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Effects of Addition of Potassium Promoter to Titania-Supported Ultrafine Particles of Iron Metal Prepared by Gas Evaporation Method

Byong-tae CHANG* and Sung-jin KIM
Department of Chemistry, Faculty of Science, Korea University,
Kodaira, Tokyo 187

Effects of addition of potassium promoter on the catalytic properties of ultrafine particles of Fe metal prepared by the gas evaporation method have been studied for CO hydrogenation. The potassium promoter was found to be very effective in enhancing the catalytic activity and light olefin selectivity of UFP-Fe/TiO_2, an optimum amount of K_2CO_3/Fe being 6 wt%. Four kinds of TiO_2 with different physical and chemical properties were used as supports for UFP-Fe, and their effects on the activity and light olefin selectivity also have been discussed.

In recent years the correlation between the activity or selectivity of a catalyst, and its particle size has been attracting a great deal of attention.[1,2] In our previous paper,[3] it has been reported that the ultrafine particles of Fe metal(UFP-Fe, particle size ca. 20 nm) prepared by the gas evaporation method can become highly active and relatively stable catalysts for CO hydrogenation, simply by mixing them mechanically with a metal oxide support, and that the sequence of catalytic activity which depends largely upon the kind of used support is $TiO_2 >$ HZSM-5 $> SiO_2 > Al_2O_3 >$ NaZSM-5. In this work, the effects of addition of potassium promoter, one of the most representative ones for iron catalysts,[4,5] on the catalytic properties of the UFP-Fe/TiO_2 have been studied, in an attempt to achieve higher activity and light olefin selectivity.

Two kinds of UFP-Fe used in the present work were purchased from Vacuum Metallurgical Co.(Lot No. 2220, average size ca. 20 nm and Lot No. 2222, ca. 10 nm). Four kinds of TiO_2(JRC-TIO-3,4,5 and an anatase type of Wako Chemicals) were used as supports. Each catalyst was prepared by mixing UFP-Fe(10 wt%) mechanically with one of the titanias in an agate mortar, adding K_2CO_3 solution to Fe/TiO_2 and then drying at 60 °C. The catalysts were offered to the CO hydrogenation without H_2 reduction. The CO hydrogenation was conducted with a flow type fixed-bed stainless steel reactor. The feed stream consisted of a mixture of H_2, CO and Ar(H_2:CO:Ar = 47.5:47.5:5). All transfer lines following the reactor were heated and led directly to a heated sampling valve of a gas chromatograph for periodic analysis of the effluent gas. CO, CO_2,and Ar were analyzed on an activated charcoal column using a TCD detecter. C_1 - C_6 and C_7 - C_{14} hydrocarbons were analyzed on a Porapak Q column and an Apiezon-L column, respectively, using a FID detecter.

Figure 1 shows changes in the CO conversion with time on stream over Fe(20 nm, 10%)/TiO_2(Wako) containing K_2CO_3 of 0-8 wt% to Fe at $t = 250$ °C, $P = 5$ kg/cm^2 and W/F

=19 g.h/mol. Stationary CO conversion values can be obtained after 6-8 h for K_2CO_3=2-6%, while the linear decrease of CO conversion with time occurs for K_2CO_3=8%.

As is obvious from Table 1, the addition of K-promoter results in little changes in the hydrocarbon distributions at least in the range of C_1-C_{14}. The hydrocarbon distributions were well-simulated by the Schulz-Flory equation(except C_2), giving chain-growth probability values of ca. 0.75 for all the catalysts studied. On the other hand, the light olefin selectivity($C^{=}_{2-4}/C_{2-4}$) increases as the amount of K_2CO_3 increases. These results indicate that an optimum value of K_2CO_3/Fe should be 6 wt%.

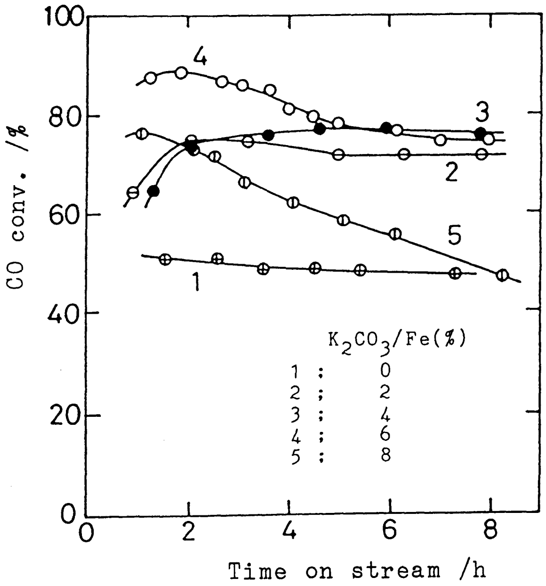

Fig.1. Changes in CO conversion with time on stream over K-promoted UFP-Fe/TiO_2(Wako) catalysts(t=250 °C, P=5 kg/cm^2 and W/F=21±2 g·h/mol).

In general, the addition of K-promoter to Fe catalysts brings about the increase of the electron density on Fe through the electron donation from potassium. This leads to the further electron donations to the bonding orbital of Fe-C and to the anti-bonding orbital of C-O in the absorbed CO molecules, consequently weakening the C-O bond and suppressing the H_2 adsorption. Thus the catalytic activity, the olefin selectivity and the average molecular weight of the products are enhanced, and also the water shift reaction is accelerated.[5-7] Such discussions are available for the effects of K-promoter on the catalytic properties of UFP-Fe although the increase of the average molecular weight of the products can not be clearly observed.

Figure 2 shows the effects of reaction temperature on the CO conversion and the $C^{=}_{2-4}/C_{2-4}$ of K-promoted(K_2CO_3=6%) Fe(20 nm)/TiO_2(Wako) catalyst at P=10 kg/cm^2. The CO conversion increases markedly with the increase of the temperature and reaches a very high value(95%) at 250 °C. Under this condition, the selectivity of C_{2-4} and $C^{=}_{2-4}$ in the total produced hydrocarbons were 50% and 36%, respectively. It should be noted that the K-promoted UFP-Fe/TiO_2 catalysts, which can be easily prepared by mechanically mixing and adding K^+, have the high activity and $C^{=}_{2-4}$

Table 1. Effects of amounts of K_2CO_3 on CO hydrogenation over UFP-Fe/TiO_2[a)]

K_2CO_3/Fe (wt%)	W/F (g.h/mol)	CO[b)] conv. %	CO_2 yield %	η^e/η^t [c)] (%)	Hydrocarbon distribution(C-wt%) C_1	C_2	C_3	C_4	C_5^+	$C^{=}_{2-4}/C_{2-4}$
0	23	48.5	21.4	56	7.3	11.3	16.9	16.3	48.2	22
2	19	72.3	33.7	53	8.3	9.5	15.3	14.6	52.3	40
4	19	76.7	37.0	52	8.7	9.0	15.4	15.1	51.8	64
6	19	75.9	38.0	50	7.4	9.3	15.8	15.1	52.4	72
8	22	55.4	27.6	50	9.7	11.8	14.6	11.6	52.3	90

a) t=250 °C and P=5 kg/cm^2. b) stationary values(excluding K_2CO_3=8%) at 7-8 h. c) η^t=(total CO conv.) and $\eta^e=\eta^t$-(CO_2 yield).

selectivity, low CH_4 selectivity(less than 10 %) and relatively good thermal stability at a moderate reaction condition of 250 °C and 10 kg/cm^2.

Four kinds of TiO_2 have been examined as supports for UFP-Fe(10 or 20 nm) in order to clarify the effects of physical and chemical properties of TiO_2 on the CO hydrogenation over K-promoted $Fe/TiO_2(K_2CO_3/Fe=6\%)$ catalysts. As given in Table 2, the highest CO conversion was obtained for Fe(10 nm)/TIO-4(an anatase type with a large surface area), whereas the highest $C^=_{2-4}/C_{2-4}$ was given by Fe(20 nm)/TIO-5 (a rutile type with a small surface area). As reported in the previous paper,[3)] TIO-5 gave the highest $C^=_{2-4}/C_{2-4}$ in the unpromoted UFP-Fe/TiO_2 catalyst,too. It seems that the small surface area of TiO_2 support and the large particle size of Fe are advantageous for the formation of the light olefins.

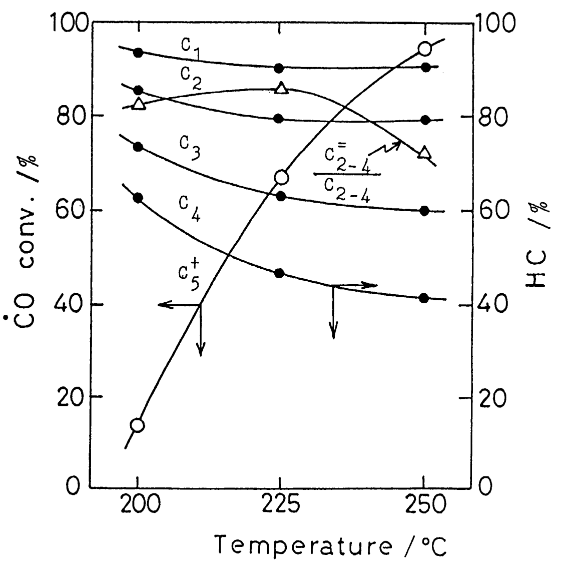

Fig.2 CO hydrogenation over K-promoted($K_2CO_3/Fe=6\%$) UFP-Fe(20 nm)/TiO_2(Wako) catalyst at P=10 kg/cm^2 and W/F=20 g·h/mol.

Furthermore, the correlations between CO conversions and $C^=_{2-4}/C_{2-4}$ under various reaction conditions have been considered for each TiO_2. As shown in Fig. 3(a) for TIO-4, there exists a good linear relationship between the CO conversion and the $C^=_{2-4}/C_{2-4}$. In other words, the selectivity of light olefins decreases linearly with the increase of CO conversion. Thus it is impossible for TIO-4 to get a high light olefin selectivity together with a high activity. As shown by the curve 1 in Fig.3(b), TIO-4 also gives the similar tendency. On the other hand, TIO-5(the curve 2) always sustains very high values of the $C^=_{2-4}/C_{2-4}$ irrespective of the CO conversion. These facts strongly suggest us that TiO_2 supports have a great deal to do with the adsorptions of CO and H_2 molecules on Fe, the chemical reactions between the adsorbed species, the desorption of the products and so on.

Titania is well-known as a support which interacts strongly with metals. Indeed the first report on strong metal-support interactions(SMSI) was concerned

Table 2. Effects of properties of TiO_2 supports on CO hydrogenation over potassium-promoted($K_2CO_3/Fe=6\%$) UFP-Fe/TiO_2 catalysts[a)]

Symbol	Particle size of UFP-Fe	W/F	CO conv.	CO_2 yield	Hydrocarbon distribution(C-wt%)						Surface area of TiO_2
	nm	(g·h/mol)	%	%	C_1	C_2	C_3	C_4	C_5^+	$C^=_{2-4}/C_{2-4}$	m^2/g
JRC-TIO-3	20	19	75.4	40.8	5.5	8.6	14.2	14.2	57.5	42	40
JRC-TIO-4	10	16	88.9	44.0	9.6	11.1	19.2	16.7	43.4	15	50
	20	18	69.3	31.7	6.5	8.0	15.1	13.6	56.8	39	
JRC-TIO-5	10	21	78.6	38.5	6.5	10.0	16.0	15.6	51.9	86	2.6
	20	22	64.3	32.1	7.1	10.0	14.3	13.3	55.3	94	
Wako	20	20	74.5	36.5	7.8	9.7	15.9	14.8	51.8	72	10

a) t=250 °C and P=5 kg/cm^2.

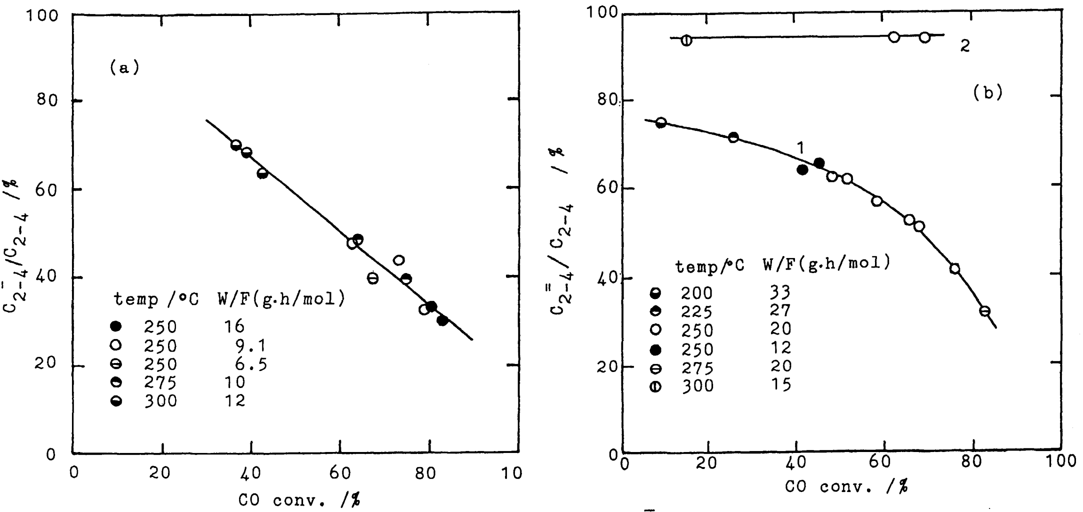

Fig.3. Correlations between CO conversion and $C_{2-4}^{=}/C_{2-4}$ values under various reaction conditions. K_2CO_3/Fe=6%, P=5 kg/cm^2. (a)Fe(10 nm)/TIO-4, (b)curve 1, Fe(20 nm)/TIO-3; curve 2, Fe(20 nm)/TIO-5.

with group 8 noble metals supported by TiO_2.$^{6)}$ Afterward, the metal-support interactions in Fe/TiO_2 catalysts reduced at various temperatures have been studied in detail.$^{7-9)}$ When the present work is compared with these previous papers, the effects of TiO_2 supports mentioned above must be attributed to the native natures of used TiO_2 and be distinguished from the SMSI effects because they have been defined as the suppression of CO and H_2 chemisorption following high-temperature (ca.500 °C) reduction of catalysts.$^{6,10)}$ As discribed above, the most remarkable difference among 4 kinds of TiO_2 appears in the light olefin selectivity and its CO conversion dependence. According to the CO hydrogenation mechanism proposed by Pettit,$^{11)}$ chemisorbed hydrogens are involved in both chain initiation and termination; the latter consists of β-hydride elimination of metal-alkyls to produce α-olefins and reduction of metal-alkyls to give paraffins, which determines the production ratio of olefins to paraffins. Although the details of behaviours and roles of surface hydrogens over CO hydrogenation catalysts remain unknown,$^{12)}$ TIO-5 might suppress the chemisorption of H_2 through electronic and/or geometric effects, leading to the high $C_{2-4}^{=}/C_{2-4}$ values.

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