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NOTES

The Effect of Crystal Structure upon the Activity of Iron in Steam Gasification

A previous publication (*1*) reported on the behavior of iron particles supported upon graphite in a hydrocarbon/steam environment. That work concentrated on the temperature range above ca. 1273 K. Catalytic behavior for the same system in the temperature range from room temperature to 1273 K is the subject of this note. Experimental procedures are the same in both studies.

Kinetic studies were made using controlled-atmosphere (transmission) electron microscopy (CAEM). Odd morphological characteristics of nucleated iron particles were observed in ethane/steam (40/1) at 843 K: one portion of the particle was quite dense and globular; the remainder took the form of a thin platelet appendage. Particles became mobile at 938 K, and the dual morphology persisted even into the temperature regime where catalytic gasification was occurring. Channeling was the mode of catalytic attack, and it occurred with the dense globular portion of the particle at the head of the channel. At 1223 K the thin portion of the particles disappeared.

Other qualitative features seen on some specimens but not considered to be reproducible events include

(a) the loss of mobility of catalytically inactive particles at 1203 K;

(b) the tendency of particles to spread and wet edges of the graphite at 1143 K, resulting in edge recession and a reduction in the number of isolated particles remaining on the surface;

(c) the finding that very occasionally channeling particles would lose their activity by a spreading and wetting action similar to that reported for nickel (*2*); and finally

(d) the observation that during channel propagation the bistructural particles could undergo rupture and still retain their unusual morphology and catalytic activity.

Kinetic analysis was performed on many channeling sequences. The variation in channeling rate of 56-nm-diameter particles as a function of temperature is presented in the form of an Arrhenius relationship in Fig. 1. These data were obtained from catalyst particles cutting channels of similar depth. Inspection of this plot shows that the catalytic rate of carbon gasification by iron particles in ethane/steam is extremely sensitive to the specimens' thermal history. During the initial reaction cycle and subsequent heating cycles, where the upper temperature has *not* exceeded 1248 K, the rate follows the pathway A and exhibits an apparent activation energy of 38.7 ± 4 kcal · mole^{-1}. If specimens were heated to temperatures in excess of 1248 K during the initial cycle, the subsequent rate of reaction follows pathway B, and on gradual cooling to below 1248 K, particles exhibited channeling rates which follow pathway C and yield an apparent activation energy of 23.0 ± 3.0 kcal · mole^{-1}. During subsequent reheating of these specimens, the channeling rate always remained on pathway C and never reached the higher initial values.

In a separate series of experiments, specimens of preformed γ-Fe on graphite were reacted with ethane/steam. Nucleation of small particles was observed to take place over the range 823 to 873 K. As the temperature was raised to 933 K, many of these

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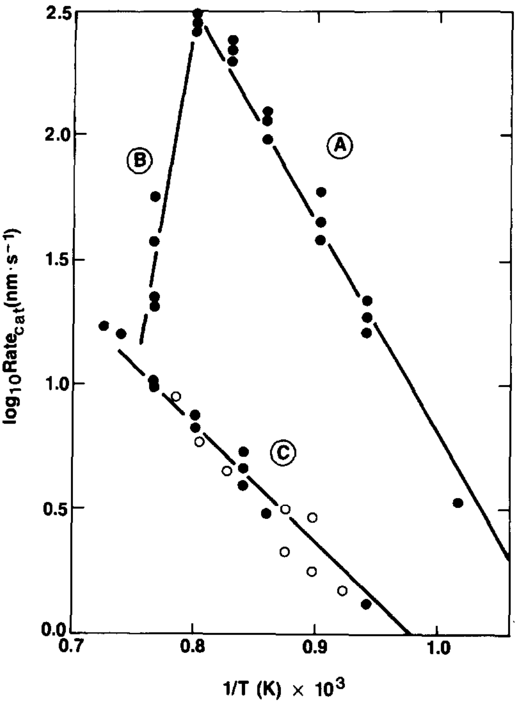

FIG. 1. Arrhenius plots of iron-catalyzed gasification (A) during initial heating cycle in 1.0 Torr ethane/steam; (B) when the upper temperature exceeded 1248 K; and (C) relationship which prevailed after these specimens were treated at temperatures in excess of 1248 K and cooled to lower temperatures. ●, data points from particles which were initially present as α-Fe^0; ○, data points from particles which were initially present as γ-Fe^0.

particles exhibited mobility on the basal plane and occasionally became relocated to edge and step sites, where they existed in a nonwetting condition. This morphology was maintained until 953 K, when the particles underwent a rapid transformation, starting to disappear as a result of a wetting and spreading action along the edges. After a short period, edge regions where this phenomenon had occurred were observed to undergo recession. As this form of attack developed, it became apparent that the edges were faceted and that these features were preferentially oriented in directions parallel to the $\langle 11\bar{2}0 \rangle$ crystal planes of the graphite. The edge recession process continued in a uniform fashion, and the rate exhibited a smooth rise with increasing reaction temperature until 1148 K when edges lost their smooth profile and gradually came to a halt as particles reformed. On continued reaction at this temperature many of these particles proceeded to create channels. The channels tended to follow straight paths moving in directions parallel to the $\langle 11\bar{2}0 \rangle$ crystallographic orientations, and channeling remained the exclusive form of attack as the temperature was progressively raised to an upper limit of 1273 K. If at this stage the temperature was lowered, then channeling activity persisted even down to temperatures where edge recession had been the original mode of attack.

TABLE 1

Mössbauer Parameters of Fe/G Reacted in C_2H_6/H_2O

Sample treatment temperature	Spectral component	Assignment	Magnetic hyperfine field (kG)	Quadrupole interaction, ε(mm/s)	Isomer shift, δ(mm/s)	Relative spectral area
973 K Fit A	Sextuplet	α-Fe	330.5	−0.004	0.003	1.0
Fit B	Sextuplet	α-Fe	329.89	−0.007	0.000	0.69
	Sextuplet	Fe_3C	207.49	0.041	0.256	0.31
1123 K	Sextuplet	α-Fe	330.84	−0.025	0.021	0.26
	Singlet	γ-Fe	—	—	−0.092	0.74
1223 K	Sextuplet	α-Fe	333.62	0.017	0.003	0.28
	Singlet	γ-Fe	—	—	−0.092	0.72

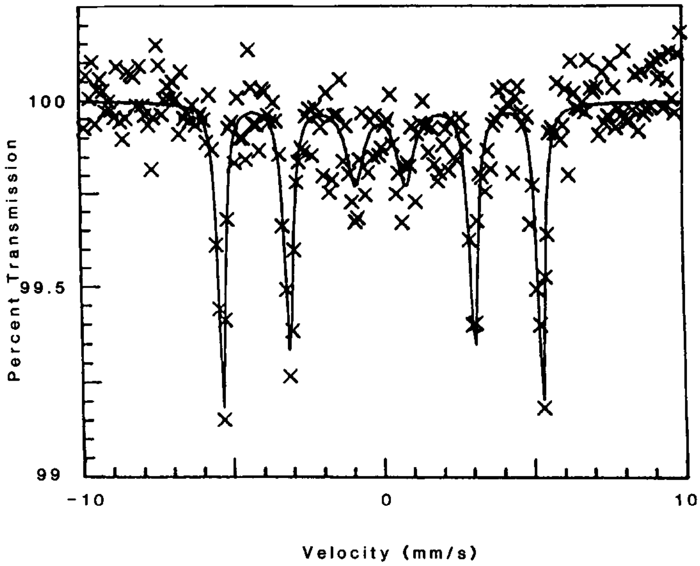

FIG. 2. Mössbauer spectrum of Fe/graphite sample treated at 973 K in C_2H_6/H_2O. ×, experimental data; solid line, fit to data using one sextuplet.

An Arrhenius plot of the data obtained from 56-nm-diameter particles cutting channels of similar depth is shown as the open circles in Fig. 1.

SP-1 graphite was impregnated with a solution of $Fe(NO_3)_3$ to produce a 10 wt% loading of metallic iron. Samples were reduced at 673 K for 3 h in a flowing mixture of 20% H_2 in Ar. The temperature was then adjusted in pure argon prior to gasification in ethane/steam/argon. The recovered materials (from gasification experiments at 973, 1123, and 1223 K) were analyzed at room temperature in a Mössbauer spectrometer (*3*, *4*). The spectra of all three samples contained α-Fe^0 as one of the components as seen in Table 1 (*5*). Figure 2 shows that the sample gasified at 973 K may also have a Fe_3C spectral component (*6*, *7*); the statistics of the fit including this component are slightly worse than those not including it.

In the samples gasified at the higher temperatures the α-Fe^0 spectral component is a minor one. As the spectrum in Fig. 3 shows, most of the spectrum consists of a γ-Fe^0 feature (*7*). Walker *et al.* (*8*) have discussed transformations which can occur in the iron–carbon system upon cooling from reaction conditions to room temperature. Application of their rationale to the present Mössbauer data suggests that under reaction conditions at 973 K α-Fe^0 was present whereas at reaction conditions above 1123 K γ-Fe^0 was present. The minor α-Fe^0 component observed in the spectra of the samples from the higher temperatures may either have been present under reaction conditions or it may have formed during cooling to room temperature.

The change in the kinetics of the reaction was noticed around 1248 K using the CAEM technique, but the formation of γ-Fe^0 was already evident at 1123 K from the Mössbauer results. It is likely that this difference is attributable to the differences in the sample geometries, method of heating, and gas flow patterns. Suppression of γ-Fe^0 formation in the CAEM could arise from a relatively slow rate of carburization of iron. Additionally when preformed γ-Fe^0 is used in the CAEM, the behavior immediately matches the behavior which was observed after heating an α-Fe^0 sample above 1248 K (as seen comparing open and filled circles in C of Fig. 1).

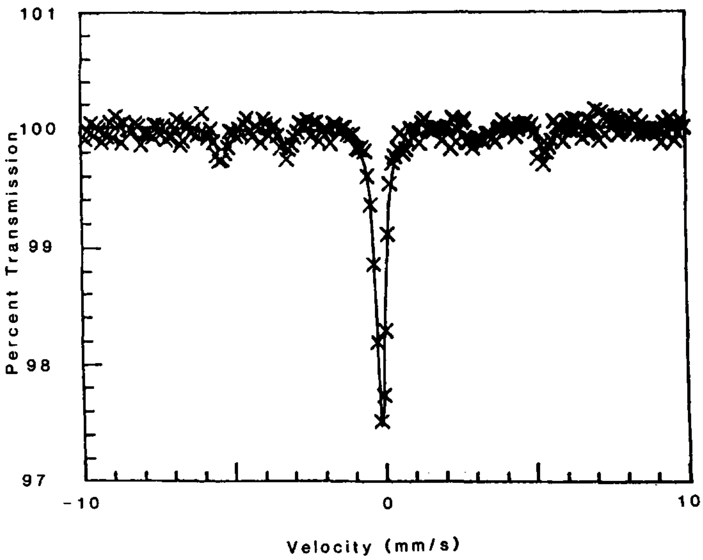

FIG. 2. Mössbauer spectrum of Fe/graphite sample treated at 1223 K in C_2H_6/H_2O: ×, experimental data; solid line, fit to data using one sextuplet and one singlet.

In summary, it has been observed that γ-Fe^0 is less active than α-Fe^0 in the gasification of graphite in a steam/hydrocarbon atmosphere. This effect may be due to differences in carbon solubility, rate of carbon diffusion, or H_2/H_2O adsorption between the two phases. Additional experimental work is planned to probe the importance of these properties.

REFERENCES

1. Baker, R. T. K., and Sherwood, R. D., *J. Catal.* **95**, 101 (1985).
2. Baker, R. T. K., and Sherwood, R. D., *J. Catal.* **70**, 198 (1981).
3. Phillips, J., Claussen, B., and Dumesic, J. A., *J. Phys. Chem.* **84**, 1814 (1980).
4. Sorenson, K., "Internal Report No. 1," Laboratory of Applied Physics II, Technical University of Denmark, Lyngby, Denmark, 1972.
5. Greenwood, N. N., and Gibb, J. C., "Mössbauer Spectroscopy." Chapman & Hall, London, 1971.
6. Huffman, G. P., and Huggins, F. E., *in* "Mössbauer Spectroscopy and Its Chemical Applications" (J. G. Stevens and G. K. Shenoy, Eds.), *Adv. Chem.* **194.** Amer. Chem. Soc., Washington, D.C., 1981.
7. Cashion, J. D., Aghan, R. L., and Doyle, E. D., *Scr. Metall.* **8,** 1261 (1974).
8. Walker, P. L., Jr., Shelef, M., and Anderson, R. A., *in* "Chemistry and Physics of Carbon," Vol. 4, p. 287 (P. L. Walker, Jr., Ed.). Dekker, New York, 1968.

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