

Kinetics and Mechanisms of Iron Sulfide Reductions in Hydrogen and in Carbon Monoxide

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Received August 7, 1986; in revised form December 22, 1986

The reduction of iron sulfides by hydrogen and by carbon monoxide has been studied using plug flow and thermogravimetric methods. The reactions were studied in the 523–723°K temperature range and were found to be first-order processes. Plug flow studies were used to correlate reaction rates between pyrite and the gases as a function of the surface area of the pyrite. The rate of H₂S formation increases with the surface area of the pyrite sample. The results of thermogravimetric experiments indicate that the reactions consist of several steps. Rate constants for the pyrite reduction by H₂ and by CO were obtained. The activation energies increased with degree of reduction. Values of E_a were 113.2 (step I) and 122.5 kJ/mole (step II) for pyrite reduction with CO and 99.4 (step I), 122.4 (step II), 125.2 (step III), and 142.6 kJ/mole (step IV) for pyrite reduction with hydrogen. © 1987 Academic Press, Inc.

Introduction

This paper presents the results of studies in which the reductions of pyrite with carbon monoxide and with hydrogen are examined and compared. The research is in support of a project which seeks to develop a coal desulfurization process (1). In the

first step of the process under development, pyrite in the coal is converted by reaction with carbon monoxide to a pyrrhotite/troilite mixture which is subsequently used to catalyze desulfurization of the organic phase of the coal. The research follows the observation that iron sulfides play important roles in coal transformation processes (2–5).

Studies of iron sulfide transformations have been an important component of coal research (6–11). For example, in an early

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study, Schwab and Philinis (12) examined the decomposition of pyrite in H_2 , CO_2 , and O_2 thermogravimetrically. They found that the reduction of pyrite by hydrogen was first order. The activation energy they obtained was about 126 kJ/mole in the 693–823°K temperature range. Attar (13) suggested that the rate-determining step in this process is the diffusion of sulfur in the solid pyrite.

In this paper we compare reduction of pyrite to troilite by hydrogen and by carbon monoxide. The results of Schwab and Philinis for the reaction with hydrogen have been generally confirmed in a lower temperature range (653–693°K). We find that the reactions, in this temperature range for both hydrogen and carbon monoxide, are first order and involve several discrete steps.

A plug flow reactor was used in studies which were designed to obtain estimates of the activation energies of the reactions. Plug flow studies of pyrrhotite formation were followed by microbalance reactor experiments which revealed the stepwise character of the reactions. Rate constants and activation energies were obtained for all of the steps observed. Curve analysis procedures developed by Gardner (19) were used to examine the mechanisms of the reactions. Plots of weight loss versus time for the reactions of CO with pyrite at different temperatures (693, 683, 673, and 663°K) were found to be affine with slopes which indicate surface reaction control. In the case of the hydrogen reactions, similar plots were not affine, indicating a more complex mechanism in which both surface reaction and solid diffusion appear to contribute.

Experimental Methods

Mineral pyrite used was obtained from Colorado Geological Industries, Denver, Colorado. X-ray analysis indicated a 1% quartz impurity. Sample preparation and

methods employed in plug flow experiments have been described previously (15). Mössbauer spectroscopy was used for determinations of residual pyrite present in partially reduced samples. In the present study 0.5 g of pyrite or of previously prepared iron sulfide (composition $Fe_{1-x}S$ to FeS) was placed in a glass-lined stainless-steel tube passing through a furnace capable of controlled temperatures up to 1273°K. Carrier or reaction gases were passed through the reactor tube at set flow rates. A gas handling system provided the means to purify the gases and control the flow rate. Product gases were then analyzed by sampling the exit stream of the reactor and passing the sample through an in-line gas chromatograph.

The Cahn 113 microbalance reactor used in this study consists of a quartz-tube reactor heated in a split-shell furnace, a quartz bucket for the catalyst sample (40 mg), and auxiliary equipment for introduction and metering of gas flow. Weight changes (with accuracy of 0.05 mg) were automatically recorded on a Sargent SR recorder. Normally, samples were preheated in He at the reaction temperature to obtain a constant weight. The temperature control system utilizes a Micricon 823 computer connected to a thermocouple suspended just below the sample pan. It maintains reactor temperatures to within 1°K during the experiments.

The reduction of the sample was initiated by adding hydrogen or carbon monoxide to the microbalance at a temperature established in the 653–693°K range. Flow of the reducing agent was 80 ml/min. The degree of reduction, α , was calculated as

$$\alpha = \Delta W / \Delta W^*, \quad (1)$$

where ΔW is the weight loss at the time t and ΔW^* is the weight loss for complete pyrite conversion to troilite, FeS, calculated from the quantity of pure pyrite placed in the reactor pan. Pyrrhotite compositions are calculated from measured

weight losses. Mössbauer spectra were taken with a Ranger Scientific MS-900 spectrometer using a ⁵⁷Co source in a rhodium matrix from Amersham International.

Results and Discussion

Pyrite is reduced by carbon monoxide and by hydrogen to troilite. In the case of carbon monoxide, carbonyl sulfide is the by-product and the overall reaction may be written as



In the hydrogen reaction, the by-product is hydrogen sulfide:



Troilite may be reduced further by hydrogen to mixtures of iron and troilite. Troilite, however, is the final product of the carbon monoxide reaction. These two reactions occur only at elevated temperatures. The reaction of pyrite with carbon monoxide begins at 520°K, while the reaction with hydrogen begins at about 600°K.

Plug Flow Reactor Study

Plug flow reactor methods were used to estimate the activation energies of the above reactions. The progress of the reactions was followed by sampling the product gas streams intermittently for hydrogen sulfide, in the case of hydrogen reductions, and for carbonyl sulfide, in the case of the carbon monoxide reductions. The concentrations of these products are directly proportional to the reaction rates (15). Data collected at several temperatures were used to construct Arrhenius plots from which activation energy estimates were obtained.

For carbon monoxide, the activation energy determined from the reaction with pyrite was 98 kJ/mole, while that determined for pyrrhotite was 108 kJ/mole. The activation energy determined for the reaction of hydrogen with pyrrhotite was 108 kJ/mole. Both reaction systems were sen-

sitive to the pyrite pretreatment. In the experiments, pyrite samples were heated under dry, flowing, oxygen-free helium for 24 hr before the reductions were begun.

In previous studies, it was found that heating pyrite at 673°K under flowing helium increases the surface area of the pyrite and increases the reaction rates of hydrogen and carbon monoxide (1). In Fig. 1, as an example, is a plot of the rate of OCS production versus the BET surface area of the pyrite sample. For both H₂ and CO, increased surface area results in increased reaction rates.

Thermogravimetric Study

The processes that occurred during the heating of pyrite in flowing helium were examined thermogravimetrically. A pyrite sample (40.00 mg) was placed in the microbalance reactor under a flow (60 ml/min) of dry, oxygen-free helium. As the temperature was increased a weight loss of 0.31 mg was observed between 373 and 383°K. This loss of 0.31 mg was attributed to loss of absorbed water and trapped gases. A second weight loss, which was attributed to sulfur loss resulting from partial pyrite reaction, was observed in the temperature range 653–673°K. The temperature was then maintained at 673°K as the experiment was continued for 12 hr. During this period

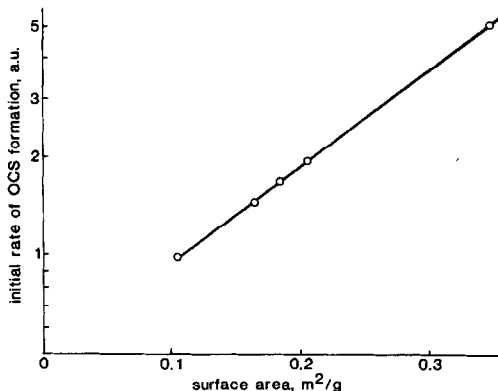


FIG. 1. Plot of the initial reaction rate of CO with pyrite versus surface area of the iron sulfides.

the weight of the sample was virtually constant. If the weight loss due to sulfur is assumed to be from the formation of troilite, then the surface area estimates indicate that the surface of the pyrite is covered by a layer of troilite.

Pyrite Reduction with Carbon Monoxide

Using a Cahn microbalance flow reactor, the weight changes in iron sulfide samples which accompany reactions with the gases were recorded as a function of time for several reaction temperatures. In the analysis of the weight change data, curves of the degree of reduction, $\alpha(T, t)$, were plotted versus time for each temperature. Relationships between the curves were examined graphically. For the reactions of CO with pyrite, the curves obtained were related by affine transformations, i.e. (16),

$$\alpha(T_m, t) = \alpha(T_n, b_m^n t), \quad (4)$$

where b_m^n is a constant, the relationship between temperature is $T_m = T_n + \Delta$, and Δ is the temperature increment. When this is the case, the rate equation for the process

$$d\alpha/dt = r(T, p, x^i, \alpha) \quad (5)$$

can be written as a product of two functions,

$$d\alpha/dt = k(T, p, x^i) \cdot f(\alpha), \quad (6)$$

where $k(T, p, x^i)$ is the rate constant which is dependent upon temperature, T .

The affine character of the curves indicates that the series of states traversed by the system in the course of the reaction is invariant with respect to intensive variables such as temperature or pressure. That is, the mechanism of the reaction is the same through the temperature range studied. Rate constants for the several temperatures are different only because of changes in the temperature increments. If, for example, $T_m = T_n + \Delta$, then the rate constants for T_m and T_n are related by

$$k_{T_m} = k_{T_n} \cdot \frac{E}{R} \cdot \frac{\Delta}{T_n + \Delta} = k_{T_n} b_m^n. \quad (7)$$

In the integrated rate equation, the multiplier b_m^n has the effect of stretching out the time scale. It depends upon the temperature involved (T_m and Δ) and upon the activation energy of the process. In general, we can write, for the rate constants at two temperatures,

$$k_m/k_n = b_m^n \quad (8)$$

for each step in the reaction.

The conformity of the kinetic curves to the affine transformation is an obligatory but not sufficient condition for a single reaction process. In such a case, the kinetic curve can be described by a single equation, with rate constants depending only on intensive rather than extensive parameters. The form of this equation can supply information concerning the nature of the process that controls the overall rate of the reaction.

Many solid-state reactions can be described by equations of the type $F(\alpha) = k \cdot t$, where $F(\alpha)$ depends on the mechanism controlling the reaction and α is the extent of the reaction variable (17–20). Gardner developed general curve analysis procedures based upon comparisons between observed rate laws for solid-state reactions and rate expressions derived from specific mechanistic assumptions. Table I lists a group of derived relationships written in a form which facilitates the analysis and an associated slope value, h , used in the analysis.

The functions $D_1(\alpha)$ through $D_4(\alpha)$ represent some of the important diffusion equations. $F_0(\alpha)$ and $F_1(\alpha)$ are the functions for zero- and first-order reactions, and $R_2(\alpha)$ and $R_3(\alpha)$ are equations for phase-boundary controlled reactions. $A_2(\alpha)$ and $A_3(\alpha)$ are the Avrami–Erofe'ev equations based on nucleation and nuclei growth. In the analysis, the group to which a controlling reac-

TABLE I

SOLID-STATE REACTION RATE EQUATIONS

Function	Equation	<i>m</i>
$D_1(\alpha)$	$\alpha^2 = kt$	0.62
$D_2(\alpha)$	$(1 - \alpha)\ln(1 - \alpha) + kt$	0.57
$D_3(\alpha)$	$(1 - (1 - \alpha)^{1/3})^2 = kt$	0.54
$D_4(\alpha)$	$1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt$	0.57
$F_1(\alpha)$	$-\ln(1 - \alpha) = kt$	1.00
$R_2(\alpha)$	$1 - (1 - \alpha)^{1/2} = kt$	1.11
$R_3(\alpha)$	$1 - (1 - \alpha)^{1/3} = kt$	1.07
$F_0(\alpha)$	$\alpha = kt$	1.24
$A_2(\alpha)$	$(-\ln(1 - \alpha))^{1/2} = kt$	2.00
$A_3(\alpha)$	$(-\ln(1 - \alpha))^{2/3} = kt$	3.00

tion step belongs is established by comparing the slopes, h , of plots of $\ln[-\ln(1 - \alpha)]$ versus $\ln(t)$ for the experimental system to those listed in Table I.

Plots of $\ln[-\ln(1 - \alpha)]$ versus $\ln(t)$ for pyrite reduction in carbon monoxide have slopes of 1.01, indicating that the reaction can be described using an equation derived from a first-order mechanism. According to Table I, the rate equation of pyrite reduction with CO is

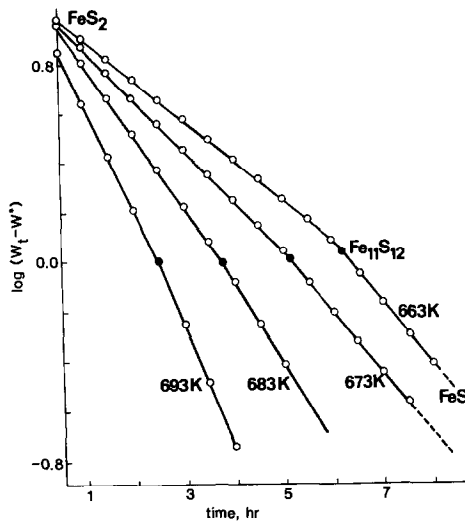


FIG. 2. Plots of $\log(W_t - W^*)$ vs time for the reduction of pyrite by carbon monoxide (solid circles identify inflection points).

$$-\ln(1 - \alpha) = k \cdot t. \quad (9)$$

In order to evaluate the rate constants k , the function $\log(W_t - W^*)$ versus time was plotted, where W^* is the weight of the sample when fully converted to FeS. The resultant correlation is given in Fig. 2, which shows that all curves, regardless of temperature, have an inflection point. The formula of pyrrhotite at the inflection point for each curve was calculated from the weight loss to be FeS_{1.085} (Fe₁₁S₁₂). Accordingly, pyrite reduction in carbon monoxide may be written as

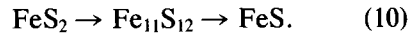


Table II presents the values of rate constants and activation energies for the two steps of the reaction.

Pyrite Reduction with Hydrogen

The rates of pyrite reduction in the hydrogen stream were measured at 653, 673, 683, and 693°K. Before reduction, the samples were conditioned in a He stream to constant weight. Based upon work described earlier, the surface areas of the pyrite samples exceeded 1 m²/g. The values of α were calculated as described above. In contrast to the observations of the carbon monoxide reactions, plots of $\alpha(T, t)$ versus time for the reactions of hydrogen with

TABLE II

THE RATE CONSTANTS ($\times 10^{-2}/\text{min}$) AND THE ACTIVATION ENERGIES (kJ/MOLE) FOR PYRITE REDUCTION WITH CARBON MONOXIDE

Temperature (°K)	k_1	k_2
663	0.60	0.79
673	0.78	0.88
683	1.06	1.22
693	1.46	1.76
E_a	113.2	122.5

pyrite were not affine. This suggests that more than a single process may be rate determining and that the separate contributions have different temperature dependencies. Utilizing the Gardner procedure (19), plots of $\ln[-\ln(1 - \alpha)]$ versus $\ln(t)$ were constructed. These plots all had slopes of 0.83. Comparison of this slope with Table I shows that the value of the slope is intermediate, falling between slopes extracted for processes following either $D(\alpha)$ or $F(\alpha)$. While Gardner's procedure in such a case does not provide variable measures of choice among the proposed rate expressions, the results suggest a mixed mechanism for the process. This confirms the indication provided by the nonaffine character of the weight versus time plots and suggests that diffusion as well as surface reactions may be involved in the rate-determining steps of the process.

Figure 3 is a plot of $\log(W_t - W^*)$ versus time for the reaction of hydrogen with pyrite. The plots exhibit inflection points which occur at the same compositions for all of the temperatures studied. Mössbauer spectra of samples at each inflection point were obtained and analyzed. Spectra of the first two inflection points showed small amounts of pyrite remaining in the samples. Using relative intensities obtained from fitted spectra, the weight of unreacted pyrite was subtracted from the sample weight, and the pyrrhotite composition calculated. The pyrrhotite compositions determined from the inflection points are Fe_7S_8 , Fe_8S_9 , and $\text{Fe}_{11}\text{S}_{12}$. All of these compositions are well known (21). Fe_7S_8 is monoclinic pyrrhotite, and Fe_8S_9 and $\text{Fe}_{11}\text{S}_{12}$ are hexagonal forms. The results indicate that pyrite reductions with hydrogen occur in several steps, each of which is first order,

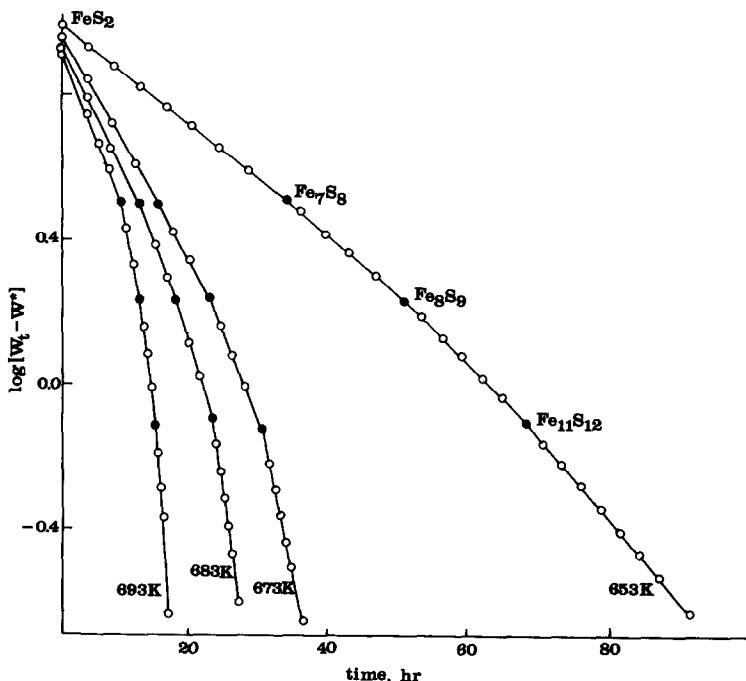
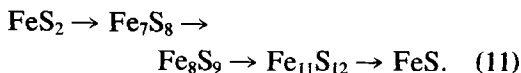


FIG. 3. Plots of $\log(W_t - W^*)$ vs time for the reduction of pyrite by hydrogen (solid circles identify inflection points).

as



The values of the rate constants for all steps of the reaction are listed in Table III. Each step exhibits a different activation energy, which are also listed in the table.

Conclusions

In the temperature range studied (653–693°K), pyrite and the pyrrhotites derived from it react substantially faster with carbon monoxide than with hydrogen. This conclusion is derived from both plug flow reactor and thermogravimetric studies. While thermogravimetric studies have provided greater detail and quantification, they have also confirmed and validated plug flow results. The reactions of both gases with pyrite and all of the iron sulfide compositions between pyrite and troilite are first order. The stepwise character of the reactions is a new finding for these systems.

The reaction of carbon monoxide with pyrite occurs in two steps. In the first step, the product is pyrrhotite, having the composition Fe₁₁S₁₂, and in the second the product is troilite. Both the rate constant and the activation energy of the second step are larger than those of the first step at each

temperature studied. This indicates significant differences in the preexponential factors of the two steps. While the increase in the activation energy of the second step tends to reduce the rate constant, a larger preexponential factor results in a faster rate.

The reaction of hydrogen with pyrite is similar to that of carbon monoxide, but more complex. Three inflection points are formed in the plot of log(W_t - W*) versus time, indicating four steps in the transformation of pyrite to troilite. The pyrrhotite composition at the inflection points is the same for each of the temperatures studied within the limits of experimental error. They are Fe₇S₈, Fe₈S₉, and Fe₁₁S₁₂. These compositions are the sequential intermediate products of the reduction, which in these experiments ended with troilite, FeS. Rate constants and activation energies determined for the four steps increase as the reduction proceeds, indicating, for this system also, a composition dependence of the preexponential factors.

Rate constants reported in this paper are taken from the slopes of the plots in Figs. 2 and 3. They are calculated from the sulfur lost in the steps of the reaction and apply to the overall processes occurring between the inflection points. The fact that the pyrrhotite with composition Fe₁₁S₁₂ is found at inflection points for both hydrogen and carbon monoxide reactions suggests that this pyrrhotite composition has a unique chemical significance which differentiates it from other nearby compositions. A similar significance can also be attached to the compositions Fe₇S₈ and Fe₈S₉, which, nevertheless, lead to inflection points only in the hydrogen reaction.

Activation energies for the reactions of pyrite with both CO and H₂ increase in a stepwise fashion as the reductions proceed. Since the activation energies for the two gases are not greatly different, we have considered possible reasons for the faster

TABLE III

THE RATE CONSTANTS ($\times 10^{-3}/\text{min}$) AND THE ACTIVATION ENERGIES (kJ/MOLE) FOR PYRITE REDUCTION WITH HYDROGEN

Temperature (°K)	k_1	k_2	k_3	k_4
653	0.66	0.84	0.93	0.97
673	1.18	1.69	1.80	2.04
683	1.41	2.31	2.42	3.30
693	1.87	3.14	3.29	4.32
E_a	99.4	122.4	125.2	142.6

reaction of CO. One reason may lie in the difference in reaction mechanism. Curve analyses indicate that the rate-determining process in the reactions of carbon monoxide with iron sulfides is a surface reaction. On the other hand, in the case of hydrogen reactions, similar analyses suggest that both surface reaction and solid diffusion provide significant contributions. The likely contribution of solid diffusion to the rate-determining process has been suggested by Attar (13), and these experiments support that assessment.

Finally, this study demonstrates that the reductions of pyrite to troilite with carbon monoxide and with hydrogen are punctuated by discrete pyrrhotite compositions. The pyrite reductions are not uniform, but proceed through well-defined intermediate compositions that include pyrrhotite solid solution.

Acknowledgments

We gratefully acknowledge partial support for this work from the Illinois Department of Energy and Natural Resources and from the Illinois Coal Research Board under Grant 7 CRG. Substantial help was furnished through the Material Technology Center and Coal Technology Laboratory at SIUC for this work, especially for partial purchase of the microbalance and for critical review of reports.

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