JOURNAL OF CATALYSIS **143**, 510–519 (1993)

Agglomeration and Phase Transition of a Nanophase Iron Oxide Catalyst

ZHEN FENG, J. ZHAO, F. E. HUGGINS, AND G. P. HUFFMAN[1]

Consortium for Fossil Fuel Liquefaction Science, 233 Mining and Mineral Resources Building, University of Kentucky, Lexington, Kentucky 40506

Received February 19, 1993; revised May 10, 1993

The agglomeration and phase transition behavior of a nanophase iron oxyhydroxide catalyst with a mean particle diameter of ~30 Å was examined using thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and Mössbauer spectroscopy. Unlike other FeOOH phases, which decompose to Fe_2O_3 at $T < 300°C$, there is no obvious phase transition between room temperature and 900°C for the 30-Å catalyst. After annealing in air for 24 h from 250 to 350°C, only part of the 30-Å catalyst sample is converted to larger α-Fe_2O_3 particles ($d > 100$ Å). Both the relative fraction and average particle size of the α-Fe_2O_3 phase increase with annealing temperature. The phase transition rate is dependent on the moisture content of the catalyst surface. After identical annealing at 250°C for 24 h in air, the as-received sample consists of 65% 30-Å phase and 34% α-Fe_2O_3 phase, whereas the sample exposed to air for 5 days before annealing consists of 26% 30-Å phase and 73% α-Fe_2O_3 phase. The results indicate that due to moist-air exposure, the catalyst particles become linked by water molecules adsorbed at the surface coordination unsaturated (CUS) sites. At elevated temperatures, these water molecules are evolved from the particle linkages, facilitating both agglomeration of the 30-Å particles and the phase transition to α-Fe_3O_3.

I. INTRODUCTION

In recent years, there has been renewed interest in iron-based catalysts for conversion of coal to liquid fuel via direct coal liquefaction (DCL) (*1–7*). Efforts have been made to produce highly dispersed iron catalysts in order to increase surface area and minimize catalyst loading. Improved dispersion and DCL conversion rates have been obtained by sulfating the iron oxide catalyst surface (Fe_2O_3/SO_4^{-2}) and by doping small amounts of other elements to the catalysts ($Mo/Fe_2O_3/SO_4^{-2}$, $W/Fe_2O_3/SO_4^{-2}$) (*4, 5*). The sulfate group (SO_4^{-2}) promotes the formation of Lewis acid and base sites or coordination unsaturated (CUS) sites at the catalyst surface and thus increases the acidity of the catalysts (*4, 8*). It has been suggested that an acidic surface may prevent agglomeration of the fine particles during calcination and reaction (*4*).

More recently, a number of investigators (*7, 9, 10*) have studied the properties of a new iron oxide catalyst (NANOCAT) manufactured by Mach I, Inc. The catalyst is highly dispersed, with an average particle diameter of 30 Å (described as 30-Å catalyst in the following). The structure of the 30-Å catalyst, as reported in the preceding paper (*9*), is identified as oxyhydroxide (FeOOH). A considerable amount of surface iron ions were found to be at coordination unsaturated (CUS) sites. The DCL activity of the 30-Å catalyst is sensitive to the surface condition. Lower DCL conversion is reported for the catalyst if it is exposed in moist air before reaction (*10*). Similar results have been obtained for the Fe_2O_3/SO_4^{-2} catalyst (*4*).

The structure of the 30-Å catalyst appears to be similar to an amorphous FeOOH cata-

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

lyst (*11*) and ferrihydrite (*12*), as reported in the preceding paper (*9*). The amorphous FeOOH catalyst has been shown to be very active and selective in the oxidative dehydrogenation of butene. Ferrihydrite is a naturally occurring oxide that has been studied extensively by mineralogists. It is a precursor to formation of α-FeOOH and α-Fe_2O_3, and the transformation to α-FeOOH and α-Fe_2O_3 can take place even at ambient temperatures in the presence of water (*12*). The mechanisms are still unclear.

In this work, the agglomeration and phase transformation of the 30-Å catalyst at high temperature have been investigated by means of transmission electron microscopy (TEM), Mössbauer spectroscopy, and thermogravimetric analysis (TGA). The results demonstrate the effect of the surface structure and surface conditions on particle agglomeration and phase transition of the catalyst system.

II. EXPERIMENTAL

The 30-Å catalyst is a free flowing powder with a reddish-brown color. According to the manufacturer, the sample can absorb as much as 15% by weight of water after a long period of exposure to air. Our test showed that after 5 days exposure to air, the sample gains 5% in weight. However, it can be reactivated by heating the sample in vacuum at 150°C for 3 h, as recommended by the manufacturer. The sample was shipped to us in a sealed can and was repacked in N_2 upon opening to avoid air exposure. In addition to the as-received sample, several samples were prepared by annealing the 30-Å catalyst in air for 24 h at temperatures from 250 to 500°C. To observe the effect of moisture, a sample from the same as-received batch was first exposed in air for 5 days at room temperature, and subsequently annealed at 250°C in air for 24 h.

Samples for TEM measurements were prepared by suspending the catalysts in ethyl alcohol (weight ratio of alcohol to sample ~1000), to form a slightly turbid suspension. This suspension was constantly agitated in an ultrasonic bath for about an hour. A drop of the well-mixed suspension was carefully placed with a syringe on a thin carbon formvar film (Ted Pella, Inc., Redding, CA) predeposited on 200-mesh copper grids. The specimen was placed in a STEM sample holder after the alcohol had evaporated, leaving the particles on the grid.

Transmission electron micrographs and microdiffraction patterns were obtained using a Hitachi H800 NA STEM system. The operating voltage was set at 200 kV. Several micrographs from different locations on the grid were taken at magnifications ranging from 50 to 200 K.

Mössbauer spectra were recorded with a constant acceleration spectrometer. The radioactive source consists of ~50 mCi of ^{57}Co in Pd matrix. Because of the small particle sizes, the Mössbauer spectra exhibit significant superparamagnetic relaxation effects (*13*). Therefore, in order to observe the magnetic hyperfine splitting, all spectra were recorded from samples at 10 K using an Air Products displex cryogenic system.

Thermogravimetric analysis (TGA) was performed with a Seiko 320 TGA/DSC system. The heating rate was set at 10°C/min from 30 to 200°C, 4°C/min from 200 to 300°C, and 10°C/min from 300 to 900°C for the 30-Å catalyst and a bulk α-FeOOH. The TGA measurement on the 30-Å catalyst was also carried out at a heating rate four-times slower.

III. RESULTS

Effect of Annealing

TGA results for the as-received 30-Å catalyst and α-FeOOH are shown in Fig. 1. At temperatures below 300°C, crystalline α-FeOOH normally converts to α-Fe_2O_3 by releasing H_2O,

$$2\text{FeOOH} \Rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}\uparrow, \qquad (1)$$

resulting in an 11% weight loss. For α-FeOOH, the phase transition occurs fairly sharply between 200 and 270°C, as shown in the figure. For the 30-Å catalyst, although an approximately 12% weight loss was ob-

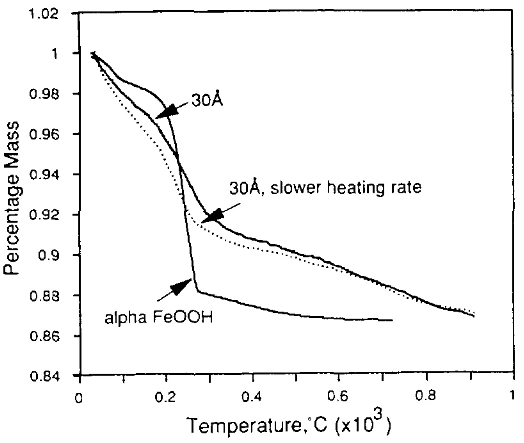

FIG. 1. Thermogravimetric analysis for α-FeOOH and the 30-Å catalyst.

served at 900°C, indicating that the above reaction does occur, no obvious phase change was observed at temperatures up to 900°C. Figure 1 also shows that the phase transition rate for the 30-Å catalyst is heating-rate dependent.

Examples of the morphologies of the samples after annealing are shown in the electron micrographs (Fig. 2). After annealing at 250°C for 24 h, a small fraction of larger particles with an average diameter of ~150 Å were formed (Fig. 2a). The relative fraction and average particle size of the larger particles increase with annealing temperature, as shown in Fig. 2. However, a considerable percentage of 30-Å particles remain even after 24 h annealing at temperatures up to 350°C. It should be noted that at this temperature, bulk α-FeOOH has been completely converted to α-Fe_2O_3. At annealing temperatures of 400°C and higher, larger particles dominate and the particle size becomes uniform. No trace of small 30-Å particles is seen after annealing at 500°C.

An electron microdiffraction spot pattern of the larger particles formed after annealing is shown in Fig. 3. The pattern exhibits hexagonal symmetry with lattice constants a = b = 5.03 Å and c = 13.75 Å and is identified as α-Fe_2O_3 (*14*). The pattern also indicates that the particle is aligned at {201} orientation. The extra spot near the center of the pattern is probably due to a neighboring grain. The average size of the large α-Fe_2O_3 particles as a function of annealing temperature is plotted in Fig. 4.

The phase change and particle growth that occurs as a result of increased annealing temperatures is also indicated by the color of the samples. The color of the 250°C annealed sample is quite close to that of the as-received sample, although small orange-colored grains can be discerned. As the annealing temperature increases, the sample color gradually changes from reddish-brown to orange, which is typical for larger α-Fe_2O_3 particles (*12*).

The shape of the TGA curve for the 30-Å catalyst (Fig. 1) appears to be typical for amorphous phases. In Ref. (*11*), a similar TGA curve was observed, leading to the identification of an "FeOOH amorphous" phase, since the phase transition of an amorphous material occurs gradually and continuously as temperature increases. If the 30-Å catalyst were "amorphous," at intermediate temperatures, the catalyst would be in a transitional state which is different from either the 30-Å catalyst or α-Fe_2O_3. However, electron micrographs and microdiffraction for the samples annealed at temperature below 400°C (Figs. 2 and 3) clearly show the presence of two phases, the 30-Å phase and α-Fe_2O_3 phase, indicating that some of the 30-Å catalyst particles have converted to larger particle α-Fe_2O_3, while others remain unchanged. It is worth noting that the XRD pattern of the "FeOOH amorphous catalyst" taken at 300°C (Fig. 1, Ref. (*11*)) also reveals the presence of two phases, α-Fe_2O_3 and the "FeOOH amorphous" phase.

The percentages of the two iron oxide phases in the samples annealed at 250°C were determined by Mössbauer spectroscopy. The spectra collected at 10 K for the as-received and the 250°C annealed sample are shown in Figs. 5a and 5b, respectively. The Mössbauer parameters and percentages of the iron phase determined by least-

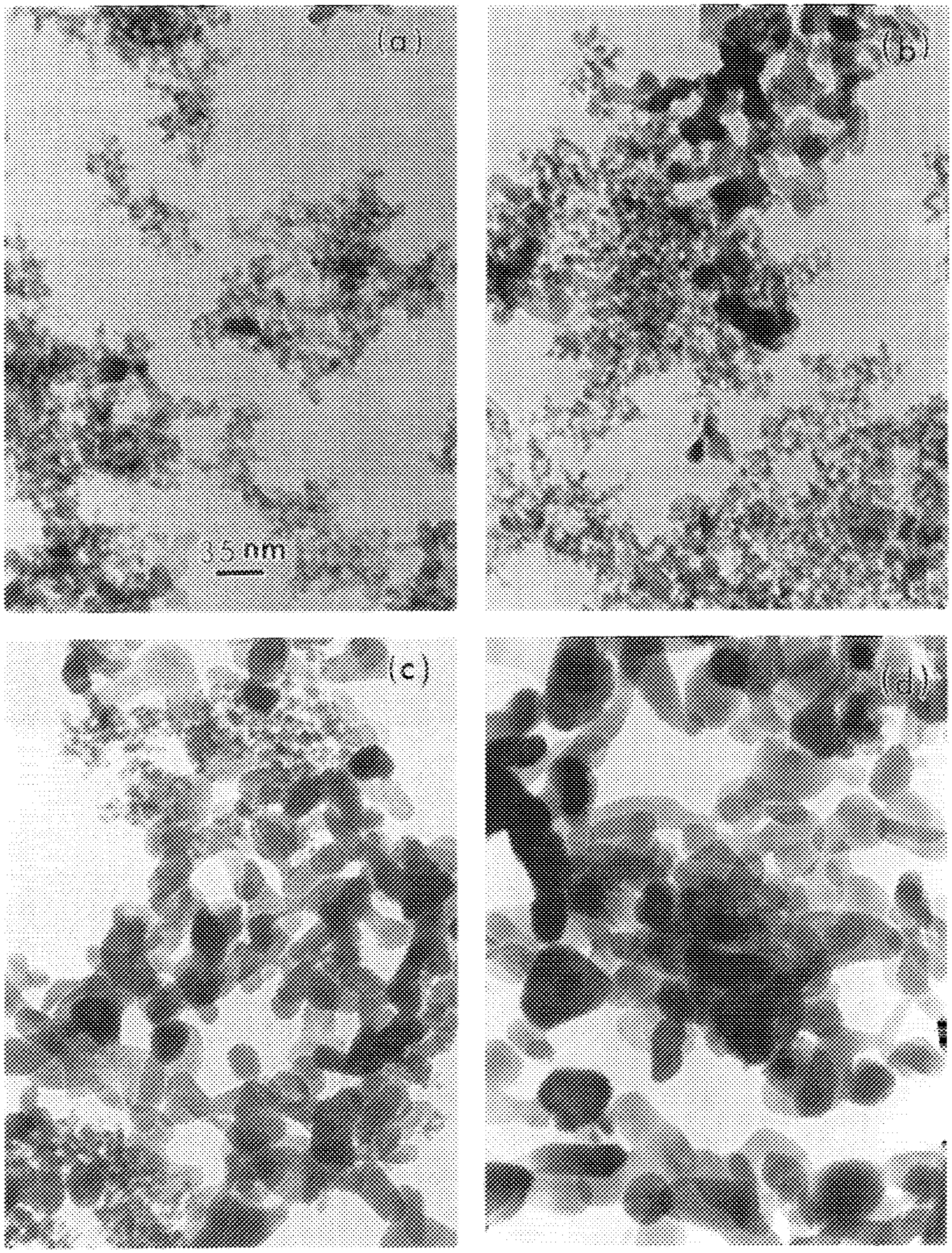

FIG. 2. Bright field electron micrographs for the samples annealed at (a) 250, (b) 300, (c) 350, and (d) 400°C in air for 24 h.

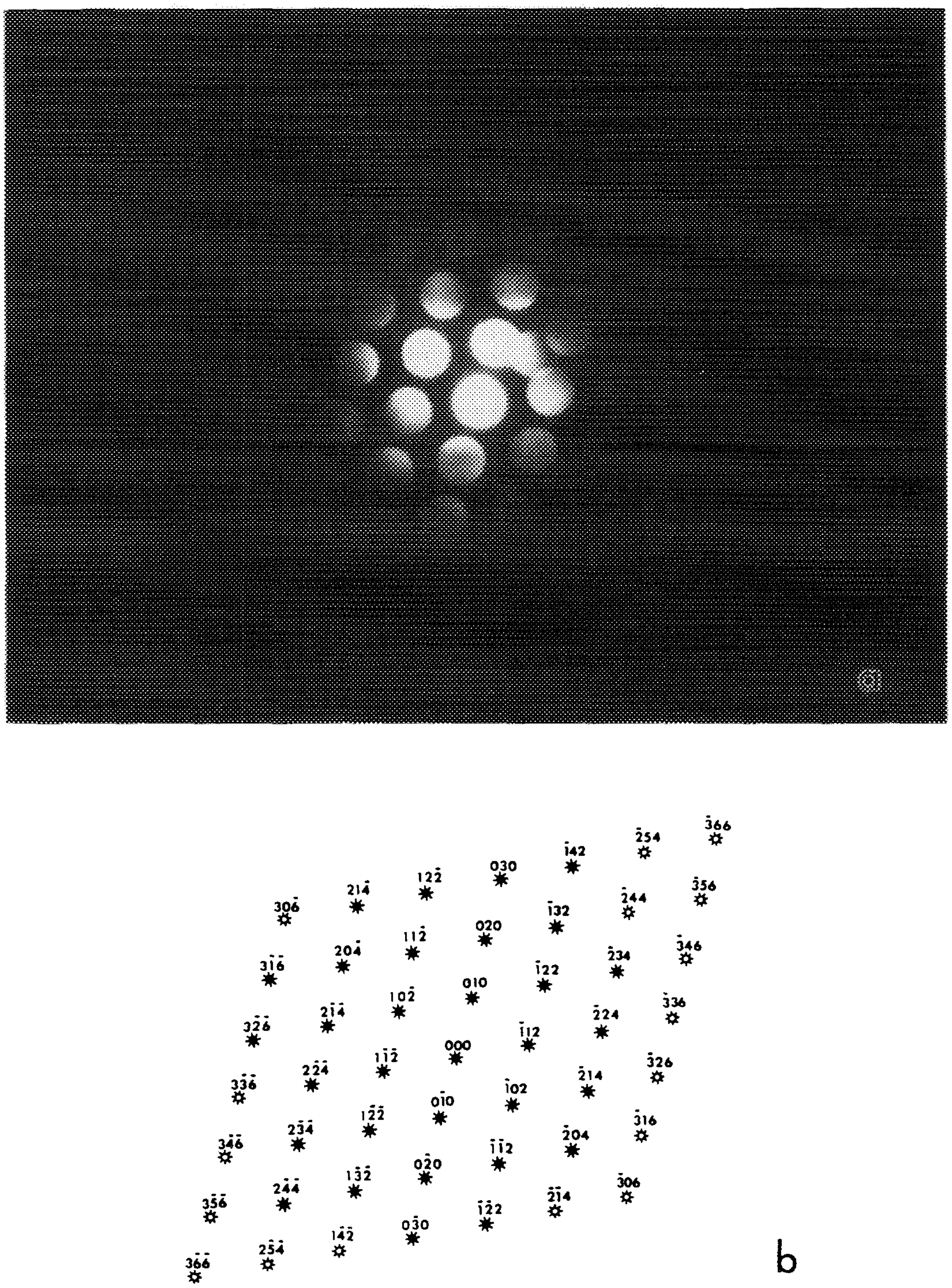

FIG. 3. (a) Spot diffraction pattern for the 500°C annealed sample. (b) The corresponding diffraction pattern for the [201] orientation for α-Fe_2O_3 (observed reflections are indicated by ✱ and the calculated reflections are indicated by ✡).

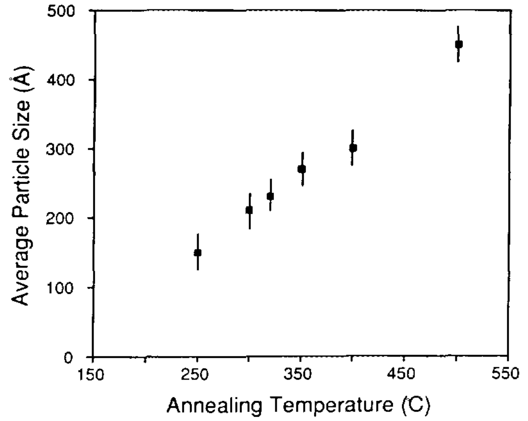

FIG. 4. Average particle size of the α-Fe$_2$O$_3$ phase as a function of annealing temperature.

squares analysis are listed in Table 1. The spectrum for the 30-Å catalyst shows broad absorption peaks, indicating a distribution of magnetic fields which may arise from the different environments for the bulk and the surface iron atoms (*12*, *13*). The spectrum is fitted with three six-line magnetic hyperfine components. The spectrum for the annealed sample shows two phases: one is the 30-Å phase and the other one, with larger magnetic hyperfine field ($H \sim 538$ kOe) and sharp peaks (width ~0.3 mm/s), is characteristic of α-Fe$_2$O$_3$. The spectrum derived from the 30-Å phase is fitted with one or two broadened (width ~0.6 mm/s) six-line magnetic hyperfine components. After 250°C annealing, the as-received sample consists of 65% 30-Å phase and 34% α-Fe$_2$O$_3$ phase (see Table 1).

Effect of H$_2$O Molecules Adsorbed on the Particle Surface

To examine the effect of moisture on the conversion of 30-Å catalyst phase to Fe$_2$O$_3$, the as-received 30-Å sample was first exposed in air at room temperature for 5 days and subsequently annealed at 250°C in air for 24 h. In contrast to the electron micrograph for the as-received sample annealed at identical conditions (Fig. 2a), the moist-air-exposed sample consists mostly of larger particles with a size of ~150 Å (Fig. 6). The larger particles are α-Fe$_2$O$_3$ as indicated by electron microdiffraction. The sample color becomes uniformly orange, consistent with the dominant larger particle α-Fe$_2$O$_3$ phase. A similar electron micrograph was also obtained from a wet sample prepared by adding several drops of water to the 30-Å catalyst sample and then annealing at 250°C for 24 h in air.

The Mössbauer spectrum of the moist air exposed sample after annealing is shown in Fig. 5c and the Mössbauer parameters obtained by least squares fitting are listed in Table 1. As a result of moist-air exposure, the percentage of α-Fe$_2$O$_3$ phase in the sample has increased to 73%, whereas the 30-Å phase decreased to 26%. Therefore, the presence of water molecules on the sample surface accelerates the phase transformation.

IV. DISCUSSION

In the preceding paper (*9*), an XAFS investigation of the 30-Å catalyst indicated that, although the structure of the bulk part of the sample is similar to FeOOH, in which iron ions are coordinated by six oxygen or hydroxyl group neighbors, a considerable fraction of iron ions at the catalyst surfaces are at sites with lower coordination. After a long period (>5 days) air exposure, the coordination number of the surface iron ions is increased. These conclusions were reached on the basis of changes observed in the pre-edge (1*s*–3*d*) peak of the *K*-edge XANES (*9*). The increase in coordination number is attributed to H$_2$O molecules adsorbed at the surface coordination unsaturated (CUS) sites. These CUS sites are also known as Lewis acid sites formed by surface dehydroxylation (*15*, *16*).

The phase transition behavior of the 30-Å catalyst appears to be governed not only by temperature but also by the surface structure and surface conditions. A dehydroxylated surface layer with CUS sites apparently prevents not only the agglomeration of the 30-Å catalyst particles,

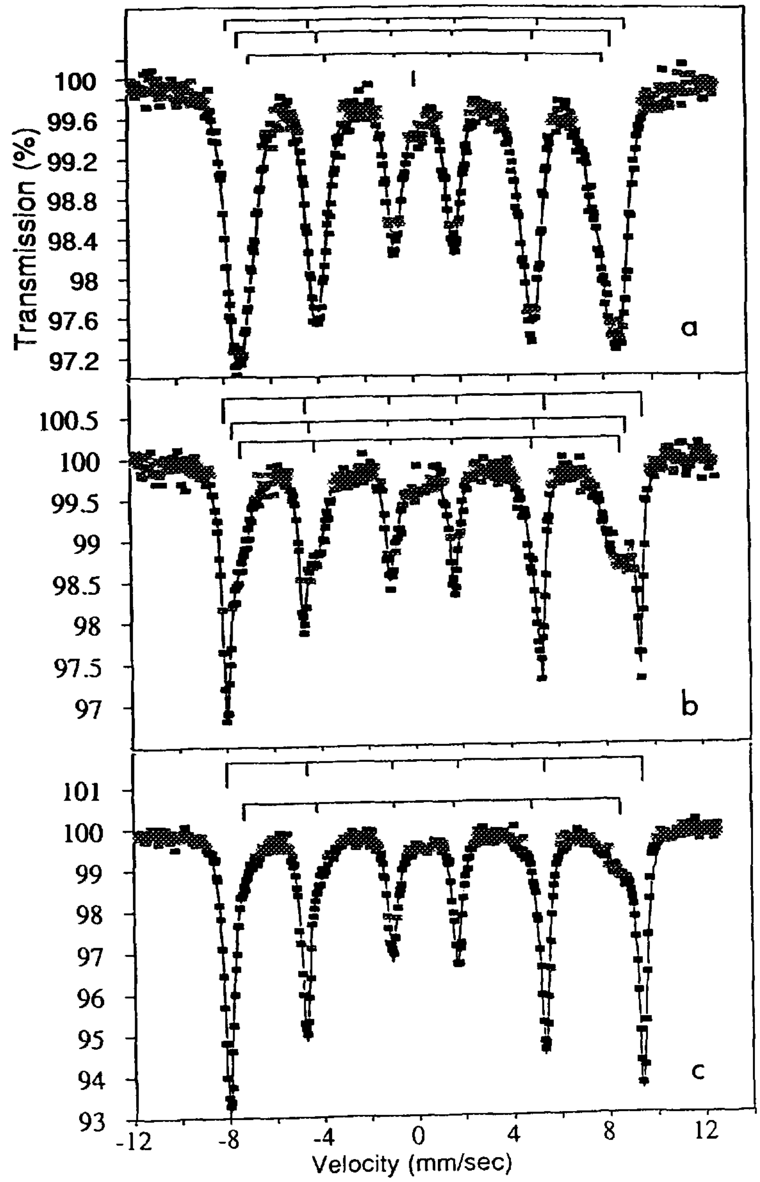

FIG. 5. Mössbauer spectra recorded at 10 K for (a) the 30-Å catalyst; (b) the 30-Å catalyst, after annealing at 250°C for 24 h; (c) the moisture-exposed 30-Å catalyst, after annealing at the same conditions.

but also inhibits dehydroxylation in the catalyst. The complete phase transition to α-Fe_2O_3 only happens at much higher temperatures (>400°C) and after prolonged annealing times. However, after the sample is exposed to moist air, the particles become linked by adsorbed water molecules and form a particle cluster. At elevated temperatures, these water molecules are readily evolved from the particle linkages, leading to agglomeration of the small particles. It appears, too, as a result of formation of

TABLE 1

Mössbauer Parameters of Three Samples at 10 K

Samples	I.S. (mm/s)	Q.S. (mm/s)	*H* (k Gauss)	Phase	Area (%)
As-received 30-Å	0.52	0.05	507		44
	0.50	0.02	477		38
	0.46	−0.02	441		18
As-received, 250°C 24 h	0.49	0.20	540	α-Fe_2O_3	34
	0.46	−0.02	514	30-Å	36
	0.43	0.05	479	30-Å	27
Moist, 250°C, 24 h	0.48	0.20	538	α-Fe_2O_3	73
	0.41	−0.10	495	30-Å	26

large particles, dehydroxylation of the bulk must occur much more readily than for isolated 30-Å particles. A scheme for this process is shown in Fig. 7. At temperatures below 350°C, the transition rate for the 30-Å catalyst is determined by the coverage of the water molecules adsorbed on the particle surface and temperature; the coverage of water molecules determines the percentage of the particles linked by water molecules whereas temperature determines the rate of dehydroxylation. Even at room temperature, transition to α-Fe_2O_3 does take place, albeit at very slow rate, as reported for ferrihydrite (*12*). For the 30-Å catalyst, we observed larger α-Fe_2O_3 particles in a sample stored in a sealed can for over six months. At temperatures

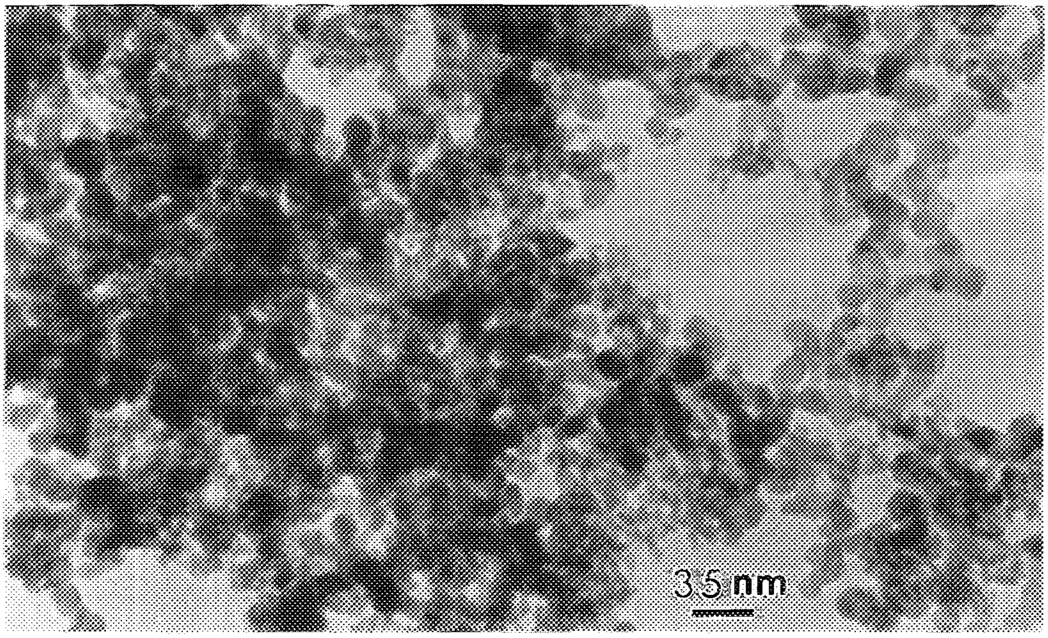

FIG. 6. Electron micrograph for the moisture-exposed 30-Å catalyst, annealed at 250°C for 24 h. Contrast with Fig. 2a.

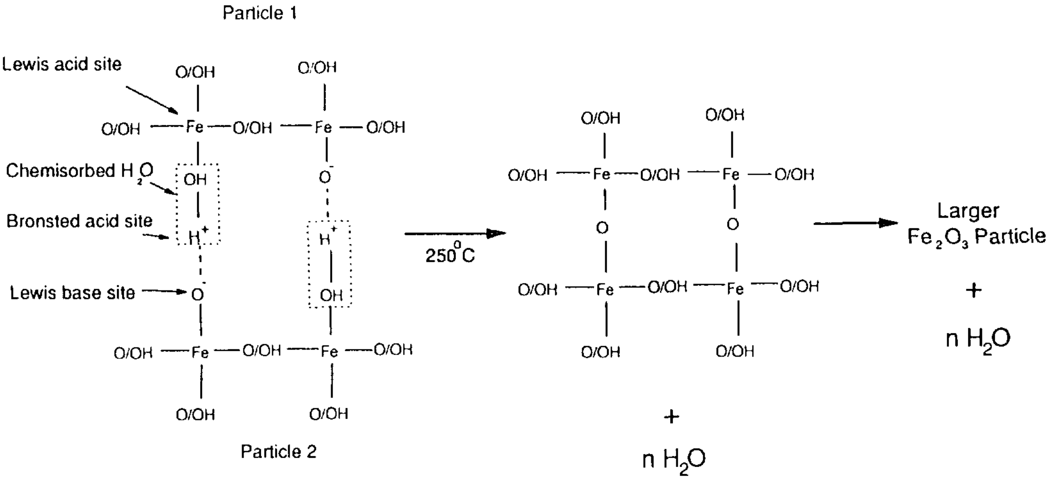

FIG. 7. Proposed scheme for the agglomeration and phase transition of the 30-Å catalyst.

above 350°C, the phase transition rate is most likely due to the dehydroxylation inside of the particle. It should be noted that only those H_2O molecules adsorbed at the CUS sites may remain on the particle surface at $T > 250°C$ or higher. Since their bonding to the particle surface is much weaker, physisorbed H_2O molecules will be detached at temperatures well below 250°C.

A novel feature of this model is the relationship that has to be inferred to exist between the particle size, surface structure, and the phase-transition mechanism. It appears that a dehydroxylated surface with CUS sites can effectively inhibit the phase transition to α-Fe_2O_3. However, once the surface is covered by chemisorbed water molecules, the phase transition to α-Fe_2O_3 can take place at very low temperatures. For direct coal liquefaction, an α-Fe_2O_3 phase with reduced surface area has shown to result in lower conversion rate (*4*). Therefore, pretreatment to remove the adsorbed water molecules, as suggested by the manufacturer, is necessary for the best effect of the catalyst. In future research, we will examine the influence of the surface structure on the catalytic performance of the 30-Å catalyst under typical DCL reaction conditions.

ACKNOWLEDGMENTS

The support of the U.S. Department of Energy for this research under Contract DE-FC22-90029 is gratefully acknowledged. This investigation was carried out as part of the cooperative research program of the Consortium for Fossil Fuel Liquefaction Science. We also acknowledge Dr. Bernard M. Kosowski of Mach I, Inc., for providing us with the NANOCAT catalyst, and Dr. Aurora Rubel, Dr. B. Ganguly, and Mr. Larry Rice, all at the University of Kentucky, for their assistance with the TGA, Mössbauer, and TEM measurements.

REFERENCES

1. Suzuki, T., Yamada, O., Takeh, Y., and Watanabe, Y., *Fuel Proc. Technol.* **10,** 33 (1985).
2. Shabtai, J. S., and Zhang, Y., *in* "Proc. 1989 Int. Conf. Coal Sci., Tokyo, 1989," Vol. II, p. 807. New Energy and Industrial Technology Development Organization (NEDO).
3. Herrick, D. E., Tierney, J. W. Wender, I., Huffman, G. P., and Huggins, F. E., *Energy Fuels* **4,** 231 (1991).
4. Pradhan, V. R., Tierney, J. W., Wender, I., and Huffman, G. P., *Energy Fuels* **5,** 497 (1991).
5. Pradhan, V. R., Herrick, D. E., Tierney, J. W., and Wender, I., *Energy Fuels* **5,** 712 (1991).
6. Derbyshire, F. J., *Energy Fuels* **3,** 327 (1987).
7. Huffman, G. P., Ganguly, B., Zhao, J., Rao, K. R. P. M., Shah, N., Feng, Z., Huggins, F. E., Taghiei, M. M., Lu., F., Wender, I., Pradhan, V. R., Tierney, J. W., Seehra, M. M., Ibrahim,

M. M., Shabtai, J., and Eyring, E. M., *Energy Fuels* **7**, 285 (1993).

8. Jin, T., Yamaguchi, Y., and Tanabe, K., *J. Phys. Chem.* **90**, 4795 (1986).
9. Zhao, J., Huggins, F. E., Feng, Z., Lu, F., Shah, N., and Huffman, G. P., *J. Catal.*, **143**, 499 (1993).
10. Farcasiu, M., unpublished results.
11. Liaw, B. J., Cheng, D. S., and Yang, B. L., *J. Catal.* **118**, 312 (1989).
12. Schwertmann, U., and Cornell, R. M., "Iron Oxides in the Laboratory." VCH, Weinheim, 1991, and references therein.
13. Ganguly, B., Huggins, F. E., Feng, Z., and Huffman, G. P., submitted for publication.
14. Galasso, F. S., "Structure and Properties of Inorganic Solids." Pergamon, Oxford, 1970.
15. Kung, H. H., "Transition Metal Oxide: Surface Chemistry and Catalyst." Elsevier, Amsterdam, 1989.
16. Knözinger, H., and Ratnasamy, P., *Catal. Rev.-Sci. Eng.* **17**, 31 (1978).