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CO Hydrogenation on Supported Ultrafine Iron Particle Catalysts Prepared by Gas Evaporation Method

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Ultrafine iron particles prepared by the gas evaporation method were found to be able to become high active and relatively stable catalysts for CO hydrogenation, simply by mixing them with supports, under the conditions of Fe contents less than 10 wt% and reaction temperatures below 250 °C. The sequence of catalytic activity, depending upon the kind of support, was as follows; TiO_2(JRC-3,4, 5 and Wako, M)>HZSM-5(US)>SiO_2(M)>Al_2O_3(M)>NaZSM-5(M).

In recent years the correlation between the activity or selectivity of a catalyst, and its particle size is attracting a great deal of attention.[1,2] Taking supported metal catalysts for instant, in general their high selectivity comes from the uniform size of metal particles, while the high activity results from the small particle size, leading to a large specific surface area.

Among various methods to prepare ultrafine particles(UFP) of metal, the gas evaporation method has several features as follows; it gives an uniform size(10-several 10 nm) of good crystalline and spheric particles without micropores, and their thermal stability is relatively high under appropriate conditions because they undergo high temperature treatments during their producing process.[3] These features suggest us that UFP of metal by the gas evaporation method could be good components of high active and/or high selective catalysts. In fact, interesting results on UFP catalysts have been presented, concerning exhaust gas treatment,[4] methanol synthesis,[5] liquid phase hydrogenation of carbon monoxide[6] and so on.

The purpose of this work is to study the activity, selectivity and stability of UFP of iron metal(UFP-Fe)/support catalysts for CO hydrogenation.

The UFP-Fe used in the present work were purchased from Vacuum Metallurgical Co.(Lot No. 2220, average size ca. 20 nm, surface area 38.5 m^2/g). The catalysts were prepared by mechanically mixing UFP-Fe with one of following supports(symbolized as M); SiO_2(Aerosil 300), γ-Al_2O_3(Aerosil Al_2O_3-C), 6 kinds of TiO_2(JRC-1,2,3, 4,5 and anatase type of Wako Chemicals), NaZSM-5 and HZSM-5(Si/Al=50) synthesized at our laboratory. Following the mechanical mixing, some of the catalysts were irradiated with ultrasonic(50 W, 40 kHz) for 30 min in acetone solvent, in attempt to improve the dispersion of UFP-Fe on the supports(symbolized as US). Besides, in the case of ZSM-5, UFP-Fe were added to sol solutions prior to zeolitization, using tetrapropyl ammonium bromide(TPA) or n-hexylamine(HA) as an organic base.[7,8]

CO hydrogenation was conducted with a flow type fixed-bed stainless steel reactor, using CO/H_2 = 1. The products were analyzed by gas chromatography. Conversion of CO and carbon based selectivity(excluding CO_2 yield) were calculated on the basis of argon as an internal standard.

Even if UFP of metal prepared by the gas evaporation method have the relatively high stability as mentioned above, the thermal stability of the catalysts still remains one of the most important problems. The stability tests were performed by pursuing the change in CO conversion with time on stream. Figure 1 shows the results on UFP-Fe/TiO_2(Wako, M). As given by curve 1, UFP-Fe(10%)/TiO_2(M) was found to be very stable under the condition of 250 °C and 5 kg/cm^2. On the other hand, fair decreases in CO conversion can be observed at 275 °C, or Fe content of 20%. Hence the Fe content of 10% and reaction temperature of 250 °C were choiced as the fundamental condition for the UFP-Fe/support catalysts. As expected, very stable activity can be also obtained for SiO_2, Al_2O_3, NaZSM-5, and HZSM-5 after the time on stream of around 4 hours as given in Fig. 2.

Effects of support on the activity of UFP-Fe catalysts are much remarkable as given in Table 1. Based on the CO conversion, the sequence of the activity of UFP-Fe(10%)/support(M) is as follows; TiO_2(Wako)>SiO_2>Al_2O_3>NaZSM-5>HZSM-5. TiO_2 gives high activity more than two times, compared with the other four supports. Furthermore, according to our experiments, an impregnated Fe(10%)/TiO_2(Wako) catalyst had CO conversion of 19.0% under the same reaction condition. The sizes of Fe particles on TiO_2(Wako) were estimated from the X-ray line broadening analysis for (111) to be 17 nm for the UFP-Fe and 31 nm for the impregnated Fe(reduced in H_2 at 400 °C for 12 h , leading to the turnover frequency(TOF) of 0.16 and 0.093 s^{-1} , respectively. For CO hydrogenation on Ni/SiO_2, Ru/Al_2O_3, and Co/Al_2O_3 catalysts, the TOF's increase with increases in the particle size.[1)] Although

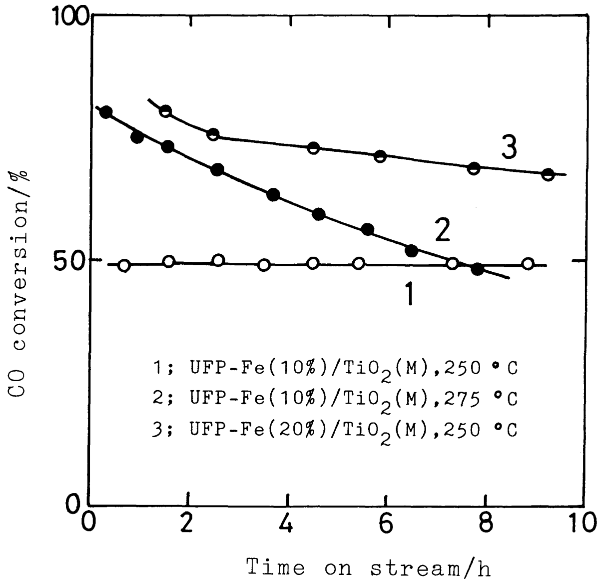

Fig. 1. Change in CO conversion with time on stream over UFP-Fe/TiO_2(Wako, M) catalysts(P=5 kg/cm^2, W/F=21±2 g·h/mol)

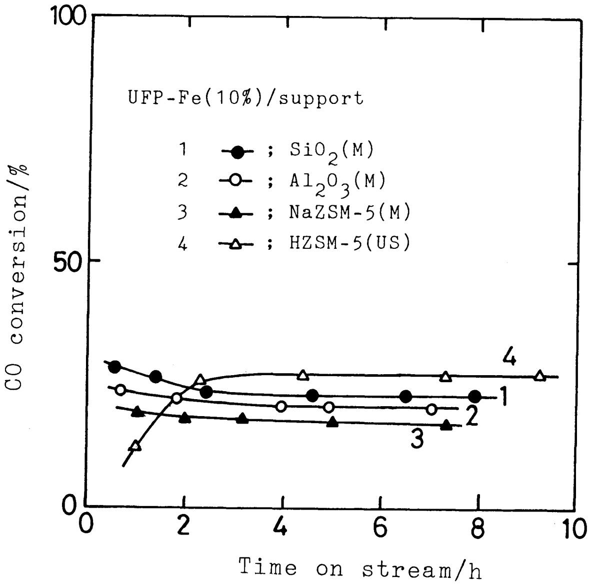

Fig. 2. Change in CO conversion with time on stream over UFP-Fe/support catalysts(t=250 °C, P=5 kg/cm^2, W/F= 29±2 g·h/mol)

the correlation between the TOF and the Fe particle size for Fe/TiO_2 catalysts remains unknown in detail at present, it should be noted that one can prepare high active and relatively stable catalysts for CO hydrogenation, simply by mixing UFP-Fe with TiO_2 support.

The ultrasonic irradiation to UFP-Fe/HZSM-5(M) exceptionally brought about the remarkable enhancement in CO conversion. The case of NaZSM-5 was completely opposite. The ultrasonic irradiation can be expected to improve the dispersion of UFP-Fe on the support and to make them attach more strongly to the surface. These effects might appear positively in HZSM-5 and negatively in NaZSM-5. The details are still unknown.

In attempt to enhance the dispersion of UFP-Fe in the ZSM-5 support, another preparation method has been examined, in which UFP-Fe were added to the sol solution for ZSM-5 synthesis under the ultrasonic irradiation, prior to the zeolitization. As given in Table 1, UFP-Fe/HZSM-5(TPA or HA) showed very low activities, probably resulting from the deactivation of UFP-Fe during the hydrothermal synthesis process of ZSM-5 in alkaline solution and/or the decomposition process of used

Table 1. CO hydrogenation over the UFP-Fe(10%)/support catalysts[a)]

Catalyst	Mixing method	W/F (g.h/mol)	CO conv. %	CO_2 yield %	Hydrocarbon distribution(C-wt%) C_1	C_2	C_3	C_4	C_5^+	Ar	$\frac{C^=_{2-4}}{C_{2-4}}$
SiO_2	M	28	23.3	5.4	6.2	8.5	13.3	12.0	59.4	-	44
Al_2O_3	M	30	20.6	3.6	8.5	11.2	16.8	15.5	48.0	-	16
TiO_2[b)]	M	23	48.6	21.1	7.3	11.5	17.0	16.2	48.0	-	18
NaZSM-5	M	29	16.9	6.4	11.9	16.2	23.4	21.7	25.2	1.6	22
	US	32	~1	-	28.8	23.1	26.1	12.5	9.5	-	57
HZSM-5	M	32	5.2	2.2	11.0	10.7	14.3	25.6	21.1	17.3	36
	US	27	27.1	9.9	7.2	5.8	11.4	22.1	23.8	29.8	35
	TPA	34	<1	-	10.6	9.3	11.1	21.1	24.5	23.4	40
	HA	32	3.4	1.6	14.8	14.6	17.5	14.9	17.0	21.2	61

a) t = 250 °C and P = 5 kg/cm^2. b) TiO_2(Wako).

Table 2. CO hydrogenation over UFP-Fe(10%) supported variuos kinds of TiO_2[a)]

Symbol	Type[b)]	Surface area m^2/g	W/F (g.h/mol)	CO conv. %	CO_2 yield %	Hydrocarbon distribution(C-wt%) C_1	C_2	C_3	C_4	C_5^+	$\frac{C^=_{2-4}}{C_{2-4}}$
JRC-TIO-1	A	73	30	≪1	-	-	-	-	-	-	-
JRC-TIO-2	A	18	25	21.5	13.7	9.8	11.6	17.9	13.6	47.1	21
JRC-TIO-3	R	40	21	47.3	27.2	10.2	12.3	20.7	16.8	40.0	12
JRC-TIO-4	A	50	21	48.8	27.3	13.9	14.0	20.2	14.8	37.1	8
JRC-TIO-5	R	2.6	23	41.6	23.3	10.8	11.2	19.4	15.3	43.3	35
Wako	A	10	25	48.6	27.5	7.5	11.5	17.0	16.2	48.0	18

a) t = 250 °C and P = 5 kg/cm^2. b) A ; anatase type, R ; rutile type.

organic base(TPA or HA) at 500 °C. Further investigation on this method is currently being proceeded, especially using UFP-Fe-Co alloy.9)

The produced hydrocarbon distributions for SiO_2, Al_2O_3, TiO_2, NaZSM-5 approximately satisfy the Schulz-Flory law with the chain-growth probability values of 0.72 ± 0.04 at 250 °C and 5 kg/cm^2. It is not the case for HZSM-5(M or US); much decreases in $C_2^=$ and $C_3^=$($C_{2,3}^=$/total $C_{2,3}$ =1%) and remarkable increases in $C_4^=$/total C_4 (71% for M and 62% for US) and aromatics can be observed. It means that, as previously pointed out at higher temperatures than 300 °C,10,11) $C_{2,3}^=$ are oligomerized to form the aromatics even at a low temperature of 250 °C, together with conversion to $C_4^=$.

As described above, TiO_2 support gives the highest activity among the five kinds of supports studied in this work. In general the effects of support on the activity and selectivity of catalysts consists of chemical ones(acid-basic properties of support, interactions between metal and support etc.) and physical ones (dispersion of metal on the surface of support, micropores of support etc.). Table 2 gives the results on CO hydrogenation over UFP-Fe(10%)/TiO_2(M), using six kinds of TiO_2 which have different chemical purity, crystal structure and physical properties. One can point out the following features; at first, except JRC-TIO-1 and 2 containing considerable large amount of SO_3, four kinds of TiO_2(JRC-TIO-3, 4, 5 and Wako) give similar CO conversion values. At second there are no significant differences in the carbon number distributions of the produced hydrocarbons. At third the rutile type with a small surface area, TIO-5, gives the highest value of light olefin selectivity($C_{2-4}^=$/C_{2-4}). This tendency becomes more remarkable when potassium promotor is added to UFP-Fe/TiO_2(M) as reported elsewhere.12)

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