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Water–Gas Shift over Magnetite Particles Supported on Graphite: Effects of Treatments in CO/CO_2 and H_2/H_2O Gas Mixtures

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The water–gas shift reaction (at 660 K) was studied over both unsupported magnetite and magnetite particles supported on graphitic materials. It was found that the turnover frequencies over the supported catalysts decreased by an order of magnitude during the first few hours of reaction. About half of the initial high activity could be restored by treatments of the catalyst in CO/CO_2 gas mixtures at 660 K. Treatment in H_2/H_2O gas mixtures did not lead to significant increases in catalytic activity. This deactivation behavior was not exhibited by unsupported samples. Mössbauer spectroscopy studies indicated that no bulk phase changes occurred during these treatments. Transmission and scanning electron microscopy showed that the magnetite particles were present as large, porous clusters. It is argued that reduction of catalytic activity for graphite-supported magnetite is caused by constriction of the pores within these clusters under water-containing atmospheres due to changes in the surface phase of the magnetite particles.

INTRODUCTION

Magnetite (Fe_3O_4) has been used industrially as a catalyst for the water–gas shift reaction for three quarters of a century (*1*); however, relatively little is known about the state of the surface of magnetite under water–gas shift reaction conditions. It is possible, for example, that a surface phase different from magnetite may exist under these reaction conditions. In this respect, it has been suggested that the surface of an iron carbide catalyst for Fischer–Tropsch synthesis is an iron oxide (*2*). With this in mind, the present investigation was undertaken to alter the surface properties of magnetite by various pretreatments (while retaining the bulk structure of magnetite) and to determine whether the catalytic activity for water-gas shift was altered accordingly.

Two classes of magnetite catalysts were investigated in this study: (i) unsupported, unpromoted magnetite, and (ii) magnetite particles supported on graphitic materials. The study of both classes of catalysts was carried out in order to vary the size of the magnetite particles. The support material was chosen to minimize the possible effects of interactions between magnetite and the support. Due to structural similarity, it may be expected that interactions between oxide particles and oxide supports may be stronger than interactions between metal particles and oxide supports. In the case of magnetite, for example, it has been shown that strong interactions take place between Fe_3O_4 and SiO_2 (*3–6*), whereas silica is commonly considered to be an inert support for metal particles. For this reason, the nonoxidic support, graphite, was used in the present work.

EXPERIMENTAL

Sample preparation. The supported samples used in this study were prepared using

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two different types of graphitic supports. For transmission electron microscopy investigations cleaved, single crystals of graphite (Ticonderoga) were used. All other studies used Grafoil (GTA grade), a high surface area graphitic material made at Union Carbide by pressing high purity, chemically exfoliated, naturally occurring graphite flakes into the form of sheets. To facilitate handling, the Grafoil was ground before use, giving a coarse powder.

Iron oxide particles were deposited on these supports using two different procedures. First, following the method of Bartholomew and Boudart (*7*), iron oxide particles were supported on Grafoil via impregnation. Sufficient iron nitrate (Baker) was dissolved in a solution of 20% ethanol and 80% benzene such that the use of 3 cm^3 of solution per gram of support produced a loading of ca. 15 wt% magnetite on Grafoil. When Grafoil was added to this solution, colloidal particles of iron formed (as evidenced by the appearance of a brown precipitate); however, this could be avoided by reducing the pH of the solution to about 1–2 by addition of nitric acid to the solution prior to impregnation. After contacting the Grafoil with the impregnation solution for about 0.5 h at room temperature, the solvent was evaporated for 24 h at 300 K in dry, flowing nitrogen, followed by evacuation for 0.5 h at this temperature. Finally, the iron nitrate was decomposed by treatment in a flowing mixture of CO/CO_2 (15/85, premixed from Matheson, 99.8% pure) for 4 h at 420 K.

Before use as catalysts for water–gas shift, the impregnated iron samples were treated in a flowing mixture of CO/CO_2 (15/85) at 660 K. This treatment has been shown to convert the iron to magnetite (*8*, *9*). The surfaces of these samples were examined by X-ray photoelectron spectroscopy and Auger electron spectroscopy before and after water–gas shift kinetics studies. These surface-sensitive techniques showed the presence of only iron, oxygen, and carbon, indicating that other possible impurities (e.g., sulfur) were not present on the samples.

For transmission electron microscopy studies, a second method was used to deposit the iron. This was accomplished by vacuum evaporation of approximately one monolayer of iron on the surfaces of the cleaved, single crystal graphite specimens. These graphite samples were approximately 30 nm thick. They were mounted on 3-mm stainless-steel grids for study.

Water–gas shift kinetics and iron oxide surface area measurements. Water–gas shift kinetics were measured in an all-glass apparatus which has been described elsewhere (*3*). The reactor was operated isothermally at conversions between 2 and 8%. A constant set of reaction conditions was chosen to allow comparison of water–gas shift activity for different samples or for a given sample after various pretreatments. These conditions were $T = 660$ K, $P = 1$ atm, 64% H_2O, 32% CO, and 4% CO_2. This was achieved by flowing premixed CO/CO_2 (89/11, Matheson, 99.5% pure) through a water saturator operating at 375 K. Small deviations in the rate due to fluctuations in reactor temperature or gas composition were corrected using the rate expression for water-gas shift developed by Bohlbro (*1*), which has been shown to be valid over magnetite at temperatures from 600 to 770 K. All reaction kinetic measurements and pretreatments were carried out at 660 K unless otherwise specified. Catalytic activities reported in this paper were calculated from the extent of CO conversion to CO_2.

The surface area of the magnetite particles supported on Grafoil was determined by measuring the amount of nitric oxide which adsorbed on the sample at 273 K, as described by Lund *et al.* (*10*). This was done volumetrically, in an all-glass apparatus which has been described previously (*10*). Prior to collection of nitric oxide adsorption isotherms, the samples were treated in the flowing CO/CO_2 (15/85) gas mixture at 660 K to ensure that the iron was present as magnetite, and then evacuated to ca. 10^{-3} Pa at 660 K for 1 h to remove adsorbed CO and CO_2 species. In separate experiments it was found that Grafoil alone adsorbs small amounts of nitric oxide (ca. 4 μmol/g) and this amount was subtracted from the NO uptakes of the Fe_3O_4/Grafoil samples.

X-Ray diffraction was used to estimate the sizes of the magnetite particles supported on Grafoil after various treatments. A Picker biplanar diffractometer operating with Cu$K\alpha$ radiation was used for this purpose. Average particle diameters were computed from the measured peak widths at half-maximum intensity according to the procedures outlined by Klug and Alexander (*11*).

Turnover frequencies, N_{CO}, were determined using two methods. In the first method NO uptakes were used. Past studies indicate that there is a one-to-one correspondence between adsorbed NO and surface iron cations (*10*); therefore, division of the rate of reaction by the NO uptake yields the turnover frequency per surface iron cation. These turnover frequencies are based on the NO uptakes determined after the sample had undergone all kinetic activity measurements.

In the second method, the number of surface iron cations was estimated from the particle diameter determined by X-ray diffraction. Assuming spherical, noncontacting particles, and a surface site density of 6×10^{18} iron cations/m^2 (10), the number of sites was calculated for a sample with a given loading and particle size. The particle diameters were determined after kinetic activity measurements were completed and are, therefore, based on the final surface area. The number of iron cations determined by this method was generally a factor of two larger than that determined by NO uptakes. This discrepancy may be due to the assumption that the particles are noncontacting spheres or to other inaccuracies in surface area determination by X-ray line broadening. The turnover frequencies determined from the particle size were multiplied by 0.5 to make them consistent with those calculated from NO uptakes.

Characterization of samples. Mössbauer spectroscopy was used to determine the chemical state of iron on the various samples following different treatments. The Mössbauer spectrometer and computer program used to fit the Mössbauer spectra have been described in detail elsewhere (*12, 13*). For these studies, the sample was loaded into a stainless-steel cell which operated at temperatures up to 700 K and pressures from 10^{-3} Pa to atmospheric (*12*). Doppler velocities were calibrated using a 25-μm metallic iron foil at room temperature, and all isomer shifts reported in this paper are relative to this standard absorber.

The size and morphology of supported magnetite particles were studied using scanning electron microscopy (SEM) for Grafoil supported samples, and transmission electron microscopy (TEM) for those supported on cleaved, single crystal graphite. For the SEM studies, a JEOL JSM-35C microscope operating at a beam voltage of 25 kV was employed. The micrographs were collected by detection of the secondary scattered electrons. The TEM studies were carried out using a JEOL 100B electron microscope operating at a beam voltage of 120 kV, as described elsewhere (*14*).

Gases. All CO/CO_2 gas mixtures used in this study were passed through a bed of glass beads at 620 K prior to use. This was done to decompose any metal carbonyls which may have been present in these gases. Hydrogen was obtained from Air Products (99.9% pure), and it was further purified by passing it through a Deoxo unit (Engelhard) followed by an activated molecular sieve trap (13×) at 77 K. Helium was obtained from Badger Welding (99.995% pure). It was passed through copper turnings at 620 K and an activated molecular sieve trap (13×) at 77 K prior to use. Oxygen was supplied by Chemetron (>99.6% pure), and it was used without further purification. The water used during

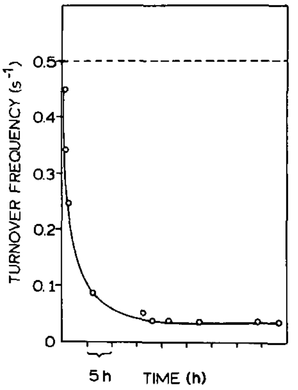

FIG. 1. Variation of the turnover frequency for water–gas shift (N_{CO}) at 660 K as a function of time for a 14.9 wt% Fe_3O_4/Grafoil Sample.

water–gas shift kinetic measurements was doubly distilled.

RESULTS

Water–Gas Shift Studies

The water–gas shift activity of Grafoil-supported magnetite was measured as a function of time under reaction conditions. A period of rapid deactivation, followed by a long period of relatively constant activity was observed. This is shown in Fig. 1 for a sample containing 14.9 wt% Fe_3O_4. During the period of stable catalytic activity, the temperature was varied from 600 to 660 K, allowing an apparent activation energy of 106 kJ/mol to be determined. This value is in good agreement with the value determined by Bohlbro (*1*) for structurally promoted magnetite.

The effects of various pretreatments on the catalytic activity of Fe_3O_4/Grafoil were then investigated. For example, the effect of treatment in CO/CO_2 is shown in Fig. 2 for a sample containing 16.8 wt% Fe_3O_4/Grafoil. In particular, the flow of water–gas shift reactants (to be subsequently denoted as "synthesis gas") to a sample which had attained a stable level of activity was interrupted for 22 h and replaced with a dry CO/CO_2 gas mixture (15/85). When the flow of synthesis gas to the reactor was resumed, the activity as indicated by Point a, was observed to be higher than that measured prior to this treatment, although it was only about one-half of the initial activity measured when the sample was first exposed to synthesis gas. From this point, the catalytic activity decreased to a stable value which was close to the activity measured before treatment in CO/CO_2. Treatments as short as 0.25 h in CO/CO_2 were found to increase activity; however, longer treatments resulted in greater extents of catalytic activation. Treatments longer than 24 h though, showed approximately the same extent of catalyst activation.

The rationale for using CO/CO_2 and H_2/H_2O gas mixtures to prepare and pretreat iron oxide catalysts is that these gas phase ratios define the thermodynamic activity of oxygen, and this activity can thereby be controlled to insure that the iron is present as magnetite. It should be noted that the CO/CO_2 ratios were also chosen such that the graphite support would not be gasified (*15*). In addition, it has been shown by Bohlbro (*1*) that these CO/CO_2 ratios do not lead to carbon deposition on magnetite.

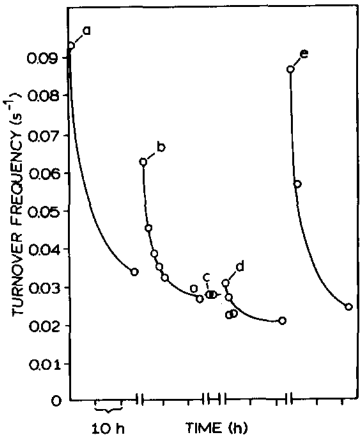

FIG. 2. Variation of N_{CO} at 660 K as a function of time after treatment in various gas mixtures for a 16.8 wt% Fe_3O_4/Grafoil sample. Activity before the first treatment: $\approx 0.023\ s^{-1}$. Pretreatments: Point a: 22 h in CO/CO_2 (15/85); Point b: 24 h in CO/CO_2 (4/96); Point c: 22 h in H_2/H_2O (40/60); Point d: 32 h in H_2/H_2O (80/20); Point e: 24 h in CO/CO_2 (15/85).

TABLE 1

Effects of Treatment at 660 K on the Water–Gas Shift Activity of a 16.8 wt.% Fe_3O_4/Grafoil Sample

Treatment gas atmosphere, time	Increase in activity[a] (%)
CO/CO_2 (15/85), 22 h	200–300
CO/CO_2 (4/96), 24 h	100–150
H_2/H_2O (40/60), 22 h	<5
H_2/H_2O (80/20), 32 h	<25
CO/CO_2 (15/85), 29 h H_2/H_2O (80/20), 21 h [b]	<25
O_2, 0.5 h CO/CO_2 (15/85), 24 h [b]	200–300
O_2, 0.3 h H_2/H_2O (80/20), 20 h [b]	200–300
Helium, 24 h	200–300

[a] Based on activity immediately preceding treatment.

[b] Second treatment immediately follows first.

While magnetite is thermodynamically stable over a range of CO/CO_2 and H_2/H_2O ratios, the oxidation state of the magnetite surface has been shown to be a function of these ratios (*16*). For this reason, the effects of varying the CO/CO_2 and H_2/H_2O ratios were investigated with respect to the extent to which these treatments increased the activity of the Fe_3O_4/Grafoil samples for water–gas shift.

As shown in Fig. 2 and Table 1, for a sample containing 16.8 wt% Fe_3O_4 on Grafoil, treatments for ca. 24 h in CO/CO_2 (15/85), Point a, and CO/CO_2 (4/96), Point b, have similar effects, with the treatment in CO/CO_2 (15/85) leading to a greater extent of catalyst activation. Treatment in H_2/H_2O (40/60) for 22 h had very little, if any, effect on the water–gas shift activity (Point c). Treatment in H_2/H_2O (80/20) for 32 h produced a greater extent of catalyst activation, as shown by Point d; however, this effect was small compared to the effects of treatments in the CO/CO_2 gas mixtures. An additional treatment of 24 h in CO/CO_2 (15/85) (Point e) was carried out to verify that the previously observed catalyst activation given by Point a could be reproduced.

Since H_2/H_2O mixtures did not significantly increase the catalytic activity, the possibility that these mixtures could, in fact, reduce the catalytic activity was examined. It was found that treatment for 29 h in CO/CO_2 (15/85), followed directly by a 21 h treatment in H_2/H_2O (80/20) had a similar effect on water–gas shift activity as a treatment for 22 h in H_2/H_2O (80/20). This indicates that treatments in H_2/H_2O not only fail to activate the samples to a significant extent, but that these treatments deactivate the catalyst following activation in CO/CO_2.

The possible effects of oxygen treatments on the catalytic activity of the Grafoil-supported catalysts were also investigated. Since treatment in oxygen is expected to convert the magnetite to Fe_2O_3, these treatments were followed by treatments in either CO/CO_2 or H_2/H_2O mixtures prior to water–gas shift activity measurements. A 0.5 h treatment in oxygen followed by 23 h in CO/CO_2 (15/85) led to an increase in catalytic activity, which was comparable to the extent of catalyst activation caused by treatment in CO/CO_2 alone. Treatment in oxygen for 0.33 h followed by treatment in H_2/H_2O (80/20) for 20 h, also caused an increase in catalytic activity which was comparable to the effect of treatment in CO/CO_2. This is in contrast to treatment in H_2/H_2O alone, or CO/CO_2 followed by H_2/H_2O, which did not lead to a significant increase in catalytic activity.

The final treatment employed in the present study was to flow purified helium over the Fe_3O_4/Grafoil samples for 24 h. The effect of this treatment was essentially the same as the treatment in CO/CO_2 (15/85): i.e., an increase in catalytic activity resulted. A summary of the treatments and their effects is given in Table 1.

Kinetic behavior similar to that reported above for impregnated Fe_3O_4/Grafoil samples has been observed for samples of Fe_3O_4/Grafoil prepared using gas phase deposition of $Fe(CO)_5$ (*12*, *13*). This suggests that the kinetic effects observed in this study are not an artifact of the preparation technique.

Studies analogous to those reported above for the Fe_3O_4/Grafoil samples were also carried out for unsupported magnetite. This sample was prepared as described elsewhere (*10*). For this unsupported magnetite, no deactivation was observed nor were increases in catalytic activity observed for any of the above treatments in CO/CO_2, H_2/H_2O or O_2. X-Ray diffraction studies of this sample indicated a particle size larger than 100 nm. The dashed line in Fig. 1 is the turnover frequency based on NO uptake observed for this unsupported magnetite sample. The stable activity of the Fe_3O_4/Grafoil sample is an order of magnitude lower than that of unsupported magnetite. In fact, the catalytic activity of the Fe_3O_4/Grafoil samples never exceeded that of unsupported magnetite.

Nitric oxide uptakes were determined after different lengths of exposure to reaction conditions for a sample containing 14.9 wt% Fe_3O_4/Grafoil (see Table 2). The uptake measured after 45 h under water–gas shift conditions and that measured after 210 h are similar, indicating that the total surface area is relatively stable once stable activity is obtained. Note that the treatment required for NO adsorptions is essentially a treatment in CO/CO_2 (15/85); therefore, the sample is in the high activity state for all NO uptake measurements.

Mössbauer Spectroscopy

Figure 3 shows room temperature Mössbauer spectra for a sample containing 16.8 wt% Fe_3O_4/Grafoil. This sample was previously used for the kinetics studies shown in Fig. 2 and has been treated in excess of 200 h under reaction conditions. The sample was transferred to a stainless-steel Mössbauer spectroscopy cell and treated for 24 h in CO/CO_2 (15/85) after which spectrum a was collected. Note that all treatments were at 660 K while all spectra were collected at room temperature. The sample was then treated in a reaction mixture containing $CO/CO_2/H_2O$ (32/4/64) for 24 h. The sample was cooled to 370 K and purged with CO/CO_2 (15/85) to avoid condensation of water. It was then cooled to room temperature and spectrum b was collected.

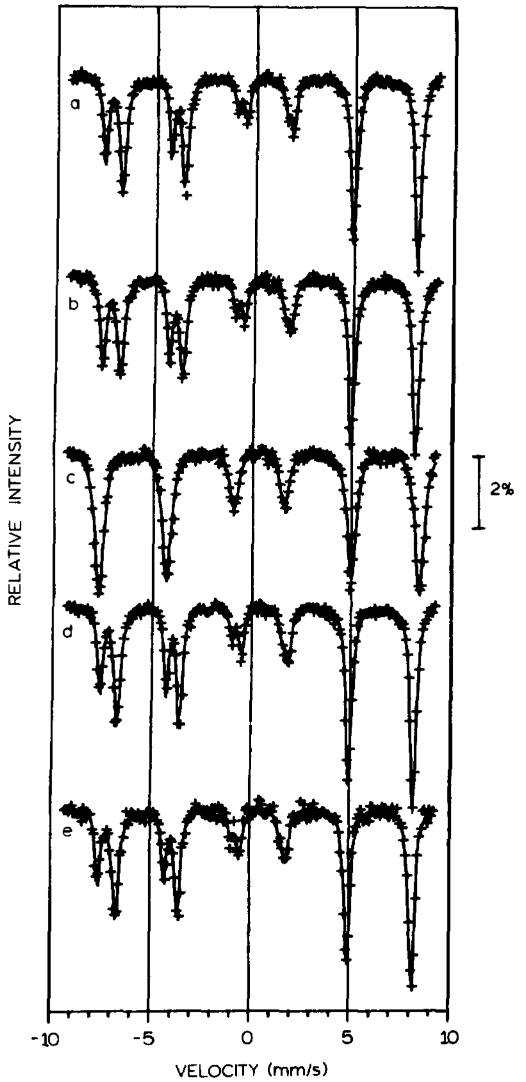

FIG. 3. Room-temperature Mössbauer spectra of a 16.8 wt% Fe_3O_4/Grafoil sample after treatment in various gas mixtures at 660 K. Spectrum a: 24 h in CO/CO_2 (15/85); Spectrum b: 24 h in $CO/CO_2/H_2O$ (32/4/64) at 660 K, followed by 1 min. purge in CO/CO_2 (15/85) at 370 K; Spectrum c: 0.3 h in O_2; Spectrum d: 24 h in H_2/H_2O (80/20); Spectrum e: 24 h in CO/CO_2 (15/85), followed by 24 h in H_2/H_2O (80/20). The vertical bar beside the figure corresponds to a 2% change in γ-ray transmission through the sample.

TABLE 2

Average Magnetite Particle Diameters, $\overline{D}$, from X-Ray Diffraction, Surface Iron Cation Densities Based on the Average Particle Diameters and NO Uptakes for Grafoil-Supported Magnetite Treated for Various Lengths of Time under Reaction Conditions

Sample	Treatment	$\overline{D}$ (nm)	Cation density (μmol/g-cat)	NO uptake (μmol/g-cat)
8.6 wt% Fe_3O_4/Grafoil	5 h, 600 K	15.6	65	—
16.8 wt% Fe_3O_4/Grafoil	>200 h, 660 K	20.0	100	—
14.9 wt% Fe_3O_4/Grafoil	5 h, 600 K	15.9	111	50
	45 h, 660 K	17.4	102	44
	210 h, 660 K	26.1	68	34

Spectrum c was obtained after treatment for 0.3 h in O_2 at 660 K. The result of a subsequent treatment for 24 h in H_2/H_2O (80/20) is seen in spectrum d. Finally, treatment for 24 h in CO/CO_2 (15/85) followed by 24 h in H_2/H_2O (80/20) gave spectrum e.

All of the above spectra, except that for the O_2 treatment, display the characteristic 12-peak spectral pattern of magnetite (*17*). Six peaks arise from ferric cations in tetrahedral sites and six peaks are due to fast electron hopping between ferric and ferrous cations in octahedral sites. The spectrum observed after treatment in oxygen is typical of γ-Fe_2O_3 (17). The Mössbauer parameters of these spectra are given in Table 3. The most important result of these Mössbauer spectroscopy studies is that the Grafoil-supported iron is present as magnetite after the different treatment conditions.

X-Ray Diffraction

Particle size determination by X-ray diffraction was carried out on all samples. The

TABLE 3

Mössbauer Parameters of 16.8 wt% Fe_3O_4/Grafoil Sample and an Unsupported Fe_3O_4 Sample

Corresponding spectrum from Fig. 3	Site[a]	H[b], kOe	δ[c], mm/s	ε[d], mm/s
(a) 24 h in CO/CO_2 (15/85)	A	493	0.270	−0.006
	B	463	0.671	−0.011
(b) 24 h in $CO/CO_2/H_2O$ (32/4/64)	A	493	0.267	−0.002
	B	463	0.666	−0.014
(c) 0.3 h in O_2		502	0.320	−0.006
(d) 24 h in H_2/H_2O (80/20)	A	493	0.275	−0.006
	B	463	0.671	−0.011
(e) 24 h in CO/CO_2 (15/85)	A	493	0.275	−0.009
followed by 24 h in H_2/H_2O (80/20)	B	462	0.671	−0.018
Unsupported Fe_3O_4	A	491	0.273	−0.002
(not in Fig. 3)	B	459	0.661	−0.010

[a] A, Tetrahedral; B, octahedral.

[b] Magnetic hyperfine field, ±1 kOe uncertainty.

[c] Isomer shift, ±0.01 mm/s uncertainty.

[d] Quadrupole shift, ±0.01 mm/s uncertainty.

average particle diameter was determined after various lengths of time under water–gas shift reaction conditions. The results of this study are given in Table 2, from which it can be seen that the particle size increased with time under reaction conditions. More importantly, it should be noted that all particles are in excess of 10 nm in diameter, and are, therefore, too large to display particle size effects normally associated with structure sensitivity.

Electron Microscopy

Samples for TEM and SEM studies were subjected to the same treatments described above. The samples were then exposed to air at room temperature and subsequently transferred to the appropriate electron microscope for study.

Consider first sample characterization by TEM. Following sample preparation via vacuum evaporation of iron onto the cleaved, single crystal graphite surfaces, two samples were treated in flowing CO/CO_2 (15/85) for 24 h at 660 K to convert the iron to magnetite. Subsequent TEM analysis showed the presence of small magnetite particles, approximately 5–10 nm in size. A representative micrograph is shown in Fig. 4a. One of these samples was treated for an additional 24 h in CO/CO_2 (15/85). No change in the average magnetite particle size was apparent. The second sample was treated for 24 h under water–gas shift reaction conditions. As can be seen in Fig. 4b, the magnetite particle size increased under water–gas shift conditions. The majority of the particles are in the size range from 15 to 20 nm. In addition, many of the particles are present as clusters of smaller particles.

The second sample above was subsequently treated for 24 h in flowing CO/CO_2 (15/85). No changes in magnetite particle size or morphology could be observed. Several areas of the sample were analyzed and located so that these same areas could be identified after further sample treatments. One of these areas is shown in Fig. 5a. The sample was then treated under water–gas shift reaction conditions for 24 h and transferred to the electron microscope. The specific areas of the sample which had been identified prior to this treatment were then analyzed by TEM after treatment under water–gas reaction conditions. For comparison, Fig. 5b shows the same field of view as that of Fig. 5a. The magnetite particle sizes and shapes appear to be essentially the same in both figures, although there is some evidence for particle mobility.

While the samples used for TEM studies were in the form of thin graphite films, Fe_3O_4/Grafoil samples could be studied by SEM without special preparation. The sample used for the SEM studies was the 16.8 wt% Fe_3O_4/Grafoil sample which had been used in the kinetic studies of Fig. 2. This sample had been treated in excess of 200 h under reaction conditions. The final treatment consisted of CO/CO_2 (15/85) for 0.5 h at 660 K. Subsequent SEM analysis indicated the presence of large particles (ca. 5 μm), as seen in Fig. 6a. Energy dispersive X-ray analysis confirmed that these particles were iron based. Higher magnification revealed that these large particles were composed of clusters of particles ca. 100 nm in size (see Fig. 6b). The clusters observed on the Fe_3O_4/Grafoil samples were much larger than those observed on cleaved, single crystal samples; however, it should be remembered that the samples were prepared by different techniques.

A sample of unsupported magnetite was prepared for SEM study by pressing the powdered magnetite onto two-sided tape. A thin layer of gold (<10 nm) was evaporated onto this sample to increase the conductance and improve the contrast. The unsupported magnetite particles were seen to be quite large (ca. 50 μm). Higher magnification again revealed that the large particles were composed of clusters of particles ca. 250 nm in size. The individual particles observed for unsupported Fe_3O_4 appeared, however, to be larger, more spherical, and less tightly packed than those of Grafoil-

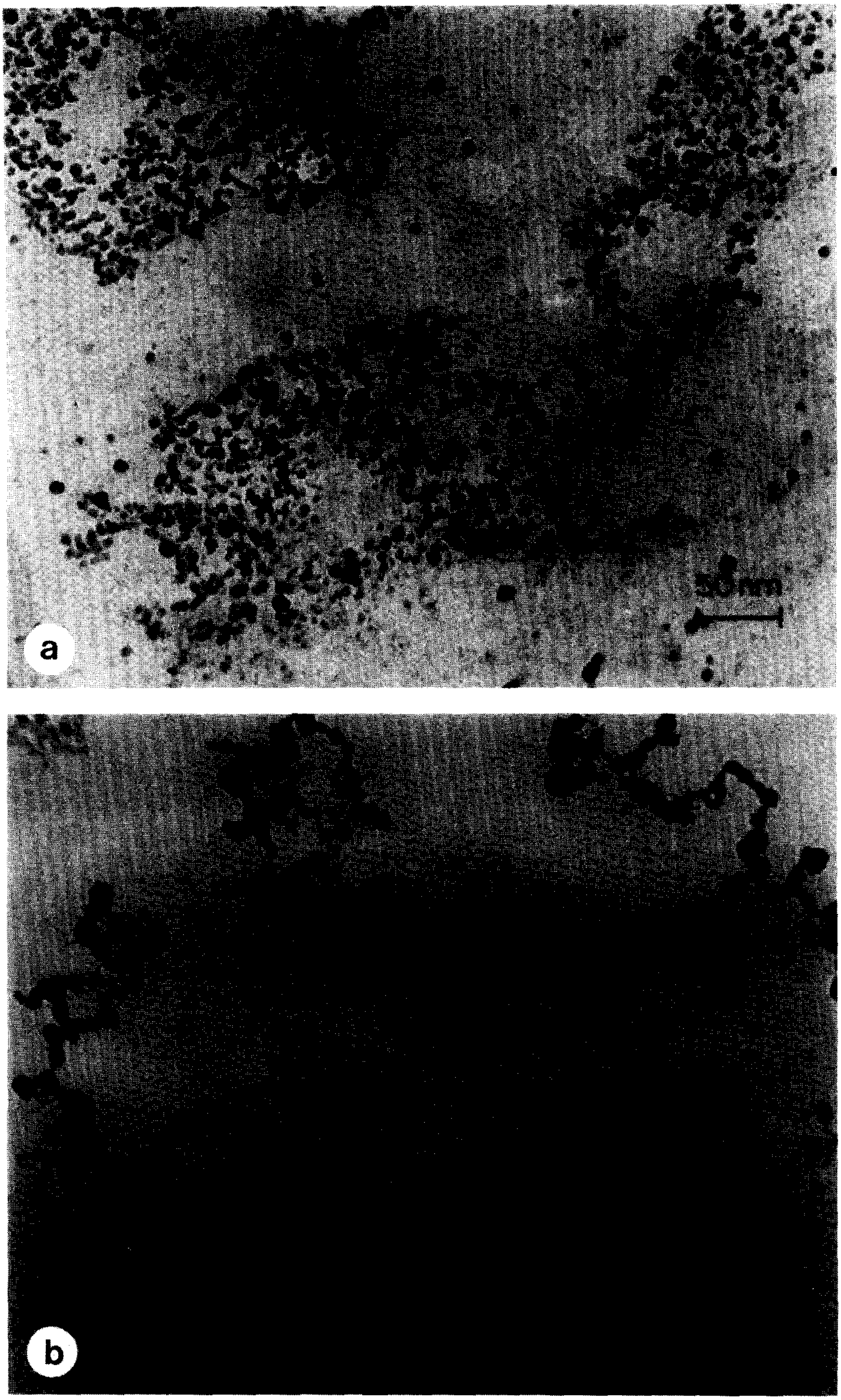

FIG. 4. Transmission electron micrographs of Fe_3O_4 particles on cleaved, single crystal graphite: (a) treated 24 h in CO/CO_2 (15/85) at 660 K; (b) treated 24 h in CO/CO_2 (15/85), followed by 24 h in $CO/CO_2/H_2O$ (32/4/64) at 660 K.

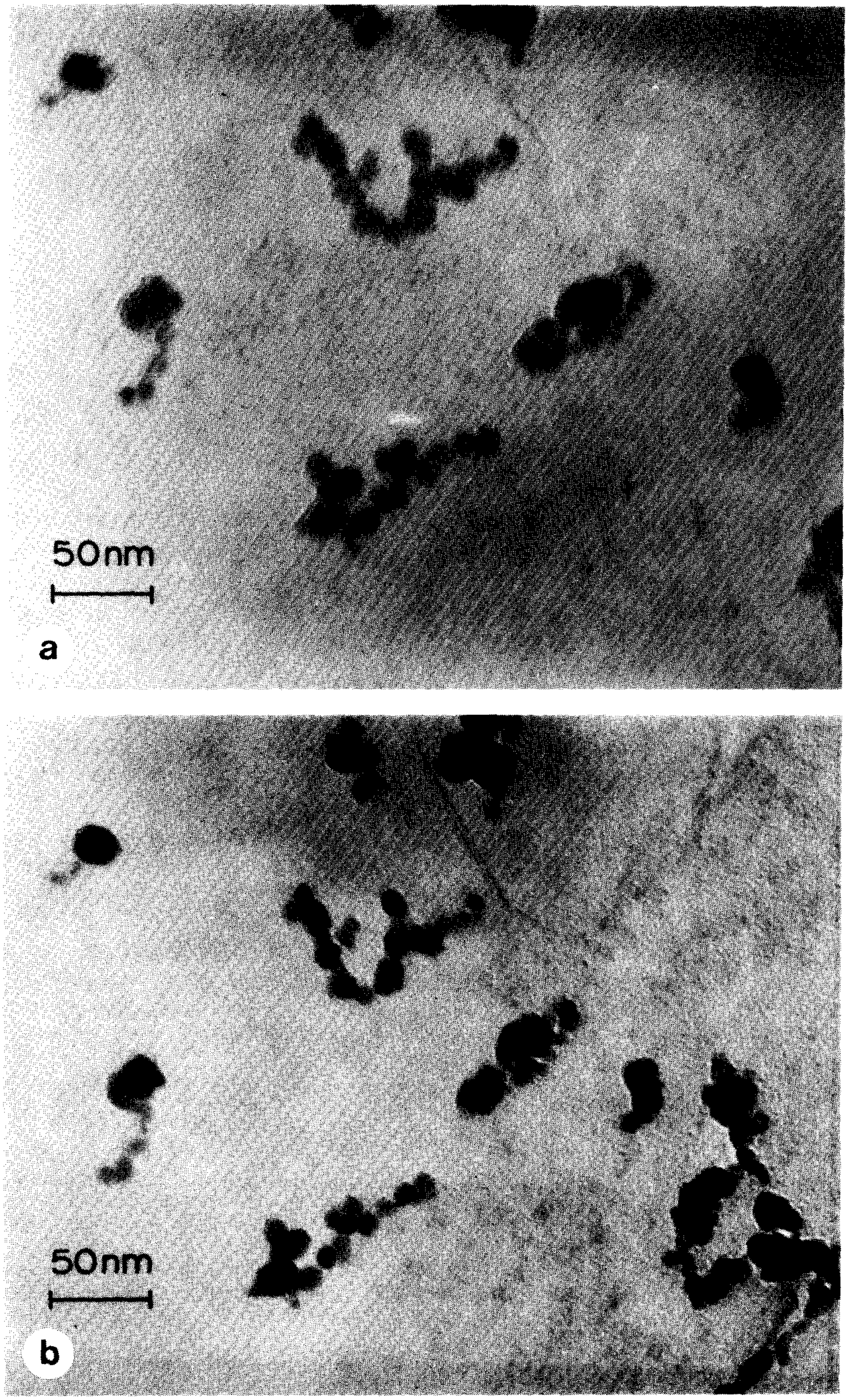

FIG. 5. Transmission electron micrographs of Fe_3O_4 particles on cleaved, single crystal graphite. (a) Same sample as Fig. 4b, treated an additional 24 h in CO/CO_2 (15/85) at 660 K; (b) same field of view after an additional 24 h in $CO/CO_2/H_2O$ (32/4/64) at 660 K.

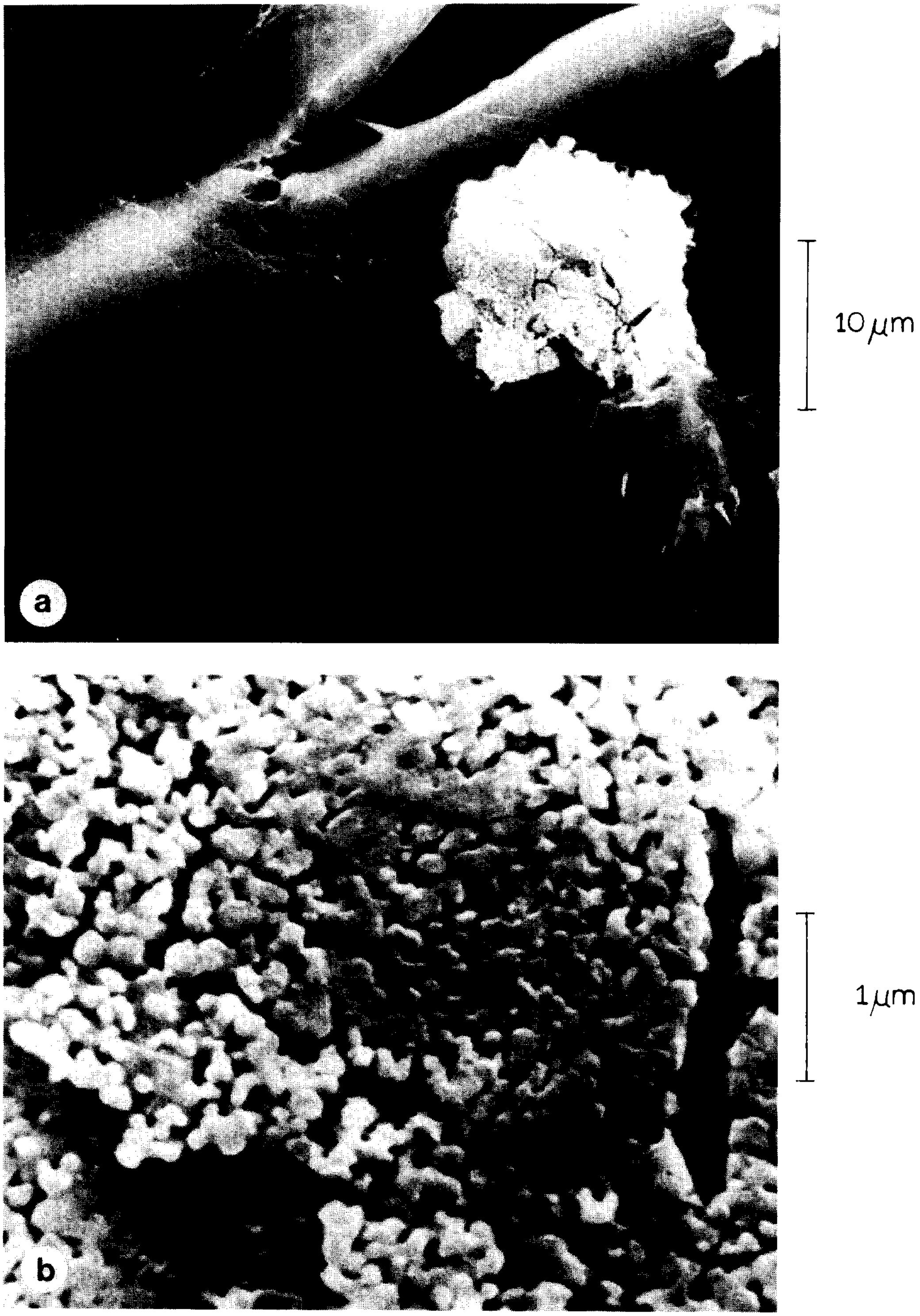

FIG. 6. Scanning electron micrographs of a 16.8 wt% Fe_3O_4/Grafoil sample which had undergone >200 h in $CO/CO_2/H_2O$ (32/4/64) at 660 K. (a) Magnification 2000×; (b) magnification 20,000×.

supported Fe_3O_4. The important conclusions from the TEM and SEM studies are that the large particles are aggregates of smaller particles, and that individual particles of supported magnetite are less than half the size of those for unsupported magnetite.

DISCUSSION

Particle Size Growth

One of the conclusions of the present study is that the size of magnetite particles supported on Grafoil or graphite is dependent on the treatment of the sample. Most notable is the growth of the magnetite particles when the sample is first exposed to water-containing gases at 660 K. For example, after a stable magnetite particle size has been reached following treatment in CO/CO_2 (15/85), a significant growth of these particles takes place when the sample is exposed to water–gas shift reaction conditions. This behavior is also manifested by a loss of catalytic activity when the sample is first used as a catalyst for water–gas shift. The water–gas shift kinetic measurements, X-ray diffraction, NO uptakes, and electron microscopy studies also suggest, however, that a relatively stable magnetite particle size is ultimately reached after prolonged (ca. 24 h) exposure to these water-containing gas atmospheres.

The mechanism for the water-induced growth of magnetite particles on Grafoil or graphite appears to be the migration of magnetite particles over the support. Evidence for this statement is the observation by TEM of clusters of magnetite particles, which have not coalesced into a single larger particle, after treatment of Fe_3O_4/Grafoil under atmospheric pressure, water-gas shift reaction conditions (see Fig. 4b).

The following general model is proposed to describe the particle size growth of magnetite on Grafoil or graphite. The initial treatment in CO/CO_2 produces a large number of small magnetite particles (e.g., 5–10 nm in size for the Grafoil-supported samples). These particles are in close proximity. During subsequent treatment in water-containing gases, these small particles become mobile and form clusters of particles. As this process continues, the clusters become larger and the distance between clusters increases. Furthermore, the mobility of magnetite may decrease as the magnetite particle size increases. These effects explain why the magnetite particle size reaches a relatively constant value after prolonged treatments under water–gas shift reaction conditions. The origin of the increase in the mobility of magnetite on Grafoil or graphite in water-containing gases may be due to hydroxylation (or hydration) of the magnetite surface, thereby weaken the bonding between magnetite and the carbon support. This type of behavior has been suggested to explain the effect of water on the interactions between iron and silica (*18*).

Water–Gas Shift Activity, General Features

The results of the water–gas shift kinetic studies indicated that the catalytic activity of Fe_3O_4/Grafoil could be altered by various treatments. Mössbauer spectroscopy studies of the Fe_3O_4/Grafoil samples showed that the iron was present as magnetite under water–gas shift reaction conditions, after treatment in CO/CO_2, and after treatment in H_2/H_2O. Furthermore, the transmission electron microscopy studies showed that the size and shape of the magnetite particles were essentially constant after the initial changes which take place when the sample is first exposed to water–gas shift reaction conditions.

A model is discussed below to interpret the changes in water–gas shift activity which were observed in the present study. Of importance are the observations that (i) the magnetite particles for the Fe_3O_4/Grafoil samples, for which the water–gas shift activity could be altered by different treatments, were present as clusters of particles on graphite, and (ii) the Grafoil-supported samples exhibit a stable activity which is an order of magnitude lower than unsupported magnetite. The presence of magnetite clusters in the present study is in agreement with the previous study of Amelse *et al.* (*19*) for iron oxide particles.

It is now suggested that the magnetite surface area contained within the pores of these clusters is accessible to reactant gases after the sample has been pretreated in CO/CO_2 (15/85). The catalytic activity of the sample is therefore comparable to that of unsupported magnetite. Under water–gas shift reaction conditions, the pores become constricted, perhaps due to a change in the structure or phase of the surface. The catalytic activity of the sample decreases accordingly. In contrast to the behavior of Grafoil-supported magnetite, unsupported magnetite is present as larger particles with correspondingly larger pores. These pores are not as susceptible to constriction by a change in the surface of magnetite, and thus unsupported magnetite is not sensitive to the effects of treatments which altered the catalytic activity of Fe_3/O_4/Grafoil.

Surface phases differing from the bulk have been reported by others for iron catalysts. As mentioned above, the surface of an iron carbide catalyst for Fischer–Tropsch synthesis has been suggested to be an iron oxide (*2*). Similarly, the surface of a metallic iron catalyst for ammonia synthesis has been described in terms of a surface nitride phase (*20, 21*). Indeed, Kubsh *et al.* (*16*) have reported that the surface stoichiometry of a magnetite sample may be altered by variations in the gas phase while the bulk phase remains unchanged.

In order to explain the effects of treatments in CO/CO_2, H_2/H_2O, and water–gas shift reaction conditions, it is necessary to discuss the nature of the surface change which is responsible for changing the sizes of the pores in the clusters of magnetite particles. The slow deposition of graphitic carbon on the surface cannot be the cause of these effects, since as mentioned above graphite cannot be removed by treatment in the CO/CO_2 gas mixtures used in the present study (*15*). In addition, a change in the oxidation state of the surface is not responsible for these effects, since the thermodynamic activity of oxygen is similar in the CO/CO_2 (15/85) and H_2/H_2O (80/20) gas mixtures while only the first of these treatments activated the sample for water–gas shift. Instead, it is suggested that a surface hydroxide phase may be formed during treatment of magnetite under water–gas shift reaction conditions or in H_2/H_2O. The bulk density of iron hydroxide is lower than that of magnetite, suggesting that the formation of iron hydroxide would result in an expansion of the surface, thereby constricting the small pores present in the clusters of magnetite particles. This would explain why treatments in dry gases such as CO/CO_2 or helium lead to increases in catalytic activity of Fe_3O_4/Grafoil, while treatments in water-containing gases such as H_2/H_2O or synthesis gas cause catalyst deactivation. This simple idea also explains the observation that a catalyst treated in a H_2/H_2O mixture having a lower partial pressure of H_2O is more active than a sample treated at a higher pressure of water.

One experimental observation of the present study cannot be explained by the above model: activation of Fe_3O_4/Grafoil samples by treatment in O_2 followed by H_2/H_2O (see Point c in Fig. 4). This treatment, however, is more complicated than the treatments in CO/CO_2 or H_2/H_2O alone, since the treatment in O_2 oxidizes Fe_3O_4 to γ-Fe_2O_3. We have no adequate explanation for this behavior at this time.

SUMMARY

Magnetite particles supported on graphitic supports have been shown to become mobile under water–gas shift reaction conditions. Large clusters of smaller magnetite particles are thereby formed. A significant fraction of the magnetite surface area is therefore contained within the pore structure of these clusters of particles. Under water–gas shift reaction conditions, these pores become constricted, resulting in a decrease in catalytic activity. A similar decrease in activity results from treatment of the catalyst in H_2/H_2O gas mixtures. Accessibility to the magnetite surface area within these pores can be increased, and the catalytic activity correspondingly increased, by treatments in CO/CO_2 or helium. These results are explained by the reversible formation of an iron hydroxide surface phase on magnetite in water-containing gas atmospheres.

In general, it may be anticipated that a variety of oxide catalysts may be composed of large clusters of smaller oxide particles. The surface areas of oxide catalysts are normally measured under water-free conditions, such as by BET or chemisorption methods. However, the accessible surface area for these samples under reaction conditions may be considerably smaller than the total surface area, especially for reactions carried out in the presence of water.

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