CO Hydrogenation over TiO_2-Supported Ultrafine Fe_3O_4 Particle Catalysts Prepared by a Colloid Chemical Method

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The properties of TiO_2 supports and the H_2 reduction temperature of Fe_3O_4/TiO_2 catalysts were found to play imortant roles in determining their activity and light olefin selectivity. For each catalyst, a good linear relationship was observed between the CO conversion and the light olefin selectivity. The sequence of the latter under identical conditions was JRC-TIO-5>TIO-3>TIO-4.

In recent years, much attention has been focused on the interactions between metal and support in various supported catalysts.[1–3] Previously we found that the catalytic activity of ultrafine particles of metallic Fe (10—20 nm), prepared by a gas evaporation method, depends largely on the nature of support (TiO_2, SiO_2, Al_2O_3, NaZSM-5 and HZSM-5), and that the physical and chemical properties of TiO_2 supports exert considerable influence on the activity, particularly the light olefin selectivity.[4,5]

According to Ito,[6] ultrafine particles (smaller than 10 nm) of several metal oxides can be prepared by a colloid chemical method. The purpose of this work was to study the catalytic properties of TiO_2-supported Fe_3O_4 prepared by this method; effects of TiO_2 support, H_2 reduction temperature and potassium-promoter on the CO hydrogenation activity and the product distribution.

Experimental

Ultrafine Particle Fe_3O_4 (UFP-Fe_3O_4) were supplied from

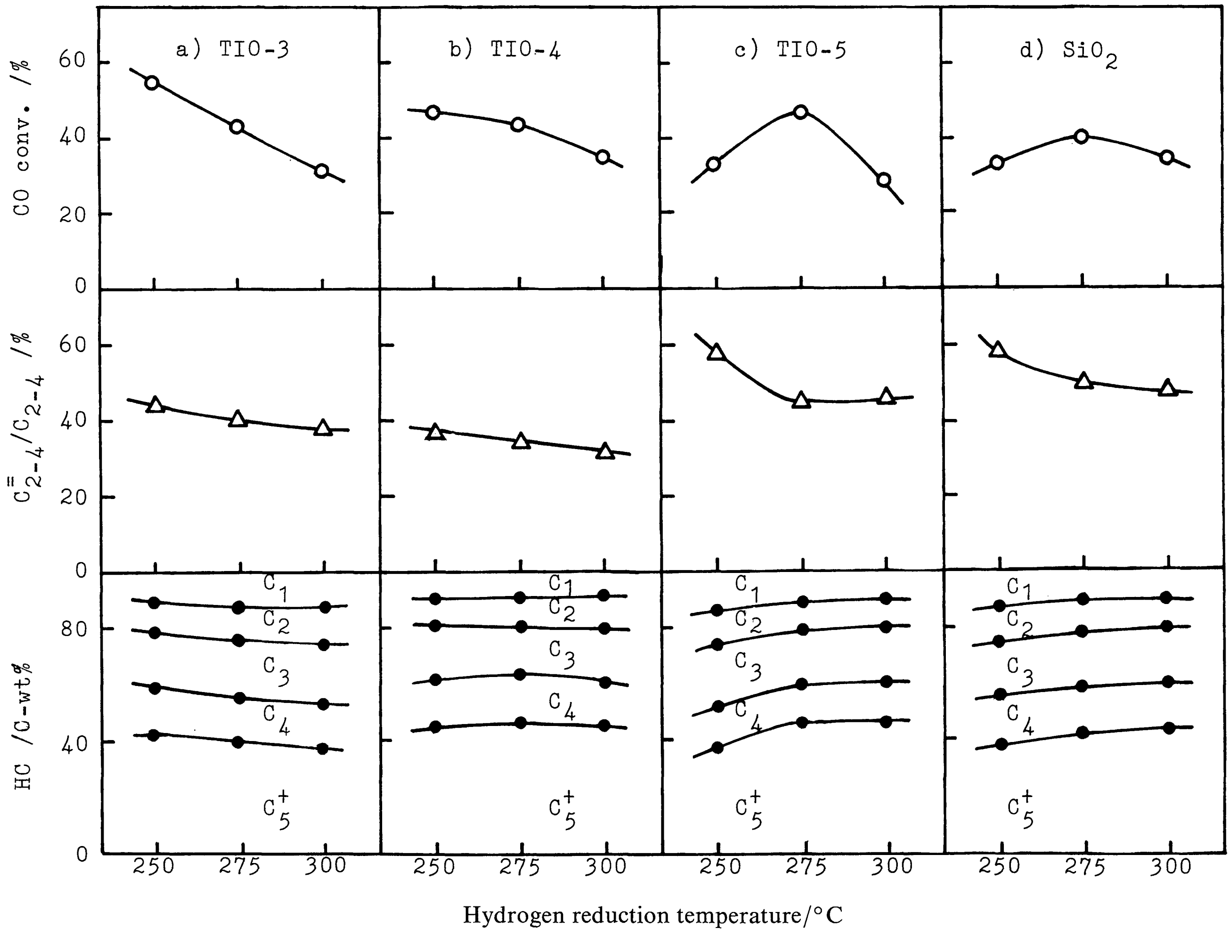

Fig. 1. Effects of hydrogen reduction temperature on the CO conversion, the light olefin selectivity, and the distribution of hydrocarbons produced over UFP-Fe_3O_4/support catalysts. CO hydrogenation conditions; t=250 °C, P=5 kg cm^{-2}, and W/F=24±3 g h mol^{-1}.

Okamura Oil Co. By chemical analysis UFP-Fe_3O_4 was found to contain Fe at 55.2 wt% together with several organics. The X-ray diffraction pattern was in good agreement with that of Fe_3O_4, and the particle size determined by X-ray broadening analysis was 9.6±0.2 nm.

Three kinds of TiO_2 (JRC-TIO-3, 4, and 5) and, for comparison, SiO_2 (Aerosil 300) were used as supports. Catalysts were prepared by mechanically mixing UFP-Fe_3O_4 (20 wt%) with one of the supports in an agate mortar, then adding a K_2CO_3 solution (K_2CO_3/Fe=6 wt%) to the Fe_3O_4/support and subsequent drying at 60 °C. Prior to the CO hydrogenation, each catalyst was reduced in situ by hydrogen at a temperature of 225—300 °C, a pressure of 2 kg cm^{-2} and a flow rate of 60 ml min^{-1} for 13 h.

The CO hydrogenation was conducted with a flow type fixed-bed stainless steel reactor, using a feed gas of CO : H_2 : Ar=47.5 : 47.5 : 5 (vol%) under the common condition of t=250 °C, P=5 kg cm^{-2}, and W/F (contact time)=19—33 g h mol^{-1} (W=weight of catalyst, F=molar flow rate of CO and H_2). The products were analyzed by gas chromatography as detailed elsewhere.[5] The conversion of CO (η_{CO}) was calculated on the basis of Ar as an internal standard.

Results and Discussion

UFP-Fe_3O_4/Support Catalysts. Figure 1 shows the effects of hydrogen reduction temperature on the CO conversion (stationary values at time on stream of 5—6 h), the distribution of hydrocarbons produced (HC, carbon-wt%) and the light olefin selectivity ($C^{=}_{2\text{-}4}$/total $C_{2\text{-}4}$). As seen in Figs. 1-(a) and (b), in the cases of TIO-3 (rutile type, 40 m^2 g^{-1}) and TIO-4 (anatase type, 50 m^2 g^{-1}), the CO conversion decreases as the reduction temperature increases. On the other hand, the TIO-5 (rutile type, 2.6 m^2 g^{-1})-supported catalyst exhibits a maximum value of η_{CO} at 275 °C (Fig. 1-(c)). A similar temperature dependence of η_{CO} was observed for the SiO_2-supported catalyst, as shown in Fig. 1-(d).

The carbon number distribution of the products, except for CO_2 with yields of 40±5% in η_{CO}, does not depend so much on the nature of support used. The probability of carbon chain growth (α) was in a range of 0.66±0.3. On the other hand, the value of $C^{=}_{2\text{-}4}/C_{2\text{-}4}$ slightly decreases with a rise of the reduction temperature regardless of the nature of support. The sequence of $C^{=}_{2\text{-}4}/C_{2\text{-}4}$ under identical conditions was TIO-5> SiO_2>TIO-3>TIO-4. The rutile type and small surface area of TiO_2 seem advantageous for the formation of light olefins, as observed for TiO_2-supported ultrafine Fe

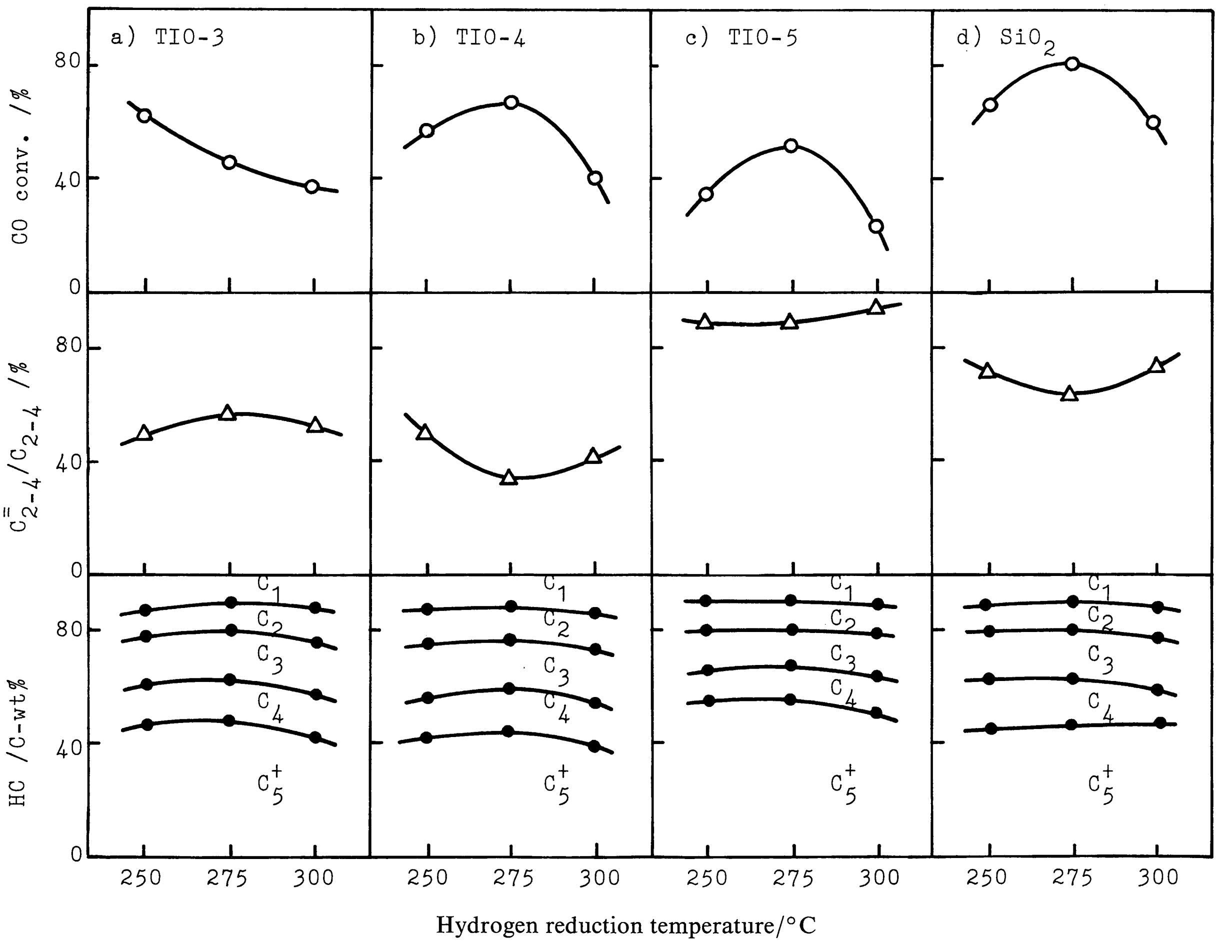

Fig. 2. Effects of hydrogen reduction temperature on the CO conversion, the light olefin selectivity, and the distribution of hydrocarbons produced over the K-promoted UFP-Fe_3O_4/support catalysts. CO hydrogenation conditions; t=250 °C, P=5 kg cm^{-2}, and W/F=23±4 g h mol^{-1}.

metal particles prepared by the gas evaporation method.[5] This tendency becomes more conspicuous when the potassium promoter is added to Fe_3O_4, as will be described below.

K-Promoted UFP-Fe_3O_4/Support Catalysts. Potassium is well known as one of the most effective promoters for CO hydrogenation on iron catalysts.[7,8] Figure 2 shows the effects of K-promoter on η_{CO}, $C_{2-4}^{=}/C_{2-4}$, and the carbon number distribution. In general, the addition of K-promoter to Fe results in an increase in the electron density on Fe through electron donation from potassium. This in turn leads to electron donation to the bonding orbital of Fe–C and to the antibonding orbital of C–O in the adsorbed CO molecules, thereby 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. Also the water shift reaction is accelerated by a similar mechanism.[7,8] As is obvious from Fig. 2, such discussions are in principle valid for the effects of K-promoter on the catalytic properties of UFP-Fe_3O_4, although the increase in the average molecular weight of the products cannot be clearly depicted except for the case of TIO-5.

The light olefin selectivity depends clearly on the support. TIO-5 gave the highest value (ca. 90%) of $C_{2-4}^{=}/C_{2-4}$ and larger amounts of C_5^+ (carbon number $\geqslant 5$) than TIO-3 or TIO-4. The α values (0.73—0.74) of TIO-5 are neatly higher than those for TIO-3 or TIO-4. These results are consistent with a view that, in the CO hydrogenation process, chemisorbed hydrogen is involved in both chain termination and addition to olefin to form paraffin.

Changes in Fe Particle Size. To clarify the effect of H_2 reduction temperature, changes in the phase of Fe_3O_4 and the particle size of metallic Fe formed during the reduction process have been examined by X-ray diffraction analysis (XRD). As given in Table 1, the reduction at 225 °C does not result in the formation of metallic Fe thick enough to be detectable by XRD. Practically no change was noted in the particle size. An extremely low value of η_{CO} indicated that catalyst has not been sufficiently activated. On the other hand, reduction at 250 °C leads to a neat increase in η_{CO}, accompanied by partial reduction of Fe_3O_4 to Fe, and a slight increase in the particle size.

On an assumption that the Fe particles are uniform and spherical, the specific activity (a_{CO}) of the catalysts can be evaluated from the particle size, the space velocity of CO, and η_{CO}. For each catalyst (except TIO-3), the a_{CO} value is maximal at 275 °C. The specific activity seems to depend on the degree of the reduction to metallic Fe and its particle size; probably the smaller the particle size, the higher the a_{CO} value.

Correlation between η_{CO} and $C_{2-4}^{=}/C_{2-4}$. In Fig. 3 are plotted the light olefin selectivity against the CO con-

Table 1. Changes in the Phase of Fe_3O_4, the Particle Size of Metallic Fe, and the Specific Activity of UFP-Fe_3O_4/Support Catalysts

Support	K_2CO_3	H_2 red. temp	Phase[a)]	Particle size of Fe	W/F	η_{CO}[b)]	a_{CO}
	wt%	°C		nm	g h mol^{-1}	%	µmol s^{-1} m^{-2}
TIO-3	0	225	O	10[c)]	33	4.0	0.023[d)]
		250	M+O	11	21	56.0	0.55[d)]
		275	M	14	24	42.9	0.47
		300	M	19	25	31.6	0.45
	6	250	M+O	13	23	62.1	0.66[d)]
		275	M	16	24	45.6	0.57
		300	M	22	27	36.8	0.56
TIO-4	0	250	M+O	11	23	46.6	0.42[d)]
		275	M	15	23	43.5	0.53
		300	M	19	25	34.3	0.49
	6	250	M+O	13	23	56.8	0.60[d)]
		275	M	16	20	66.3	1.00
		300	M	22	26	41.1	0.65
TIO-5	0	250	M+O	11	27	32.5	0.25[d)]
		275	M	15	23	46.9	0.58
		300	M	19	26	29.5	0.41
	6	250	M+O	13	28	35.9	0.31[d)]
		275	M	17	27	51.7	0.61
		300	M	19	31	36.2	0.42
SiO_2	0	250	M+O	10	26	33.0	0.24[d)]
		275	M	10	24	40.4	0.32
		300	M	11	24	34.6	0.30
	6	250	M+O	11	22	67.4	0.63[d)]
		275	M	12	19	80.4	0.95
		300	M	14	24	56.1	0.62

a) O; oxide (Fe_3O_4), M; metal (Fe). b) t=250 °C and P=5 kg cm^{-2}. c) Particle size of Fe_3O_4. d) a_{CO} was calculated for total (M+O).

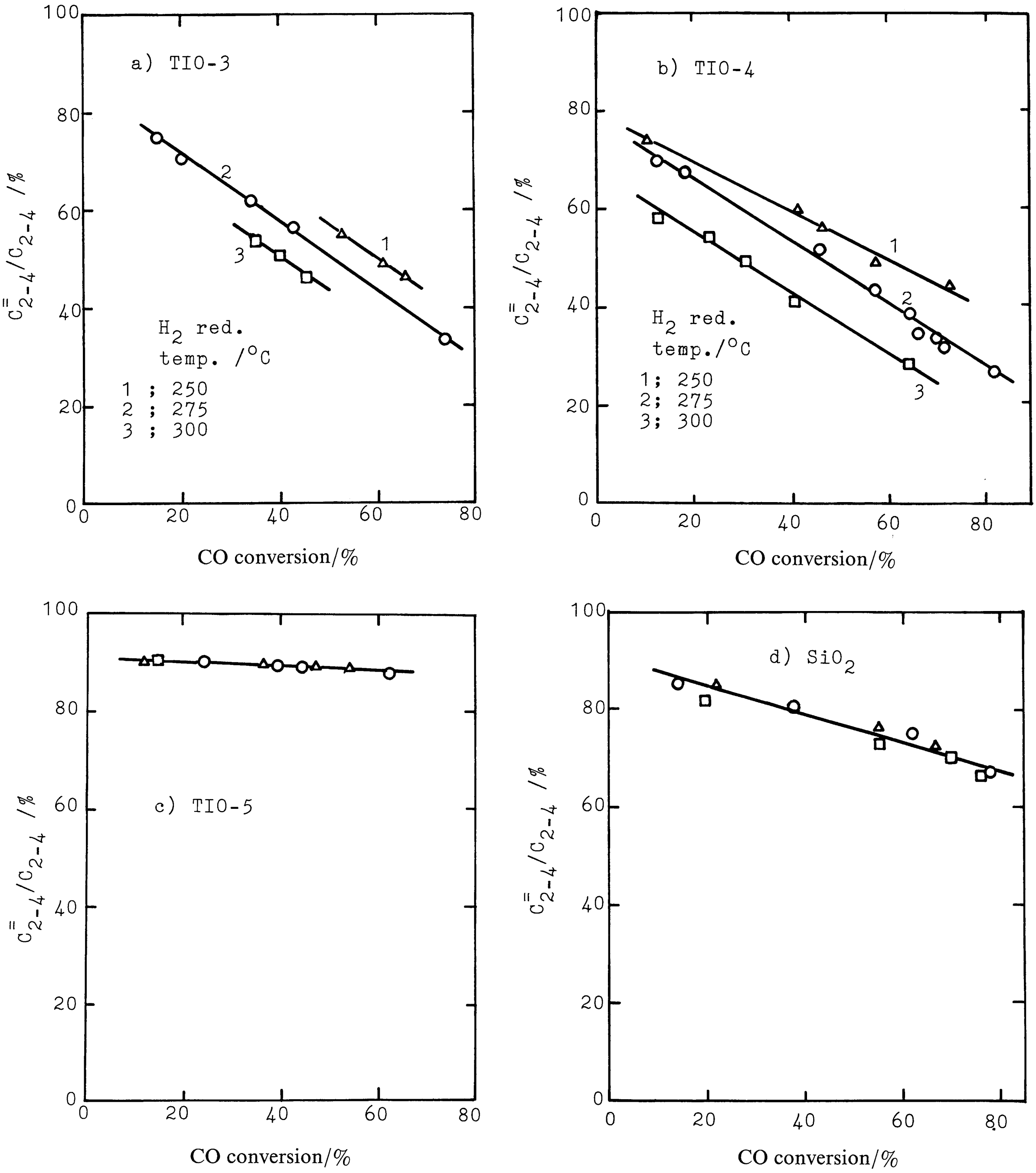

Fig. 3. Correlations between the CO conversion and the light olefin selectivity for the K-promoted UFP-Fe_3O_4/support catalysts under various reduction and CO hydrogenation conditions.

version over the K-promoted catalysts, observed under the reaction conditions in a range of t=225—275 °C, P=5—10 kg cm^{-2}, and W/F=10—33 g h mol^{-1}. For each catalyst a good linear relationship is seen, with a slope characterstic of the support used. In the cases of TIO-3 and TIO-4, the light olefin selectivity abruptly decreases with an increase in η_{CO}, so that it is impossible to carry out the reaction with high activity and high light olefin selectivity at the same time. The clear shift of the correlation line by a change in the H_2 reduction temperature could be attributed mainly to a change in the Fe particle size and consequently in the magnitude of a_{CO}.

In contrast, TIO-5 always exhibits very high values of $C^{=}_{2-4}/C_{2-4}$ almost independently of η_{CO}. Under the same conditions, the sequence of $C^{=}_{2-4}/C_{2-4}$ is TIO-5>SiO_2>TIO-3>TIO-4, as is the case for the unpromoted catalysts. In comparison with SiO_2, which is expected to interact weekly with metallic Fe, TIO-3 and TIO-4 render the Fe active sites more hydrogenating, while TIO-5 does so to a lesser extent. These findings strongly suggest that TiO_2 supports exert significant influence on the CO hydrogenation process on Fe metal. According to Vannice,[9)] the rate-determining step of CO hydrogenation on Fe catalysts is the adsorption and dissociation of H_2 on Fe surface. Also the properties (amount, activity etc.) of adsorped hydrogen play an important role in controlling the formation ratio of olefin to paraffin.[10)] In view of this, the support effects observed in this work could be ascribed to promotion (TIO-3 and TIO-4) or suppression (TIO-5) of the H_2 adsorption and dissociation by the TiO_2 support.

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