Catalytic Hydrogasification of a Carbon Material with Dodecacarbonyltriiron(0) and Iron(III) Nitrate: Effects on Surface Area, Pore Structure, and Hydrogen Adsorption

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The catalysis of adsorbed dodecacarbonyltriiron(0) was used to develop the pore structure of a carbon through its partial gasification with hydrogen. The catalytic gasification at 500 °C increased the volumes of pores, in particular those of 3—5 nm in diameter. In contrast, such an effect was not observed when iron(III) nitrate was used as a catalyst. The adsorbability of hydrogen on carbon-supported iron particles obtained after gasification was examined by temperature-programed desorption (TPD). The TPD spectrum of hydrogen, in particluar, at temperatures above 200 °C, for a cluster-derived sample differed from that for a nitrate-derived sample. In addition, the apparent activation energy for the desorption of hydrogen in a low-temperature peak at around 90 °C for the former sample was larger than that for the latter. Heat treatments caused the TPD characteristics of the cluster-derived sample to become very similar to those of the nitrate-derived sample.

Metal cluster compounds are an attractive precursor for supported metal catalysts. To prepare iron/carbon catalysts, some research groups have used iron carbonyl clusters and found interesting catalytic and adsorptive properties.[1-10] Stevenson et al. showed that the thermal decomposition of dodecacarbonyltriiron(0) adsorbed on a carbon support yielded unusually finely dispersed iron particles.[1] These iron particles had a peculiar morphology and showed an unexpected behavior, like the formation of pentacarbonyliron(0) during carbon monoxide adsorption.[1,2] Suzuki et al. used a few iron clusters as the precursor of a catalyst for coal gasification and noted their significance for preparing such binary catalysts as iron–sodium.[7,8] Takahashi et al. noted the activity of iron catalysts prepared from iron carbonyls as well as other organometallic compounds for the gasification of carbons.[9,10]

The above-mentioned studies have aroused further interest in the catalysis of carbon-supported iron cluster compounds; our effort was aimed at the catalysis of dodecacarbonyltriiron(0) on a carbon material in the present work. The activity of the iron carbonyl for carbon gasification has been applied to the control of the pore structure of carbon by its partial gasification with hydrogen. In addition, the cluster-derived small metallic iron particles obtained after the gasification have been characterized by the temperature-programed desorption (TPD) of hydrogen, as well as X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). To see the features of the triiron cluster, the results obtained for the cluster-derived samples were compared with those for samples prepared by a conventional method with iron(III) nitrate.

Experimental

Materials and Sample Preparation. The carbon material used was carbon black, Seast-3H, with an average particle size of 27 nm and a specific surface area of 75 $m^2\,g^{-1}$ supplied by Tokai Carbon Co. Ltd. The carbon powder was heat treated under vacuum at 150 and 500 °C, in hydrogen at 500 °C, and in steam (12 vol% in nitrogen) at 500 °C each for 3 h to modify its surface; it was then impregnated with iron as follows.

The dodecacarbonyltriiron(0) cluster was adsorbed on carbon powder from its hexane solution containing about 0.03 wt% iron for the amount of iron loaded to be a few wt%. The carbon was soaked in the solution for several days until the color of the solution changed from deep green to clear. After filtration, carbon impregnated with dodecacarbonyltriiron(0) was dried at room temperature for a few days. All of these procedures were carried out in nitrogen in a glove box. The prepared samples were stored in the nitrogen atmosphere before gasification and characterization. These procedures were in accordance with those by Stevenson et al.[1] The amounts of iron actually loaded were estimated from the ignition residues of carbon samples both with and without the iron carbonyl cluster.

For a comparison, other iron/carbon samples were prepared by conventional impregnation with iron(III) nitrate. The carbon powder was kept immersed overnight in its aqueous solution at room temperature and the nitrate was deposited on the surface of the carbon by evaporating the solvent at about 50 °C under reduced pressure for less than 1 h. The loading of iron was fixed to 2 wt%, being smaller than that for the samples prepared by the iron carbonyl cluster because small iron particles would also be formed in the samples with iron(III) nitrate. For this method of metal impregnation, the amount actually loaded was in good agreement with the nominal value.[11]

Hydrogasification. The iron/carbon samples were gasified in flowing hydrogen at 65 ml min^{-1} up to 500 °C in 1 h and kept at this temperature for 3 h using a stainless-steel reactor. To measure the weight loss during gasification, the samples were also subjected to thermogravimetry in hydrogen and in helium under similar conditions with a quartz reactor. The catalytic weight loss was calculated by subtracting the weight loss observed in helium from that in hydrogen.

Surface Area and Porosity. A nitrogen adsorption method was used to measure the surface area and pore volume of the carbon materials both before and after the partial gasification. The samples were pretreated in flowing nitrogen at 150 °C for 3 h and then subjected to measurements with Shimadzu-Micromeritics Model 2400 and 2200 apparatus.

TPD of Hydrogen. TPD of hydrogen was used to examine the hydrogen adsorbability and the degree of metal dispersion for the carbon-supported iron samples after the gasification. Hydrogen was flowed through the sample bed (0.15 g) at 30 °C for a certain period of time, mainly 15 min, and switched to argon, which was flowed for about 15 min. Then, the adsorbed hydrogen was desorbed with argon at a flow rate of 30 ml min^{-1} by heating the sample at 30 °C min^{-1}. The maximum temperature of the heating was limited to 450 °C in order to avoid any sintering upon repeated measurements. For selected samples, the apparent activation energy for hydrogen desorption was determined by the method of heating-rate-variation in the range from 8 to 90 °C min^{-1}.[12] It was calculated from the slopes of two semilogarithmic plots of $\ln(\beta/T_p^2)$ vs. $1/T_p$ and $\ln N_p$ vs. $1/T_p$, in which β, T_p, and N_p are heating rate, peak temperature, and peak height, respectively. The values of the two slopes were in agreement within 10% for each measurement. The apparatus and procedures used for the TPD were previously described in more detail.[13]

XPS and TEM. A Shimadzu ESCA-750 was used to examine the state of iron in the samples after gasification. The data for Fe $2p_{3/2}$ binding energy were charge-referenced to a C 1s binding energy of 285 eV.[14] The ratio of the Fe $2p_{3/2}$ peak area to the C 1s peak area was used to estimate the amount of iron atoms exposed in each sample examined. The size of iron particles obtained after gasification was examined by a Hitachi H-300 TEM. The detectable particle size was larger than 1—2 nm.

Results

Hydrogasification. Table 1 presents the results of catalytic gasification at 500 °C for 3 h, including the measured amounts of iron loaded from the iron carbonyl cluster. The rate of reaction was observed to decrease with time; the extent of gasification appeared to level off within 3 h for all of the samples examined. The weight loss data given in Table 1 are the maximum (ceiling) values that can be attained at 500 °C. The weight loss observed for the samples with dodecacarbonyltriiron(0) is over 10%, being much larger than that for the samples with iron(III) nitrate, which could gasify only a few per cent of the carbon. The results indicated some influence of carbon pretreatments on the extent of gasification. Larger carbon conversions could be obtained for treatments with hydrogen and steam. These pretreatment effects are in agreement with the previous results concerning the nickel-catalyzed gasification of a pitch coke.[15]

Surface Area and Porosity. Table 2 shows the surface areas and pore volumes of the carbon samples before iron loading and the iron/carbon samples after gasification, indicating significant changes of samples with dodecacarbonyltriiron(0). The gasification resulted in increases in the surface area and pore volume by factors of 2.0—2.5 and 1.4—2.6, respec-

Table 2. Changes of Surface Area and Pore Volume with Hydrogasification at 500 °C

Sample[a)]	Surface area		Pore volume	
	before	after	before	after
	$m^2 g^{-1}$	$m^2 g^{-1}$	$ml\, g^{-1}$	$ml\, g^{-1}$
Original	75	77	—	—
FC-1	77	155	0.23	0.55
FC-2	88	170	0.37	0.50
FC-3	82	202	0.20	0.51
FC-4	393	442	0.65	0.81
FN-1	84	94	0.34	0.31
FN-2	263	263	0.37	0.31

a) "Original" is the raw carbon black material and the abbreviations are the same as in Table 1.

Note. The influence of pretreatments on carbon depended on the weight of the carbon sample used; the weights of the samples used for FC-4 and FN-2 were different and this resulted in differences of surface area and pore volume.

Table 1. Weight Loss of Carbon on Catalytic Hydrogasification at 500 °C

Pretreatment[a)]		Precursor	Immersion time[b)]	Iron loading[c)]	Weight loss[d)]		Symbol[e)]
Atmosphere	Temp				W1	W2	
	°C		h	wt%	wt%	wt%/mgFe	
Vac	150	$Fe_3(CO)_{12}$	92	4.1	10.7	2.6	FC-1
Vac	500	$Fe_3(CO)_{12}$	92	3.2	13.5	4.2	FC-2
H_2	500	$Fe_3(CO)_{12}$	115	2.8	17.0	6.1	FC-3
H_2O	500	$Fe_3(CO)_{12}$	64	3.5	18.2	5.2	FC-4
H_2	500	$Fe(NO_3)_3$	43	2.0	1.0	0.5	FN-1
H_2O	500	$Fe(NO_3)_3$	43	2.0	2.7	1.4	FN-2

a) Performed for 3 h before the loading of metal. b) For $Fe_3(CO)_{12}$ carbon black powder was immersed in the solution until its color changed to almost clear and for $Fe(NO_3)_3$ it was immersed in the solution for a certain period of 43 h. c) Measured values for $Fe_3(CO)_{12}$ and nominal values for $Fe(NO_3)_3$. d) Due to the catalysis by $Fe_3(CO)_{12}$ and $Fe(NO_3)_3$. e) For the iron/carbon samples after the gasification; will be used in Tables 2 and 3 and Figures 1, 2, and 3.

tively, for the carbons pretreated with hydrogen and under vacuum. It also increased the surface area and pore volume of carbon pretreated with steam, although it had a larger area and pore volume before gasification. In contrast, little change was observed for samples with iron(III) nitrate.

The changes of pore size distribution of the carbons with the gasification are given in Fig. 1. Small pores grew in samples gasified by the iron carbonyl cluster; pore volumes of 3—5 nm in diameter were increased the most. For the samples with iron(III) nitrate, little change was observed for the hydrogen-pretreated carbon and a slight increase in the volume of pores smaller than 10 nm in diameter was observed for the steam-pretreated carbon.

TPD of Hydrogen. The TPD spectra of hydrogen adsorbed on the iron/carbon samples are shown in Fig. 2. The desorption peaks can be seen at about 90 °C for all of the samples examined, irrespective of the precursor and carbon pretreatment. (This peak will be referred to as the low-temperature peak in the following.) However, the amounts of hydrogen which desorbed above 150 °C were markedly different between the samples with dodecacarbonyltriiron(0) and iron(III) nitrate. Regarding the former samples, the desorbing amounts increased with the temperature while for the latter little desorption occurred up to about 300 °C; the desorbing amounts then increased with the temperature above 300 °C, being even

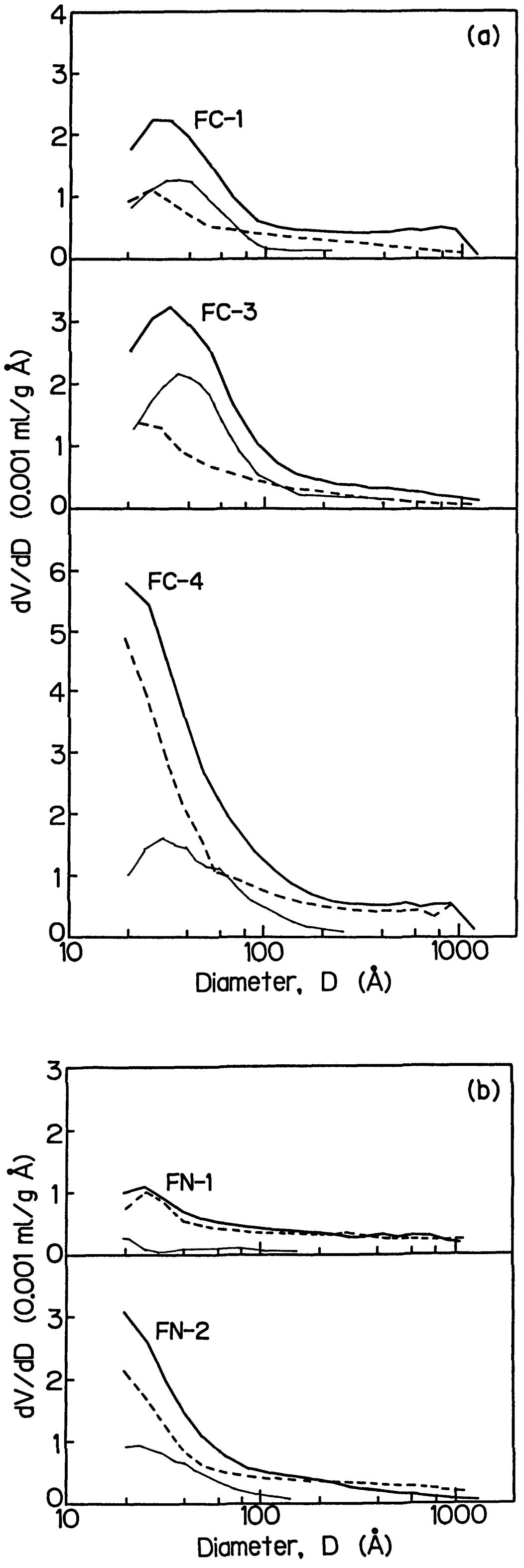

Fig. 1. Pore size distributions of carbons (broken lines) and iron/carbon samples (bold lines) after the gasification at 500 °C. (a): Samples prepared from dodecacarbonyltriiron(0), (b): those from iron(III) nitrate (the abbreviations are the same as in Table 1). Fine lines indicate the differences in pore volumes between iron/carbon samples and carbons, showing the changes due to the catalytic gasification.

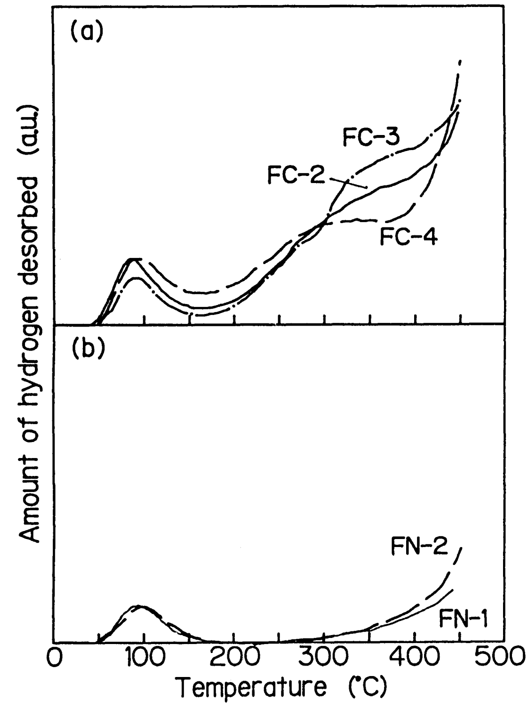

Fig. 2. TPD spectra of hydrogen adsorbed on iron/carbon samples (0.15 g) prepared with (a) dodecacarbonyltriiron(0) and (b) iron(III) nitrate (the abbreviations for the samples are the same as in Table 1).

Table 3. Apparent Activation Energy for the Desorption of Hydrogen in the Low-Temperature Peak

Sample[a)	Activation energy	Coverage[b)
	kJ mol^{-1}	—
FC-1	37 (28)[c)	0.72
FC-3	37 (27)[c)	0.72
FC-4	36 (30)[c)	0.74
FN-1	26	0.70
FN-2	27	0.58

a) For abbreviations, see Table 1. b) Calculated by the ratio of amount of hydrogen desorbed for an adsorption time of 15 min to that of 90 min. c) Determined after subsequent heat treatments in flowing argon at 600, 650, and 700 °C for 1 h each.

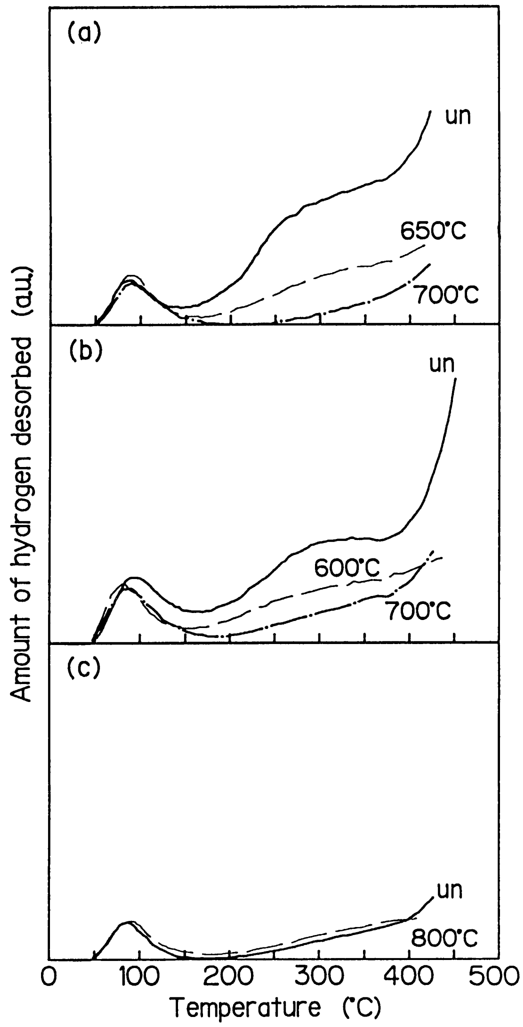

Fig. 3. Influence of heat treatment on TPD spectra of hydrogen for the three samples of (a) FC-3, (b) FC-4, and (c) FN-1 (for abbreviations, see Table 1). Heat treatments were made in flowing argon at temperatures given. un: Untreated.

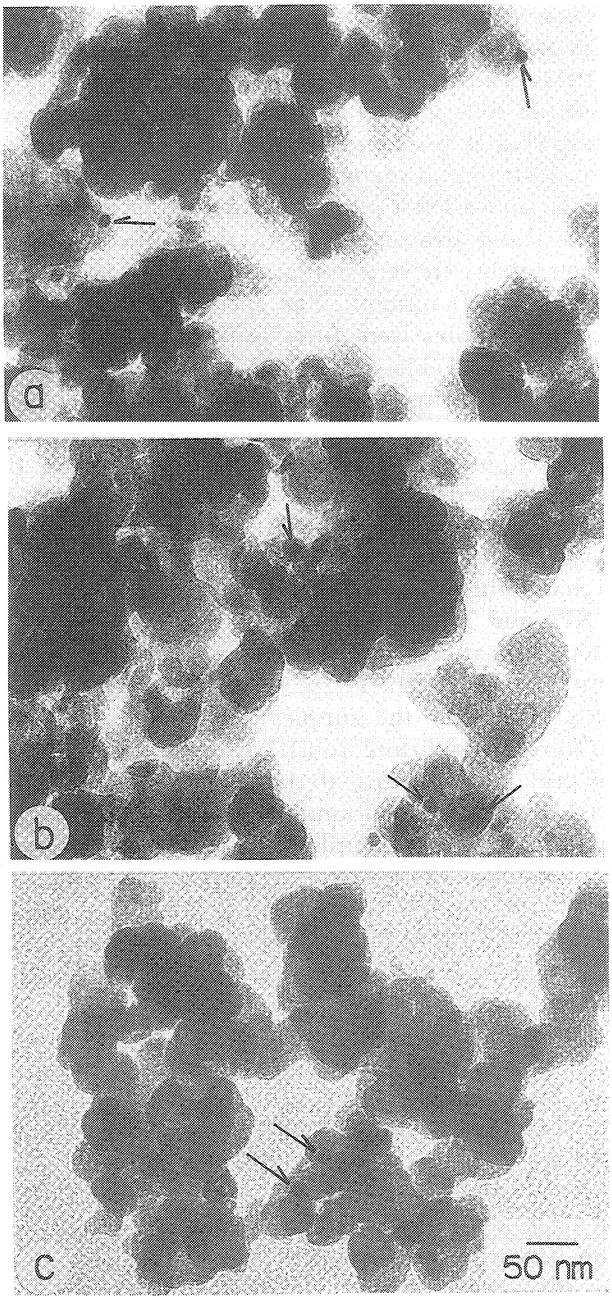

Fig. 4. Transmission electron microscope images of FC-3 (a) and FC-4 (b) samples after heat treatment at 700 °C and of FN-1 (c) sample before heat treatment (for abbreviations, see Table 1). Arrows indicate iron particles.

smaller than those for the former. Table 3 indicates the apparent activation energy for the desorption of hydrogen in the low-temperature peak when the adsorption time was 15 min, giving similar initial coverages. The activation energies are different depending only on the precursor used; it is 37 kJ mol^{-1} for samples prepared with dodecacarbonyltriiron(0) being larger by about 10 kJ mol^{-1} than those prepared with iron(III) nitrate. It is thus demonstrated that the hydrogen adsorbability of cluster-derived iron/carbon samples is markedly different from that of nitrate-derived samples.

In addition, we examined the influence of a heat treatment on the TPD of hydrogen. The iron/

carbon samples were heated in flowing argon at 600, 650, and 700 °C for 1 h each and then subjected to a TPD measurement after each step of heating. Figure 3 shows typical TPD spectra for the cluster-derived samples after heat treatments. The amount of hydrogen desorbing at the temperatures examined, in particular above 150 °C, was decreased by the treatments. After being treated at 700 °C, the samples showed spectra that were very similar to those for the samples with iron(III) nitrate. The spectra for the nitrate-derived samples were little influenced by the heat treatments. Table 3 also includes the activation energy for the cluster-derived samples after a treatment at 700 °C. The samples showed similar values of 27—30 kJ mol^{-1}, which were close to those for the nitrate-derived samples. It follows that the heat treatments caused the hydrogen adsorbability of the cluster-derived iron/carbon samples to become similar to that of the nitrate-derived samples.

XPS and TEM. The state of iron in the samples after gasification was examined by XPS. No significant difference in the Fe $2p_{3/2}$ binding energy could be detected between the samples prepared with dodecacarbonyltriiron(0) and iron(III) nitrate. The ratios of the peak area of Fe $2p_{3/2}$ to that of C 1s for the cluster-derived samples were found to be larger than those for the nitrate-derived samples. This suggests that the former samples have more iron atoms exposed than do the latter, being in accordance with the above-mentioned TPD results and TEM observations that it was impossible to see iron particles in the cluster-derived samples.

In addition, the XPS indicated that the heat treatment of the cluster-derived samples at 700 °C decreased their peak area ratios of Fe $2p_{3/2}$ to C 1s by more than 30%. Figure 4 shows TEM images of selected samples, demonstrating that the heat-treated cluster-derived samples include iron particles comparable in size to those of the untreated nitrate-derived samples. That sintering took place with the heat treatment for the cluster-derived iron/carbon samples was shown by those results as well as the changes in the TPD spectra.

Discussion

The present results demonstrate that the carbon can be gasified by hydrogen with adsorbed dodecacarbonyltriiron(0) and the gasification results in the development of smaller pores. The hydrogen adsorbability of the iron/carbon samples obtained after the gasification is markedly different from that of the samples prepared conventionally with iron(III) nitrate where the extent of gasification and the resulting change of porosity are even smaller compared with the cases for the iron carbonyl cluster. The following discussion will begin with the hydrogen adsorbability and then deal with gasification activity.

The Hydrogen Adsorbability. The difference in the hydrogen adsorbability between the iron/carbon samples prepared with dodecacarbonyltriiron(0) and iron(III) nitrate may be due to a difference in the particle morphology that has recently been discussed by Stevenson and Dumesic.[2] They reported that iron particles in the cluster-derived samples were even smaller, more spherical, and had more surface atoms being coordinately unsaturated, compared with conventionally prepared samples with iron(III) nitrate.

As shown in Fig. 2, the TPD spectrum for each cluster-derived sample has two regions that are below about 150 °C (low-temperature peak) and at higher temperatures. Larger amounts of hydrogen desorbed at higher temperatures are a salient feature of the cluster-derived samples. Figure 5 shows plots of the amounts of hydrogen desorbed at temperatures up to 450 °C and in the low-temperature peak against the product of the XPS intensity ratio of Fe $2p_{3/2}$/C 1s by the surface area of the sample. This product may be used as a measure of the amount of iron atoms exposed in unit weight of the samples. Figure 5(b) gives a relatively good correlation which includes the results for samples with the carbonyl cluster and the nitrate; Fig. 5(a) dose not. This suggests that all of the hydrogen dose not desorb from the surface of iron

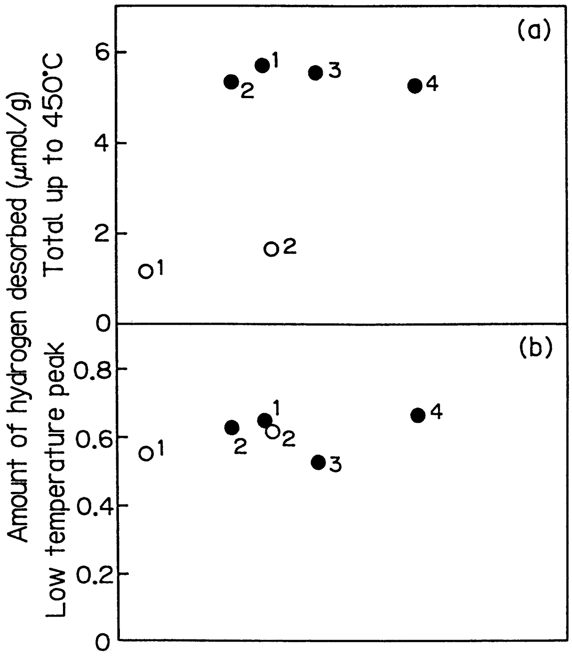

Fig. 5. Plots of the amounts of hydrogen desorbed at temperatures up to 450 °C (a) and in the low temperature peak (b) against the product of XPS intensity ratio of Fe $2p_{3/2}$/C 1s by the BET specific surface area (SSA) for the iron/carbon samples prepared with dodecacarbonyltriiron (0) (●) and iron(III) nitrate (○) after the hydrogasification at 500 °C. Figures given refer to the kinds of the sample (see Table 1).

particles, although the total amount of hydrogen desorbed under the present conditions is rather smaller than expected from the amount of metal loading and the high degree of metal dispersion. We assume that there occurs a hydrogen spillover from the iron particles onto the carbon support in our samples; hydrogen desorbed in the low-temperature peak is adsorbed by the particles and that desorbed at higher temperatures is spilt-over hydrogen. In the literature, hydrogen spillover was reported in many studies for carbon supports[16—22] and others.[23,24]

From the present TPD data below 450 °C, the amount of spillover of hydrogen per unit weight of sample is about 5 $\mu mol\,g^{-1}$ for the cluster-derived samples, depending little on the support used. Probably, hydrogen spillover occurs at similar rates for these samples and the number of acceptor sites on their carbon surfaces are enough for the amounts of spilt-over hydrogen under the present conditions. The amount of spillover of hydrogen per unit surface area of support is estimated to be 0.01—0.03 $\mu mol\,m^{-2}$. Compared with these cluster-derived samples, the estimated amounts of spillover of hydrogen are much smaller for the nitrate-derived samples. Hydrogen spillover would easily occur in samples prepared with dodecacarbonyltriiron(0), and their iron particles with the above-mentioned morphological characteristics may be favorable to this phenomenon. Figure 2(a) shows the differences in the TPD spectrum above 300 °C among the cluster-derived samples. This might indicate the influence of the surface properties of the carbon support on the spillover of hydrogen. As for the hydrogen adsorption, further information will be obtained by additional studies under different adsorption conditions; further studies along this line are now in progress.

When the cluster-derived iron/carbon samples were heat-treated, their TPD spectra and activation energies became very similar to those for the samples with iron(III) nitrate. These results indicate that the heat treatments cause some changes in the particle morphology, the degree of iron dispersion, and/or the state of iron-carbon contact for the cluster-derived samples, in which very samll iron particles are probably easier to undergo such a change than larger particles in the nitrate-derived samples. It was proved by TEM and XPS that sintering occurred in the cluster-derived samples with the heat treatments.

The Hydrogasification and the Development of Pores. Dodecacarbonyltriiron(0) is highly dispersed on the surface of carbon[1] and it changes into small metallic iron particles during the heating in hydrogen up to the gasification temperature. The formed iron particles are also highly dispersed,[1] and active for the hydrogasification. Not only the high degree of iron dispersion but also the ease of hydrogen spillover may be responsible for the high gasification activity in the cluster-derived samples. The important role of hydrogen spillover in the gasification of carbons was previously pointed out in several studies.[18—22] In the present cases, the gasification results in the development of pores, particularly, those of 3—5 nm in diameter. It is probable that the gasification occurs near the interfacial areas of carbon-iron particles; dissociatively adsorbed hydrogen atoms migrate from the particles onto these areas and react with the carbon, as discussed by Tomita and Tamai.[19] Thus, one can suppose that the carbon near the iron particles would be gasified and pits would be formed near them, resulting in the development of pores. The sizes of developed pores, 3—5 nm in the present cases, are larger than the iron particles in the cluster-derived samples, for which neither such small particles nor larger ones could be detected with TEM. This might suggest that, compared with sizes of the iron particles present, larger carbon-particle interfacial areas are a reaction locus; in other words, hydrogen atoms would migrate on the carbon relatively long distance before the reaction. It is difficult at present to make any further detailed discussion about the mechanism of hydrogasification with dodecacarbonyltriiron(0); additional studies will be required for this.

In contrast, iron(III) nitrate is less active in the gasification and little influences the porosity of carbon. These may be due to a lower degree of iron dispersion and the difficulty of hydrogen spillover, resulting possibly from the fact that the initial dispersion of iron precursors is lower and/or they are more difficult to reduce to metallic iron, compared with the cases of the iron carbonyl cluster.

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