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Magnetite Formation on Silica and Alumina

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Iron(III)hydroxoacetate (IHA) was precipitated on (i) silica and (ii) alumina and heated, under conditions at which IHA yields magnetite, according to a new, recently published route for magnetite preparation. In the presence of silica, magnetite formation is prevented. Magnetite obtained by heating IHA deposited on alumina is less crystalline and has a lower Fe(II)/Fe(III) ratio than the unsupported material. Magnetite coatings on alumina are uneven, a feature which is related to the heterogeneity in the morphology of alumina particle surfaces: rougher surfaces are more intensely coated than smoother ones. © 1994 Academic Press, Inc.

INTRODUCTION

The great majority of industrial processes use supported catalysts; silica and alumina are the most common catalyst supports.

Alumina is inert to most reacting systems and can exist in a variety of forms with surface areas ranging from less than 1 m^2/g up to about 300 m^2/g (1). It is a refractory oxide with a high melting point (above 2000°C), conveniently used to mantain particles of a finely divided catalytic material separated from each other, preventing their aggregation or coalescence. It is amphoteric and, in the form of α-alumina, it is a hard material stable under high pressure and abrasive conditions (2). Because of these characteristics alumina is generally the first choice as a catalyst carrier. It has been used in several important industrial processes such as reforming (3), hydrogenation (4), dehydrogenation and selective dehydrogenation (5), low-temperature shift reaction (6), and methanol synthesis (7).

Silica is not used as frequently as alumina, but it is useful in some cases in which alumina does not fit (8). Silica is more resistant to acidic media than alumina (9). Like alumina, silica occurs in many forms, for which the temperature ranges overlap. However, silica is more sensitive to pressure changes than alumina. Moreover, it can sublime at high temperatures and pressures of 1 mPa or below (2). Silica gel is available with surface areas up to about 800 m^2/g. Diatomaceous earth (kieselguhr), a naturally occurring form of silica, has surface areas of about 50 m^2/g. Silica gel and kieselguhr are useful supports (1). Silica is industrially used in Fischer–Tropsch synthesis (10), sulfuric acid production (11), and ethylene polimerization (12).

Although supports are frequently considered as inert materials having the simple role of dispersing the catalysts, they can alter the activity and selectivity of these. Experience shows, for instance, that there is some kind of interaction between metallic particles and their supports due to electronic transfer or local electrical modification on metal (13). This is evident from changes in chemisorption and activity (14).

Catalysts and their supports may interact in several ways. A good example is given by the reducibility of iron (III) compounds. These can be reduced completely to the metal by hydrogen on silica and carbon supports, but this treatment generally fails when they are supported on alumina. Another type of interaction between a metal and its support has been observed for platinum on alumina under high-temperature reduction with hydrogen. Some alumina is taken into solid solution with platinum (15).

Iron catalysts supported on silica or alumina have shown activity in the water high-temperature shift reaction (16, 17) dehydrogenation of ethylbenzene (18) as well as in Fischer–Tropsch synthesis (19, 20). In all the cases changes in activity and selectivity have been noted, which were believed to be due to interactions between the catalyst and the carrier. In the dehydrogenation of ethylbenzene, hematite on different supports showed an increase in selectivity as the strength of the metal-support interaction decreases (18). In addition, magnetite on alumina has shown a decrease in activity in the water gas shift reaction as compared to the chromia promoted magnetite catalyst (16). In the Fischer–Tropsch synthesis, it was shown (19, 20) that the nature of the catalyst-support interaction strongly affects the rate of reduction of magnetite to metallic iron which in turn has a major influence on the catalytic activity and selectivity. Indeed, a direct relationship was found (19) between the temperature at which the oxidic catalyst precursor was reduced and the initial overall catalytic activity of the solids.

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The methods employed for the catalyst preparation are known to have a large influence on the catalytic behavior, not only because of the metal morphologies (21–23) but also due to the ability of the metal atoms in assuming several oxidation states according to the preparation conditions (24). Since iron can be active in several forms (as hematite, magnetite, or metallic iron) (16–20), much work has focussed on its reduction behavior (13, 20, 25). These studies revealed that the supported iron catalysts show an inferior reducibility than the unsupported one, probably due to the stabilization of ferrous cations by the formation of surface compounds (26).

In order to develop methods of preparing supported iron oxide catalysts, the influence of silica and alumina on magnetite formation is investigated in this work. Recent work showed that this oxide can be conveniently obtained by heating iron(III)hydroxoacetate (IHA) under nitrogen (27, 28). This may provide an inexpensive and reliable route for the preparation of magnetite for industrial uses, especially for water gas shift catalysts, whose active phase is magnetite. In the commercial processes, hematite is reduced to magnetite *in situ* and this exothermic reaction has to be carefully controlled since it may lead to the production of metal iron. This metal can catalyse the Fischer–Tropsch synthesis causing a decrease in the activity and selectivity of the catalyst towards the water gas shift reaction (29).

In the present work, an unsupported IHA sample was compared to solids produced in the presence of silica and alumina. The materials thus obtained were heated at several temperatures, in the range 150–400°C. The products were characterized by chemical analysis, infrared (IR) spectroscopy, X-ray diffraction (XRD), surface area measurement, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). IHA thermolysis was also monitored by thermal analysis (DSC and TGA). Related work on the catalytic properties of these solids is currently in progress.

METHODS

Analytical grade reagents were used throughout.

IHA was prepared at room temperature by adding 125 ml of 25% ammonium hydroxide solution to 250 ml of an aqueous solution containing 101 g of $Fe(NO_3)_3 \cdot 9\ H_2O$ under vigorous stirring. The resulting mixture pH was 12. After 15 min the dispersion was centrifuged (2000 rpm, 5 min) and the gel was rinsed six times with 600 ml of 5% (m/v) ammonium acetate solution in order to promote acetate sorption on iron(III)hydroxide gel and to remove ammonium and nitrate ions. The IHA gel was dried in an oven at 120°C. After this, the material was heated under nitrogen in the range 150–400°C for 2 h.

Supported samples were prepared by the method described above but the hydrolysis of iron nitrate was carried out in the presence of silica (46.9 g of Silica gel 60 for chromatography, Merck) or alumina (39.8 g of Aluminum Oxide 90 for chromatography, Merck).

Iron contents [Fe(total) and Fe(II)] were determined by $K_2Cr_2O_7$ titrimetry on samples dissolved in 18% aqueous HCl under reflux. To determine total iron, Fe(III) was reduced to Fe(II) with tin(II) chloride prior to titration (30).

Carbon analyses were carried out in a Leco instrument, model 761-100.

Surface areas were measured by the BET method from the amount of nitrogen adsorbed at liquid-nitrogen temperature using a CG-2000 (São Paulo) surface area meter.

X-ray analysis was performed using a Phillips PW 1130 diffractometer employing Co$K\alpha$ generated at 36 kV and 20 mA. A Model 1430 Perkin–Elmer spectrophotometer was used for recording infrared spectra of the samples in the range 200–4000 cm^{-1} from CsI discs.

DSC and TGA experiments were carried out at a heating rate of 10°C $\cdot$ min^{-1} under a nitrogen atmosphere (100 ml $\cdot$ min^{-1}), using a Model 9900 DuPont apparatus.

Scanning electron microscopy studies were performed on a Model JSM-T300 Jeol microscope operating at 20–30 kV. Transmission electron microscopy was done in a ZEISS EM 902 instrument operating at 80 kV.

RESULTS

Chemical Analysis

Unsupported solids heated under nitrogen changed to black and became magnetic. Figure 1 shows that the Fe(II)/Fe(III) ratio increases faster above 250°C, and at about 400°C it achieves a value of 0.47, which is near the stoichiometric value for magnetite (0.50). Samples containing alumina show similar behavior but the Fe(II)/Fe(III) ratio reaches a lower value (0.40) at about 350°C. However, solids with silica did not become magnetic and the Fe(II)/Fe(III) ratio remained at values lower than 0.35 (Fig. 1).

From the carbon analysis results (Table 1) we can see that only a small amount of organic carbon remained in solids heated to 400°C. These carbon contents are probably acceptable even in Fischer–Tropsch catalysts, in which there is carbide formation during the reaction, from the hydrocarbon produced (10). On the other hand, in the water gas shift reaction carbon is desirable since it acts as a plasticizing agent during pelletization in commercial catalysts (31).

X-ray Diffraction

Diffractograms of IHA samples with alumina heated at several temperatures for 2 h are shown in Fig. 2. There are

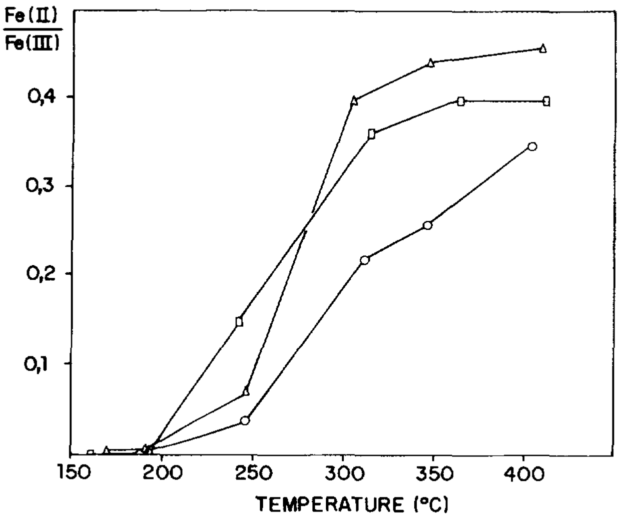

FIG. 1. Fe(II)/Fe(III) ratio in iron(III)hydroxoacetate (IHA) as a function of temperature: (Δ) IHA without support, (□) IHA with alumina, and (○) IHA with silica.

no sharp diffraction lines for solids heated at temperatures below 196°C. Diffuse lines appear at 267°C and become more intense in the samples heated at higher temperatures, in which we can identify the X-ray powder pattern of magnetite (32).

On the other hand, samples containing silica do not show any diffraction line, as seen in Fig. 3.

We can also note that the alumina-supported magnetite gives diffraction lines broader than those of the unsupported IHA.

The values of the interplanar spacing (Table 2) of magnetite on alumina are the same as in the unsupported magnetite, showing that the nature of the catalyst oxide is preserved, in this support.

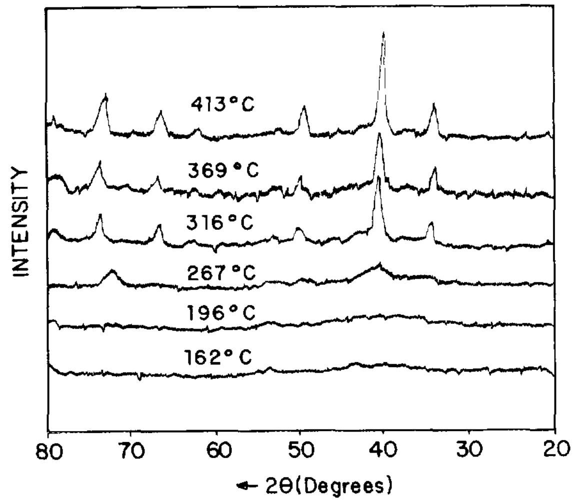

FIG. 2. X-ray diffractograms of iron(III)hydroxoacetate supported on alumina, after heating at several temperatures for 2 h under nitrogen.

TABLE 1

Carbon/Iron Molar Ratio of Iron(III)hydroxoacetate (IHA) after Heating at Several Temperatures for 2 h under Nitrogen

Calcination temperature (°C)	Carbon/iron ratio		
	IHA without support	IHA on alumina	IHA on silica
170	0.70	0.88	0.54
185	0.63	0.77	0.49
245	0.24	0.38	0.29
310	0.06	0.18	0.15
350	0.04	0.13	0.10
410	0.04	0.09	0.04

Surface Area Measurement

Unsupported IHA samples as well as those containing alumina show similar surface area vs heating temperature curves (Fig. 4). Surface areas increase at temperatures lower than 200°C and then decrease to steady values. For IHA samples with silica the surface areas change under increasing temperatures, reaching the value of 295 m^2/g at about 400°C, below the surface area of the silica gel used in the sample preparation (352 m^2/g).

Thermal Analysis

The DSC thermogram of the unsupported sample (Fig. 5) presents an endothermic peak at temperatures below 100°C which can be assigned to the loss of volatile components. At temperatures greater than 205°C there are two peaks which are associated with magnetite formation. As

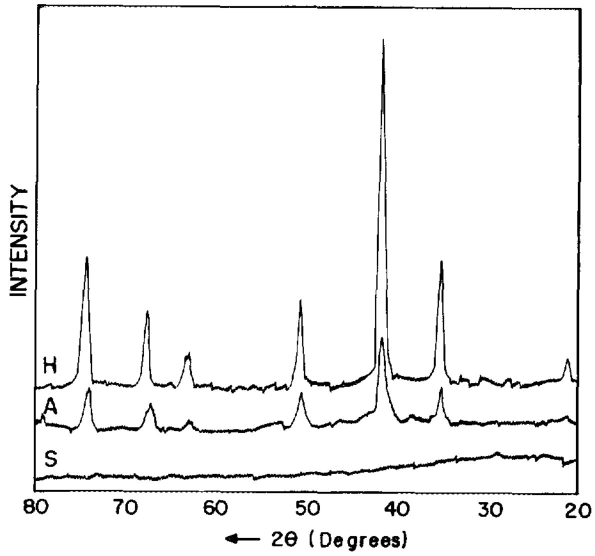

FIG. 3. X-ray diffractograms of iron(III)hydroxoacetate (IHA) after heating at 400°C, for 2 h under nitrogen: sample H, unsupported IHA; sample A, IHA on alumina; and sample S, IHA on silica.

TABLE 2

Interplanar Spacings (*d*) of Unsupported Magnetite and Magnetite on Alumina

	d (Å)		
hkl	ASTM card no. 19 269	Unsupported magnetite	Magnetite on alumina
111	4.85	4.85	4.86
220	2.97	2.96	2.97
311	2.53	2.56	2.54
400	2.10	2.10	2.10
422	1.71	1.71	1.71
333/511	1.61	1.61	1.62
440	1.48	1.48	1.48

indicated in Fig. 1, most of Fe(II) is formed in this temperature range. In alumina-containing material the thermogram has a similar profile, but in the presence of silica, the exothermic peaks are not observed.

Infrared Spectra

Infrared spectrum taken from an IHA sample with silica heated at 403°C (Fig. 6) shows absorptions at 1010 and 800 cm^{-1} assigned to Si–O stretching mode (33). A low-frequency band (460 cm^{-1}) is due to Si–O bending vibrations (34, 35). The absorption at 970 cm^{-1} in the plain silica spectrum is assigned to silanol groups (34).

The spectra of the solids (Fig. 6), obtained by heating both unsupported and alumina-supported iron hydroxoacetate at 400°C, present low-frequency bands at 580 and 370 cm^{-1} due to Fe–O vibrations on magnetite (35).

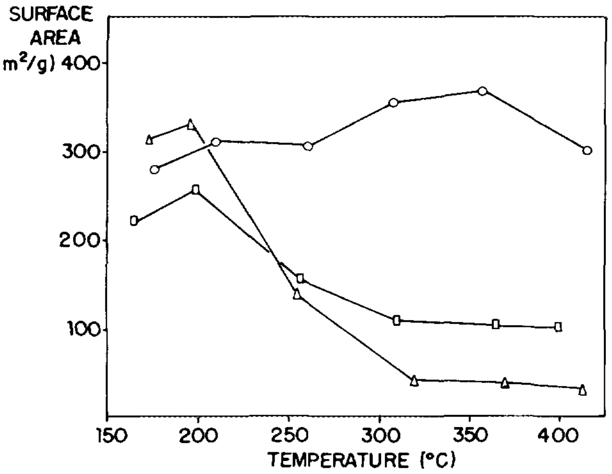

FIG. 4. Iron(III)hydroxoacetate (IHA) surface area as a function of heating temperature: (Δ) unsupported IHA, (□) IHA on alumina, and (○) IHA on silica.

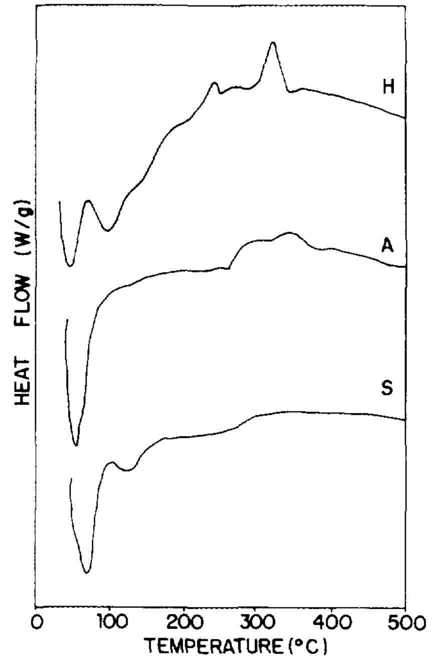

FIG. 5. Iron(III)hydroxoacetate (IHA) DSC thermograms: sample H, unsupported IHA; sample A, IHA on alumina; and sample S, IHA on silica.

Scanning Electron Microscopy

All samples presented particles in a large variety of sizes and shapes, as we can see in Fig. 7 and 8. In the backscattering picture of Fig. 8, we can also note the contrast among dark and clear areas on the particles, which means that there is a nonuniform deposit of magne-

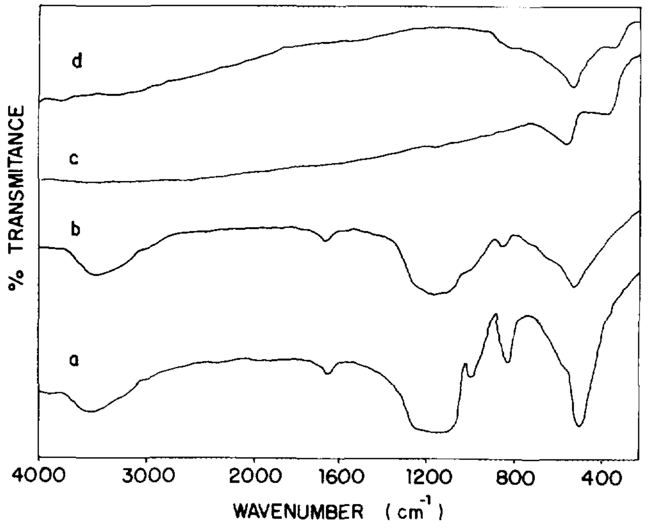

FIG. 6. Infrared Spectra of (a) IHA on silica heated at 403°C, (b) silica gel used in sample preparation, (c) unsupported magnetite, and (d) magnetite on alumina.

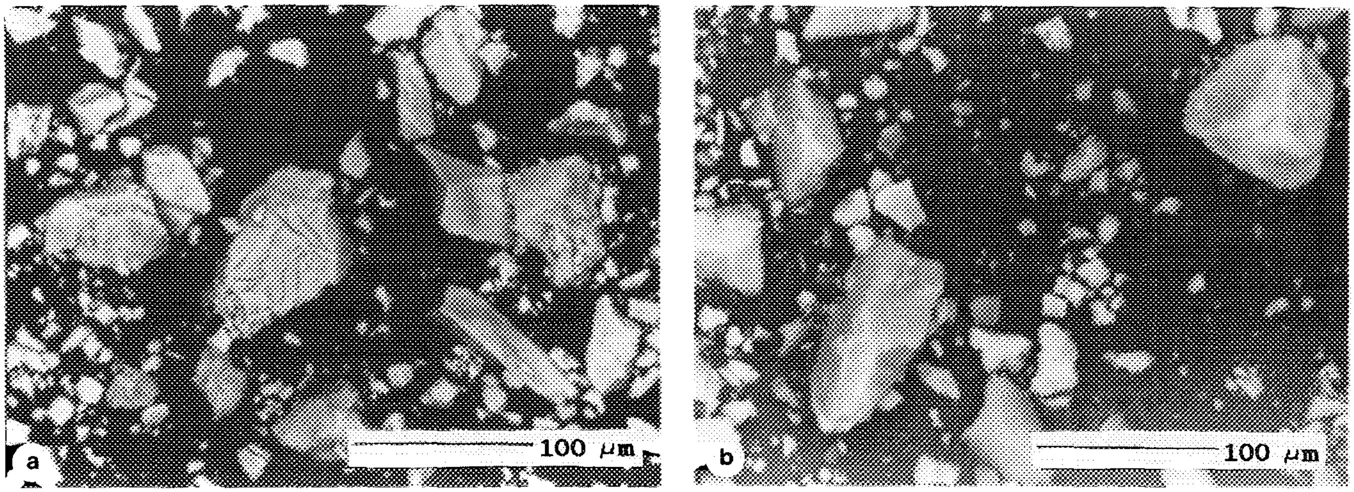

FIG. 7. Scanning electron micrographs taken from IHA heated at about 400°C: (a) unsupported IHA and (b) silica-supported IHA.

tite on alumina. In this case, dark areas correspond to magnetite, while the clear areas are plain alumina.

The pattern of magnetite deposition on alumina was studied by fractionating a sample, by means of a pocket-type magnet, into three parts: (i) a highly magnetic one (M1), which amounts to 50% of the total solid weight; (ii) a moderately magnetic one (I1), 25%; and (iii) a weakly magnetic one (N1), 25%.

The least magnetic fraction (N1) was dispersed in ethanol and again fractionated into two other parts: (i) one is weakly magnetic (M2) and amounts 30% of the N1 sample weight, and (ii) the other is nonmagnetic (N2), 70%.

The alumina of samples M1 and N2 was recovered by washing supported magnetite fractions with concentrated HCl under reflux for 8 h. Figure 9 shows the difference between the surface of these two samples. In the solid in which alumina was almost completely covered with magnetite (Fig. 9a) electron micrographs reveal rough surfaces, but in the other (Fig. 9b), in which this deposit was smaller, we can see smooth surfaces.

Transmission Electron Microscopy

Transmission electron micrographs were taken from magnetite samples prepared by heating IHA alone as well as in the presence of alumina. The powders were dispersed in ethanol, allowed to settle for some minutes, and the supernatant was applied to the microscope grids. Figure 10 shows that the finer particles in these solids are acicular as well as isometric, as are some found in unsupported IHA.

DISCUSSION

By heating IHA in the presence of alumina, one can get magnetite nonuniformly deposited on this support. As compared to unsupported materials, obtained under similar conditions, these solids are not as well crystallized and have a lower Fe(II)/Fe(III) ratio. Furthermore, they require higher temperatures to reach the stoichiometric Fe(II)/Fe(III) ratio. Overall, the (amorphous) iron(III)hidroxoacetate → magnetite transformation is slower in the presence of alumina than in its absence.

On the other hand, silica inhibits magnetite formation and silicates containing ferric and ferrous ions are produced instead.

These differences can be explained by considering some differences between silica and alumina.

The surface structure of silica gel is widely accepted as consisting of hydroxyl (silanol) groups and oxide (siloxane) linkages (36). Due to interactions between

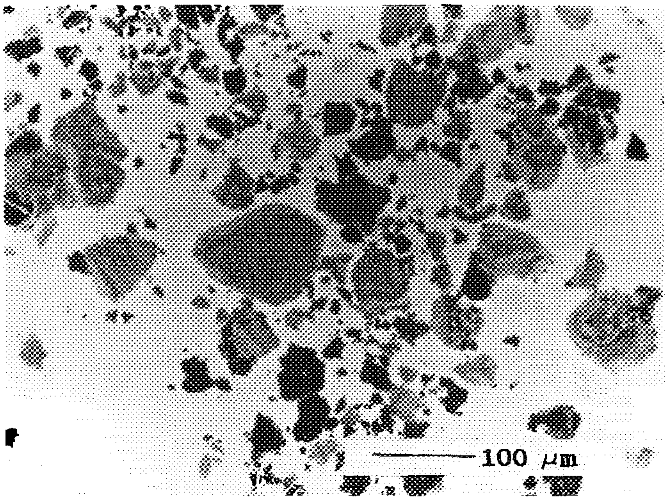

FIG. 8. Scanning electron micrograph of magnetite on alumina taken with backscattered electrons and chemical composition contrast.

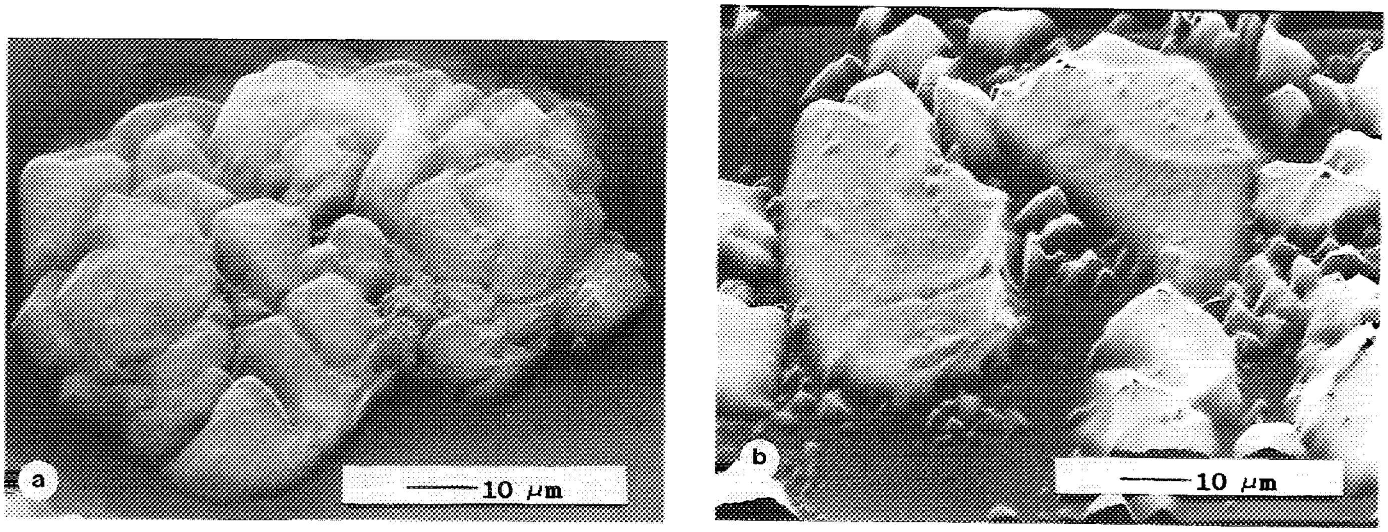

FIG. 9. Scanning electron micrographs (raster mode) taken with backscattered electrons and contrast by topography (alumina obtained from supported IHA samples): (a) alumina recovered from heavily IHA coated particles and (b) alumina recovered from lightly IHA coated particles.

silica and water, there is a conversion of siloxane to silanol surface sites. The presence of these groups allows the anchoring of IHA polymeric chains so that silica particles can bind IHA fragments, as illustrated in Fig. 11. Under heating, Fe(II) is formed by reduction with acetate and Fe(III) as well as Fe(II) ions bind to silicate groups, thus preventing the formation of crystalline magnetite.

The alumina surface also has OH groups but these are less reactive than those of silica (37) toward cations. The isoelectric point of alumina is 7.43 (38), whereas this value is 3.1 for silica (39). Therefore the silica surface becomes more negatively charged than alumina at alkaline pH's, which favors Fe^{3+} cation adsorption as well as the adhesion and growth of IHA particles on silica.

During IHA precipitation in the presence of alumina, the amorphous swollen hydroxoacetate particles adsorb and adhere to alumina. Of course, the adhesion is stronger in rough, coarse facets of alumina particles

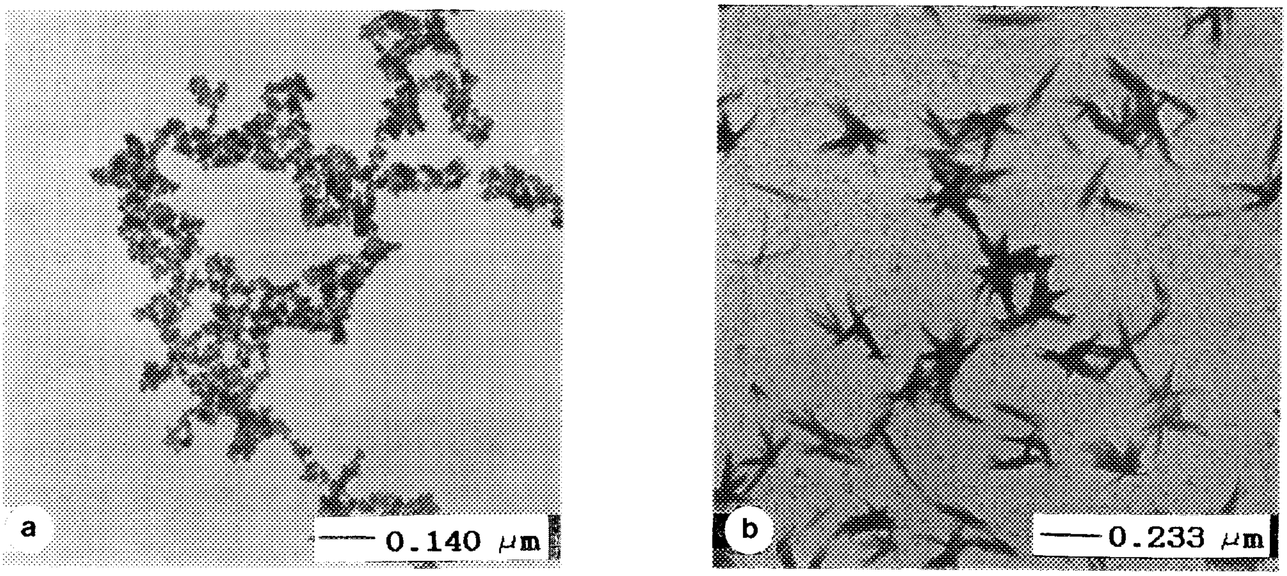

FIG. 10. Transmission electron micrographs of fine particles in alumina-supported IHA, heated at 369°C.

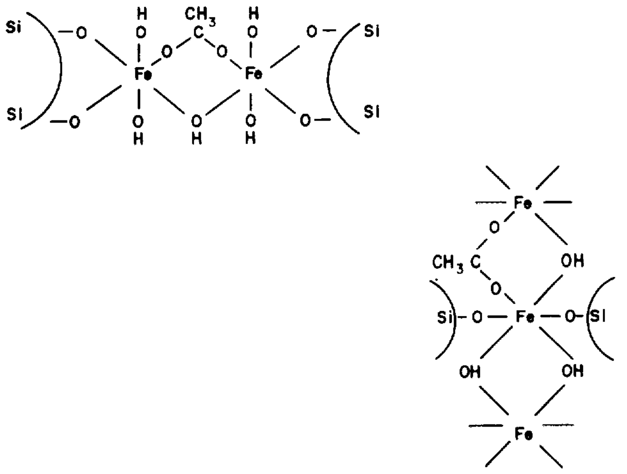

FIG. 11. Scheme showing IHA anchoring of IHA on silica particles.

than in smooth ones. For these reasons, IHA coatings are uneven, as well as the resulting magnetite coatings. As there is no shift in the position of the supported magnetite diffraction peaks, when compared to unsupported samples, we conclude that aluminum is not significantly incorporated into the magnetite structure. Therefore, IHA does not strongly interact with alumina, as it does with silica.

These results are in accordance with previous studies (20, 26) in which it was noted that ferrous ions strongly interact with silica. However, the formation of iron aluminate detected by Ren-Yuan *et al.* (25) or the incorporation of aluminum into the supported iron particles as noted by Jung and Thomson (16) were not observed in this work. We conclude that the method used in impregnation plays an important role in determining the metal-support interactions.

These observations suggest that the evenness of catalyst spreading on supports may probably be controlled by using suitable support pretreatments, to achieve desirable surface morphologies. Evaluation of catalysts prepared as described in this work is currently in progress and will be reported in the near future.

CONCLUSIONS

Heating of iron(III)hydroxoacetate (IHA) supported on alumina is a convenient method to produce supported magnetite. The magnetite thus obtained is less crystalline and has a lower Fe(II) content than other magnetite samples including those prepared by IHA thermolysis. Magnetite coatings on alumina are uneven and their formation is more pronounced on rough than on smooth surfaces. Alumina incorporation in the magnetite structure is not observed.

On the other hand, IHA strongly interacts with silica and magnetite formation is prevented, in this support.

Alumina can be used to stabilize poorly crystallized magnetite. This may prove useful in achieving higher activities, in iron oxide-based catalytic systems.

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