}Prepared from Fe(NO₃)₃. ^{c)}Prepared from K [HFe₃(CO)₁₁]; The K/Fe weight ratio is ca. 0.23. ^{d)}(C₂ + C₃) mol%.
^{e)}Martín-Martínez and Vannice, 1991. ^{f)}Venter et al., 1987. ^{g)}Kaminsky et al., 1985. ^{h)}Venter et al., 1989b. *: This Study.

Table 8. Apparent activation energies

Catalyst	E _{HC} [kJ/g-mol]	E _{CH₄} [kJ/g-mol]	E _{CO₂} [kJ/g-mol]
F-16	58	67	64
KF-0.4-16	86	100	80
KF-0.8-16	68	92	80
KF-1.6-16	55	76	78

with temperature was seen. In contrast, the OPR for the catalysts containing higher potassium content increased with temperature, i.e., from 3.4 to 13.7 for the KF-0.8-16 catalyst and from 3.6 to 18.1 for the KF-1.6-16 catalyst. This complicating behavior is not well understood at present. However, it has been suggested that for a carbon-supported catalyst which has a high K/Fe ratio only a portion of the potassium is present on the iron surface [Chen et al., 1989], but the K-promoted catalysts employed in this study have much lower potassium content than those studied by Chen et al. [1989], so most of the potassium will probably be present on the iron surfaces as indicated by the CO chemisorption results and the product distribution. It has also been suggested that the potassium spreads over the iron surfaces during reduction and the synthesis reaction [Dry, 1981]. Although the role of potassium in the chemistry of chain propagation and olefin hydrogenation is not precisely known and location of potassium in the catalyst is somewhat uncertain, the observation that variation of the OPR with temperature depends on the potassium content may be presumed to be related with the location of potassium or the nature of iron-potassium contact which would become different depending on the temperature and the potassium content.

As mentioned earlier, addition of potassium increased the rate of CO₂ formation markedly. Variation of the r_{CO₂}/r_{HC} ratio with temperature appeared to depend again on the potassium content. For the F-16 and KF-0.4-16 catalysts the ratio remained almost constant or decreased slightly with temperature, whereas a tendency of increase of the ratio with temperature was noticed for the catalysts having higher potassium content. This parallelism of enhancement of both olefin and CO₂ production may be attributed to an increased heat of chemisorption for CO by potassium, which depresses chemisorption of H₂ and promotes CO disproportionation [Sachtler et al., 1985; Venter et al., 1987, 1989b]. If

the goal is to attain high selectivity to C₂ to C₄ olefins with minimal CO₂ production and carbon deposition, improvements may be obtained by operation at high pressures [Venter et al., 1987], and optimum choices of the potassium content and reaction conditions have yet to be determined.

Apparent activation energies for CO conversion to HC (E_{HC}), methanation (E_{CH₄}) and CO₂ formation (E_{CO₂}) are listed in Table 8. Over well-dispersed, carbon-supported Fe-only catalysts, activation energies for CO conversion to HC reported in the literature are in the range from ca. 70 to 90 kJ/mol in most of the cases and those for methanation are in the range from 63 to 93 kJ/mol [Jung et al., 1982; Venter et al., 1987, 1989b; Martín-Martínez and Vannice, 1991]. The activation energies over the F-16 catalyst are somewhat lower than those in the literature, and this is considered probably due to the relatively higher temperature range employed in this study. Pore diffusion control of activity would give activation energies half as large as those measured under kinetic control, but this clearly did not occur; analyses using the Weisz criterion [Weisz, 1957] with a reasonable assumption of the pore sizes gave values well below 1, and analysis results reported in the literature about Fe/carbon catalysts which have physical characteristics and activities similar to the catalysts employed in this study have shown negligible influence of pore diffusion [Martín-Martínez and Vannice, 1991].

It has been observed that addition of potassium increases the activation energies E_{HC} and E_{CH₄} by about 10 to 40 kJ/mol [McVicker and Vannice, 1980; Venter et al., 1987, 1989b], and the results of this study are consistent with those of previous studies. The KF-0.4-16 catalyst exhibited large increases of the activation energies, but they were decreased as the potassium content increased further. The reason for this might also be related to the fore-mentioned effect of potassium on the selectivity.

Over unpromoted, carbon-supported iron catalysts E_{CO₂} is usually higher than E_{HC} and typically ranges from 83 to 100 kJ/mol in the temperature range of 493-583 K, and with addition of potassium it becomes higher [Venter et al., 1987, 1989b; Martín-Martínez and Vannice, 1991]. The results of this study are consistent with those of previous studies, although the values in this study are somewhat lower than those in previous studies. In contrast to the E_{HC} and E_{CH₄}, the E_{CO₂} did not appear to be influenced by further increase of the potassium content.

4. XRD and TEM Results

XRD analyses showed that only the (110) α -Fe peak was clearly observed for all the fresh, reduced catalysts, but its intensity was weak in spite of the relatively high loading of Fe. At the bottom of the sharp (110) α -Fe peak, however, a broad peak was overlapped. This indicates that both large and small iron particles are present, and this was consistent with the TEM results shown later. Besides the α -Fe peak, two weak, broad peaks were observed at around $2\theta = 35.5$ and 62.5° . Although the peaks were fairly broad (the half widths were about $3\text{--}5^\circ$), these peaks may indicate a small portion of iron is present as magnetite, Fe_3O_4 . This is consistent with the observation by Mössbauer spectroscopy in a previous study that a small portion of the iron in carbon-supported, reduced iron catalysts is present in an Fe^{3+} state [Chen et al., 1987]. The particle size of magnetite estimated from the half width using the Scherrer equation was roughly 2 nm.

For the used Fe-only catalyst the magnetite peaks were still observed, but the (110) α -Fe peak was not observed. Instead, two broad peaks at around $2\theta = 26$ and 43° appeared. For the used K-promoted catalysts no magnetite and α -Fe peaks were observed, but similar to the Fe-only catalyst two broad peaks at around $2\theta = 26$ and 43° appeared and the peak intensity was greater than that for the Fe-only catalyst. These two peaks are not peaks of any iron carbide or iron oxide, and the species corresponding to these peaks could not be precisely identified. For the moment these peaks are considered to come from the deposited carbon. However, failure to observe the peaks for iron carbides or iron oxides does not necessarily rule out their existence as they might be present in a form beyond the detection limit of XRD.

The TEM results for the fresh catalysts showed that most of the iron particles in all the four catalysts were in the range from 5 to 30 nm. The size distributions appeared almost the same and the average particle sizes were about 15 nm. It is not unusual that the average particle size estimated from the chemisorption results appears to be smaller than that from the TEM results, probably because highly-dispersed particles cannot be clearly imaged by TEM even though other evidence indicates their existence [Chen et al., 1987], or because highly-dispersed iron particles supported on carbon may be present in raft-like structures rather than spheroids [Phillis et al., 1980; Kaminsky et al., 1985].

The TEM pictures for the used catalysts revealed that the iron particle sizes were practically unchanged compared to those in the fresh catalysts and there was no evidence of sintering. On the used catalysts, however, formation of filamentous carbon was clearly observed. On the used Fe-only catalyst the amount of filamentous carbon was very small and the carbon filaments were very short. On the used K-promoted catalysts, the amount of filamentous carbon was significant and the carbon filaments were long and tortuous, as shown in Fig. 3. The widths of the carbon filaments were almost the same as the particle diameters, and many particles were observed to be located at the head of the filament. The same phenomenon has been observed with a variety of metals including iron, nickel, cobalt, and platinum with a variety of gases including carbon monoxide and hydrocarbons. The carbon filament is considered to be formed by deposition of carbon on one side of the catalyst particle, followed by solution and diffusion of carbon through the particle and precipitation on the other side [Rostrup-Nielsen and Trimm, 1977; Satterfield, 1980; Bartholomew, 1982]. It is clear that the catalyst bed expansion and pressure build-up is due to the carbon deposition. No inherent

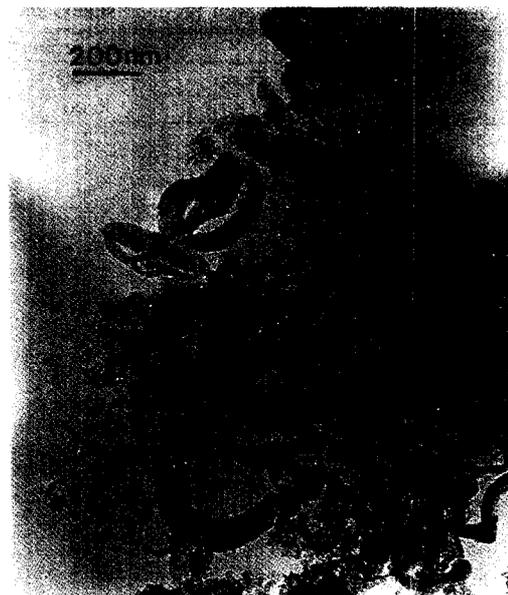


Fig. 3. Transmission electron micrograph of the used KF-1.6-16 catalyst.

activity and selectivity changes with carbon deposition may be explained by the fact that the shape of deposited carbon is filamentous rather than in a lump of carbon which could influence the activity and selectivity by the effects of mass transport through it.

CONCLUSIONS

K-promoted Fe/carbon catalysts having low K/Fe ratios and a Fe/carbon catalyst were prepared by using a conventional incipient wetness method and the effects of potassium on the catalytic behavior in CO hydrogenation were investigated. CO chemisorption results on the fresh catalysts showed that the iron was well-dispersed and that the fraction of iron exposed decreased as the potassium content increased. The turnover frequency of CO conversion to hydrocarbons increased with the potassium content, but the specific activities were about the same regardless of the potassium content.

With the low doses of potassium the promotional effects were noticeable, especially on the olefin-to-paraffin ratio. The C_2 to C_4 olefin selectivities of the K-promoted catalysts were as high as 51 to 66 mol%, and these are quite favorable values. Changes of the OPR and $r_{\text{CO}_2}/r_{\text{HC}}$ with temperature depended on the potassium content; that is, over the Fe-only catalyst and the K-promoted catalyst having a K/Fe weight ratio of 1/40 the OPR and $r_{\text{CO}_2}/r_{\text{HC}}$ remained roughly the same with temperature, while over the K-promoted catalysts having higher K/Fe ratios they increased with temperature. Addition of potassium also increased the activation energies of CO hydrogenation and CO_2 formation, even though the activation energies were somewhat lower than those in previous studies.

It was observed that beds of the K-promoted catalysts were expanded and the reaction pressure was built up during the activity maintenance experiments. It is concluded that this is due to carbon deposition as the TEM pictures clearly showed formation of significant amounts of filamentous carbon in the used K-promoted catalysts. However, the carbon deposition did not appear to

deactivate the catalysts or to alter the hydrocarbon selectivities.

ACKNOWLEDGEMENT

This study was supported by the Korea Science and Engineering Foundation and the Research Center for Catalytic Technology.

REFERENCES

- Amelse, J. A., Schwartz, L. H. and Butt, J. B., "Iron Alloy Fischer-Tropsch Catalysts. III. Conversion Dependence of Selectivity and Water-Gas Shift", *J. Catal.*, **72**, 95 (1981).
- Anderson, R. B., "Catalysis", Vol. 4, p. 119, Emmett, P. H., ed., Reinhold, New York, 1956.
- Anderson, R. B., "The Fischer-Tropsch Synthesis", Chaps. 3, 4 and 5, Academic Press, Orlando, 1984.
- Bartholomew, C. H., "Carbon Deposition in Steam Reforming and Methanation", *Cat. Rev.-Sci. Eng.*, **24**, 67 (1982).
- Boudart, M., Delbouille, A., Dumesic, J. A., Khammouma, S. and Topsøe, H., "Surface, Catalytic and Magnetic Properties of Small Iron Particles. Part I. Preparation and Characterization of Samples", *J. Catal.*, **37**, 486 (1975).
- Chen, A. A., Vannice, M. A. and Phillips, J., "Effect of Support Pretreatments on Carbon-Supported Fe Particles", *J. Phys. Chem.*, **91**, 6257 (1987).
- Chen, A. A., Phillips, J., Venter, J. J. and Vannice, M. A., "The Genesis of C-Supported Fe-Mn and K-Fe-Mn Catalysts from Stoichiometric Metal Carbonyl Clusters. II. Characterization by Mössbauer Spectroscopy and STEM/EDS", *J. Catal.*, **118**, 443 (1989).
- Dry, M. E., "The Fischer-Tropsch Synthesis", in "Catalysis: Science and Technology", Vol. 1, Chap. 4, Anderson, J. R. and Boudart, M., eds., Springer, Berlin, 1981.
- Emmett, P. H. and Brunauer, S., "Accumulation of Alkali Promoters on Surfaces of Iron Synthetic Ammonia Catalysts", *J. Amer. Chem. Soc.*, **59**, 310 (1937).
- Jung, H. J., Walker, P. L., Jr. and Vannice, M. A., "CO Hydrogenation over Well-Dispersed Carbon-Supported Catalysts", *J. Catal.*, **75**, 416 (1982).
- Kaminsky, M., Yoon, K. J., Geoffroy, G. L. and Vannice, M. A., "Carbon-Supported Fe-Ru Catalysts Prepared from Stoichiometric Mixed-Metal Carbonyl Clusters", *J. Catal.*, **91**, 338 (1985).
- Martín-Martínez, J. M. and Vannice, M. A., "Carbon-Supported Iron Catalysts: Influence of Support Porosity and Preparation Techniques on Crystallite Size and Catalytic Behavior", *Ind. Eng. Chem. Res.*, **30**, 2263 (1991).
- McVicker, G. B. and Vannice, M. A., "The Preparation, Characterization, and Use of Supported Potassium-Group VIII Metal Complexes as Catalysts for CO Hydrogenation", *J. Catal.*, **63**, 25 (1980).
- Ott, G. L., Fleisch, T. and Delgass, W. N., "Carbon Deposition and Activity Changes over Fe-Ru Alloys during Fischer-Tropsch Synthesis", *J. Catal.*, **65**, 253 (1980).
- Phillips, J., Clausen, B. and Dumesic, J. A., "Iron Pentacarbonyl Decomposition over Grafoil. Production of Small Metallic Iron Particles", *J. Phys. Chem.*, **84**, 1814 (1980).
- Raupp, G. B. and Delgass, W. N., "Mössbauer Investigation of Supported Fe Catalysts. III. In Situ Kinetics and Spectroscopy during Fischer-Tropsch Synthesis", *J. Catal.*, **58**, 361 (1979).
- Rostrup-Neilson, J. and Trimm, D. L., "Mechanisms of Carbon Formation on Nickel-Containing Catalysts", *J. Catal.*, **48**, 155 (1977).
- Sachtler, W. M. H., Shriver, D. F., Hollenberg, W. B. and Lang, A. F., "Promoter Action in Fischer-Tropsch Catalysis", *J. Catal.*, **92**, 429 (1985).
- Satterfield, C. N. "Heterogeneous Catalysis in Practice", p.142, McGraw-Hill, New York, 1980.
- Storch, H. H., Golubic, H. and Anderson, R. B., "The Fischer-Tropsch and Related Syntheses", p. 234, Wiley, New York, 1951.
- Stork, W. H. J. and Pott, G. T., "Studies of Compound Formation on Alkali/ γ -Aluminum Oxide Catalyst Systems Using Chromium, Iron and Manganese Luminiscence", *J. Phys. Chem.*, **78**, 2496 (1974).
- Vannice, M. A., "The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals", *J. Catal.*, **37**, 449 (1975).
- Vannice, M. A., "The Catalytic Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen", *Cat. Rev.-Sci. Eng.*, **14**, 153 (1976).
- Vannice, M. A., "The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals. V. The Catalytic Behavior of Silica-Supported Metals", *J. Catal.*, **50**, 228 (1977).
- Vannice, M. A., "Titania-Supported Metals as CO Hydrogenation Catalysts", *J. Catal.*, **74**, 199 (1982).
- Venter, J., Kaminsky, M., Geoffroy, G. L. and Vannice, M. A., "Carbon-Supported Fe-Mn and K-Mn-Fe Clusters for the Synthesis of C_2-C_4 Olefins from CO and H_2 ", *J. Catal.*, **103**, 450 (1987).
- Venter, J. J., Chen, A. and Vannice, M. A., "The Genesis of C-Supported Fe-Mn and K-Fe-Mn Catalysts from Stoichiometric Metal Carbonyl Clusters. I. Characterization by DRIFTS", *J. Catal.*, **117**, 170 (1989a).
- Venter, J. J., Chen, A. A., Phillips, J. and Vannice, M. A., "The Genesis of C-Supported Fe-Mn and K-Fe-Mn Catalysts from Stoichiometric Metal Carbonyl Clusters. III. Characterization by Chemisorption, Calorimetry and Kinetic Analysis", *J. Catal.*, **119**, 451 (1989b).
- Weisz, P. B., "Diffusivity of Porous Particles. I. Measurements and Significance for Internal Reaction Velocities", *Z. Phys. Chem.*, **11**, 1 (1957).