

THE RATE AND THE MECHANISM OF CATALYTIC COAL LIQUEFACTION BY IRON SULFIDES: PART I.

THE SYSTEM $\text{FeS}_x : \text{H}_2 : \text{H}_2\text{S}$, RATES OF REACTION AND SURFACE CONVERSION

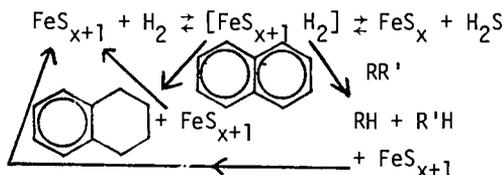
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INTRODUCTION

The systems $\text{FeS}_2\text{-H}_2\text{-H}_2\text{S}$ and $\text{FeS}_2\text{-hydrogen donor-H}_2\text{S}$ play a critical role in the catalysis of coal liquefaction by naturally occurring minerals. Consequently, there is a tremendous incentive to understand the exact mechanism and rates of reaction which affect the catalysis of coal liquefaction by FeS_x .

Examination of the data available in the literature and studies from our own laboratory suggest that the dominant catalytic action is due to the formation of an intermediate compound, possibly $[\text{FeS}_{x+1}\text{H}_2]$ which can react according to the scheme:



The main function of the FeS_{x+1} is to permit conversion of molecular hydrogen to organically bound hydrogen, either in the form of donor molecules and/or coal derived molecules. The $[\text{H}_2\text{S}]/[\text{H}_2]$ plays a critical role in this system since its value determines the equilibrium distribution of the active catalytic intermediate, $[\text{FeS}_{x+1}\text{H}_2]$, and the less active species FeS_{x+1} and FeS_x .

This mechanism explains many of the observations in the system coal-solvent- FeS_2 . The most important facts are:

1. Catalytic action by Fe salts is observed only when H_2S is present in the reactor. The level of the catalysis depends on the ratio $[\text{H}_2\text{S}]/[\text{H}_2]$.
2. Regardless of the starting material, when the FeS_x is allowed to catalyze the reaction long enough, a fixed ratio of Fe to S is achieved, typically of the order of $\text{Fe/S} \approx 1/1.09$. Such a ratio could be the result of the thermodynamic equilibrium achieved for the coal at the prevailing $[\text{H}_2\text{S}]/[\text{H}_2]$.
3. The type of pyrite used to catalyze the reaction influences mainly the rate of the initial stages of the reaction but has little effect on the results of long time liquefaction.

Since the ratio $[\text{H}_2\text{S}]/[\text{H}_2]$ (gas) and the ratio Fe/S (solid) play such a critical role in the liquefaction, it appeared useful to quantitize the rate of the individual reactions involved. To achieve reasonable data, it appeared essential that the same sample of FeS_2 be tested so that it would be possible to avoid questions related to the conversion of the surface and so that small differences in reactivity could be determined. In this paper preliminary results are presented on the system $\text{FeS}_x\text{-H}_2\text{-H}_2\text{S}$.

EXPERIMENTAL

In order to have more or less the same surface area and the same surface conditions, a pulsed differential reactor (PDR) was used, similar to that described by Attar (1979). The only difference was that a S.S.

packed bed reactor 1/4" ID x 1 ft packed with -100+120 mesh FeS₂ particles was used as the reactor. Helium was used as the carrier gas and pulses of H₂, H₂S or CO were used to investigate the effect of the surface conversion of the pyrite on its reactivity, the activation energies for the reaction, etc. Figure 1 is a schematic diagram of the reaction system.

In a typical experiment, a pulse of H₂ was injected into the He carrier and the product pulse, which consists of unreacted H₂ and H₂S + S₂ was separated on a Chromosorb 105 column and the components were determined by a TC detector.

ANALYSIS OF THE DATA

The relative rate of reaction, r_j , in the j -th pulse was determined from the consumption of the hydrogen, i.e.,

$$r_j = \frac{W_{H_2}^0 - W_{H_2j}}{W_{H_2}^0} \quad (1)$$

where $W_{H_2}^0$ is the number of moles of H₂ injected and W_{H_2j} are the number of moles of incorporated H₂. The temperature was programmed during most of the experiments, in order to allow the determination of the variations of r_j with the temperature. To a first order approximation, since the surface was barely converted in each pulse, one may write, assuming Arrhenius dependence of the rate constant on the temperature:

$$r_j = k_0 \exp\left(-\frac{E}{RT}\right) [\overline{H_2}] \quad (2)$$

or roughly:

$$\log r_j = \log \left[1 - \frac{W_{H_2j}}{W_{H_2}^0}\right] = \log k_0 [\overline{H_2}] - \frac{E}{RT} \quad (3)$$

$[\overline{H_2}]$ is the average concentration of H₂ near the surface and E is the activation energy. Figure 2 shows some of the data obtained. Curves A, B and C were done on the same pyrite sample by successive injection of H₂ pulses in three cycles of heating and cooling of degassed FeS₂. The data indicate that as the surface is being converted, the activation energy rises slightly, from 26.4 to 27.4 kcal/mole for about 1% surface conversion and that the preexponential factor decreases. This is due to the accumulation of FeS_{2-y} near the surface which resists to the diffusion of S⁼ in the solid (see ref. 2).

Curve D was obtained using a different sample of iron pyrite while curve E was derived with a specially prepared sample of FeS₂. The last curve indicates that sample D is a much more reactive specimen, with an activation energy of 22.7 kcal/mole and a larger preexponential factor than the raw FeS₂.

SUMMARY

A new mechanism is proposed for catalytic coal liquefaction using FeS_x. The mechanism includes many of the observed facts on the role of Fe, S, H₂ and H₂S in such a system. Preliminary data are presented on one of the subsystems, i.e., FeS₂ + H₂ and the role of surface conversions in deactivation of the reaction of FeS₂ with pure H₂ is demonstrated. Specially prepared samples of FeS₂ appear to have a much larger activity toward H₂, and as will be shown in a future paper, much larger catalytic effect on the rate of coal liquefaction.

REFERENCES

1. Attar, A., Rev. Sci. Inst., 50 (1), 111 (1979).
2. Attar, A., Fuel, 58, 201 (1978).

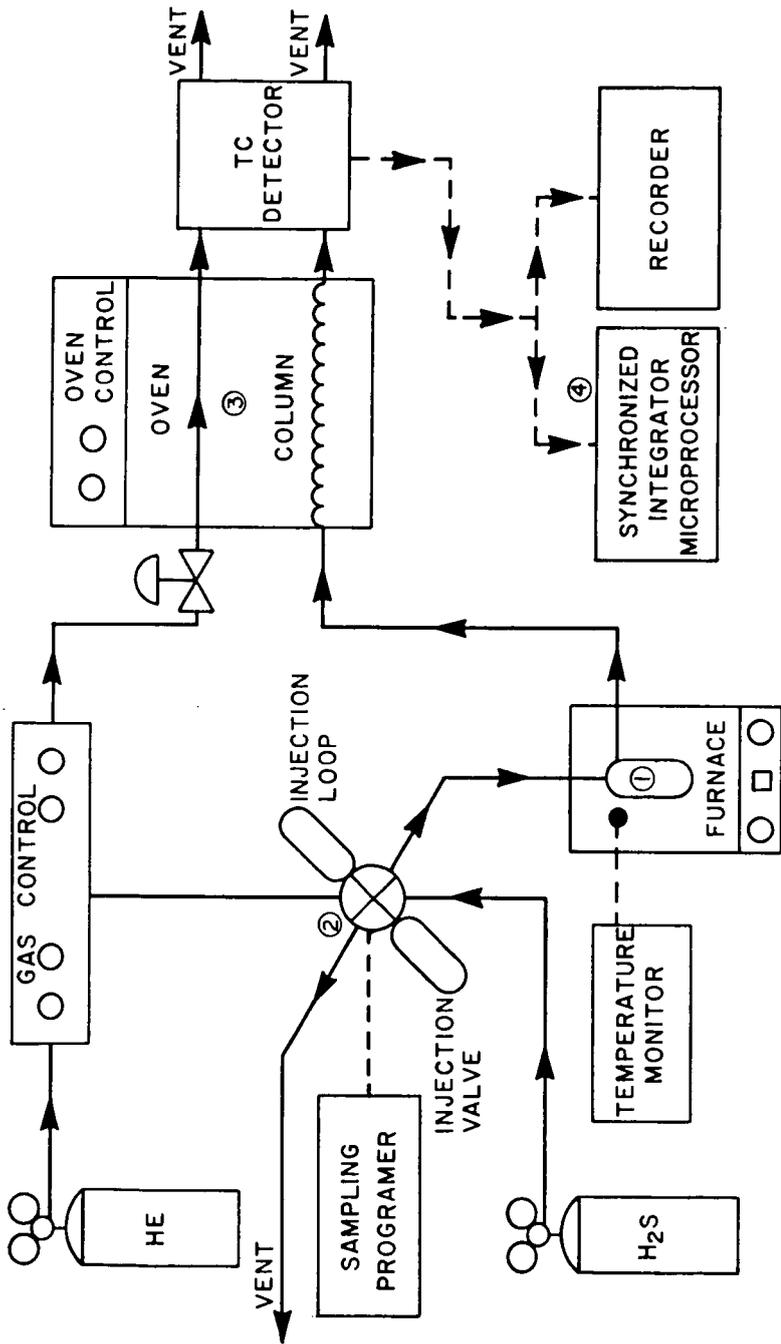


FIGURE 1

Figure 2

TEMPERATURE DEPENDENCY OF PYRITE REDUCTION
PULSE DIFFERENTIAL REACTOR SYSTEM

Activation Energy (kcal/mol)
(Temp. range 400-450°C)

Run	1	2	3	4
Symbol	○	□	△	◇
Energy	26.4	27.0	27.4	37.2

