

**Complex Iron Catalytic Systems: Relative Catalytic Activity
of Various Components.**

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Key words: catalytic hydrocracking, iron-sulfur catalysts, active phase.

ABSTRACT

Fine particle (6-8nm) iron-sulfur systems with complex chemical compositions are formed when a 3 nm iron oxide is heated with sulfur in the presence of 9,10-dihydrophenanthrene for 1 hour. These systems form small-particle pyrrhotite when heated at 320°C. The fine particle pyrrhotites are very active hydrocracking catalysts, but agglomerate rapidly during reaction at 320°C.

INTRODUCTION

The use of iron-based catalysts in reactions of interest for direct coal liquefaction usually involves the addition of iron compounds to the reaction mixture and the in-situ activation of the iron compounds to form iron catalysts. The composition of active iron-based catalysts has been a subject of considerable interest and several reviews have been published on the subject (1,2). It was reported that the hydrocracking of monoaromatic model compounds at temperatures of 425-435°C is catalyzed by iron-sulfur systems in the presence of hydrogen sulfide (2). The catalytic activity was tentatively explained by an interaction of pyrite with pyrrhotite and hydrogen sulfide.

We have studied the activity of some iron-sulfur catalytic systems formed in the reaction of fine-particle iron oxides with elemental sulfur and a hydrogen donor, 9,10-dihydrophenanthrene (9,10-DHP), at low temperature. In this paper we will discuss the systems formed when the above compounds are heated at low temperatures (200 - 320°C). We have found that the iron-sulfur systems formed under these conditions are very active in low temperature, selective hydrocracking of C_{ar}-C_{aliph} bonds, when the aromatic carbon is a part of a condensed polycyclic aromatic hydrocarbon. The composition of the iron-sulfur systems and the variation of their compositions with time under various reaction conditions have been studied by a variety of methods. We report

here our findings concerning the catalytically active components in the above described iron-sulfur system.

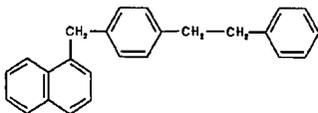
EXPERIMENTAL

General. Reagent grade chemicals and HPLC grade solvents were used as purchased unless stated otherwise. Methylene chloride was dried over 4 Å molecular sieves. Ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), obtained from Mach I, Inc., King of Prussia, Pennsylvania, was vacuum dried for ca. 3 hours at 150 °C, then stored in a desiccator. The particle size reported by the vendor (3-5 nm) was confirmed by microscopic analysis and is consistent with the surface area determination by the BET method. Compound I was available from our previous work (3).

The reactions were conducted in sealed 7mm o.d. heavy walled glass tubes (Corning Glass) in a Lindberg Type 59344 muffle furnace equipped with a thermocouple.

Chromatographic analyses were conducted on a Hewlett-Packard Model 5890 Series II Gas Chromatograph equipped with a split-vent injector and connected to an HP 3396A integrator, on a J&W 30 m x 0.248 mm fused silica capillary column coated with 0.25 μm silicone SE-52, with a head pressure of 20 psi (136 KPa). The column temperature was increased from 80°C to 310°C at a rate of 8°C/min. Identification of the components was described in a previous publication (3).

Catalyst Preparation and Activity Measurement. In a typical experiment, ferrihydrite (2.5 mg) dried as indicated above, sulfur (2.5 mg), and 9,10-DHP (100 mg) were loaded into the glass tube which was sealed without excluding the air. The length of the sealed tube was ca. 14 cm. The tube was heated at the desired temperature for the duration indicated below, then it was cooled and stored at room temperature until use. For catalyst testing, the tube was cracked open (CAUTION: pressure buildup in the tube occurs, particularly for experiments at higher temperatures), 25 mg of the reactant, 4-(1-naphthylmethyl)bibenzyl (I), was added and the tube was resealed and heated as indicated



below. In the alternative procedure, compound I was added together with the catalyst precursors such that catalyst preparation and reaction of I were conducted in one operation. For the analysis of

products, the tube was cooled to room temperature and carefully opened, the organic materials were dissolved in the minimum amount of methylene chloride possible and filtered through a layer of anhydrous MgSO_4 (ca. 0.3 g) supported by a glass wool plug in a micropipette. The tube was rinsed twice with methylene chloride (ca. 0.5 mL each time) and the washings were filtered through the same microcolumn for drying. The combined solution was concentrated to ca. 1 mL and analyzed by GLC (0.5 μL of sample was used for each injection).

Catalyst Characterization. The particle size, chemical composition, and the crystallographic properties of the iron species formed under various experimental conditions were determined as described by Eldredge et al.(4), using XRD and Moessbauer spectroscopy. The surface area was determined by the BET method (5) from the adsorption isotherms for N_2 at 77K. The samples were first outgassed for 18 hr at 95°C and less than 10^3 torr. A Coulter Omnisorp 100CX gas sorption analyzer operated in the fixed-dose, static-flow volumetric mode was used to measure the adsorption isotherms. Equilibration of the sample with a nitrogen dose was defined as five consecutive readings with a variance of less than 0.1 torr over a 3 second interval. A value of 0.162 nm^2 was used for the cross-sectional area of nitrogen.

RESULTS AND DISCUSSION

The catalyst prepared in-situ from ferric oxide (20-80 nm) and sulfur in the presence of 9,10-DHP and reported previously (6) was found active in hydrocracking reactions of compound I at temperatures of 420-430°C. In the present study, the reactions were performed at temperature and conditions where no thermal reaction of I occurs (3). In work reported here, we have used an oxide with smaller particles (3-5 nm) as the catalyst precursor. Our goal was to prepare an iron-sulfur catalyst in an initial step, and then add the substrate I and perform the hydrocracking reaction. The temperature was varied independently in the two steps (between 200°C and 320°C for the first step and between 200°C and 400°C for the second step) and each step was normally conducted for 1 hour. Alternatively, the two steps were combined by adding the substrate from the beginning and thus synthesizing the catalyst in-situ. The conversion of I, defined as the selective cleavage of the bond adjacent to the naphthalene ring, is presented in Table 1 for both of these approaches. It can be seen that the catalyst is active even at temperatures as low as 250°C. Moreover, conversion of I reaches a maximum value of 92% in one hour at 350°C (Table 1)

The data in Table 1 also show that reaction of I at any temperature between 250 and 400°C gives the same conversion with the catalyst generated in-situ or with the material pre-synthesized at 200°C. Synthesis of the catalyst in a prior step at higher temperatures gave less active catalytic systems.

Under our experimental conditions, specifically with the reactant dissolved in 9,10-DHP, there is likely no mass transfer limitation and the rate of formation of the active phase by the

reaction of iron oxide with sulfur (or more likely with the hydrogen sulfide formed from S and the H-donor) is faster than the hydrocracking reaction. Such favorable conditions might not be available if the catalyst were generated in a very complex heterogenous medium with large excess of solids, as is the case in coal liquefaction. Therefore, preparation of active, small particle catalysts, prior to the actual coal liquefaction, is desirable.

The structural study of this Fe-S material formed after pretreatment of 3-5 nm particles of ferrihydrite for 1 hour at 200°C indicates the presence of at least four distinct components: pyrrhotite, magnetite, unreacted ferrihydrite (or hematite), and a new iron sulfide phase identified as marcasite with pyrite stacking faults (4). The composition, as determined by Moessbauer spectroscopy, is reported to be (7): 15% pyrrhotite, 19% unreacted ferrihydrite, 29% magnetite, and 37% for the new iron sulfide phase. The particle size of the pyrrhotite component in this material was in the range of 6.5-8 nm (XRD) and its calculated surface area was 150-182 m²/g. The direct surface area determination for all the components gave a surface area of 180 m²/g. The marcasite/pyrite phase is unstable at 200°C and is converted to pyrrhotite upon longer heating at that temperature. Pyrrhotite is also formed at the expense of the new phase when catalyst synthesis is conducted at higher temperature. In both cases, larger particles are obtained. When catalyst preparation was conducted at 320°C, only pyrrhotite was observed even at a short reaction time of 20 minutes. The particle size of the pyrrhotite obtained under the latter conditions was ~30 nm, with a corresponding calculated surface area of ~40 m²/g. Pretreatment at 200°C, followed by treatment for 10 minutes at 320°C, or direct pretreatment for 10 minutes at 320 °C gives pyrrhotite with particle size of 22-25 nm (corresponding surface area of 54-48m²/g). After pretreatment of 1 hour at 320°C, the particle size of the pyrrhotite was in the range of 38-50 nm (XRD) and a surface area of ~24 m²/g was calculated.

The catalytic activity of the iron-sulfur system formed at 200°C may be due to one, some, or all of the components present; i.e., to pyrrhotite, the newly identified iron sulfide phase, magnetite, or to the unreacted ferrihydrite. The ferrihydrite used alone in tests with I in the presence of 9,10-DHP was found to be catalytically inactive. For identification of the active phase in this system, we studied the conversion of compound I at 320°C as a function of time in the presence of the iron-sulfur system presynthesized at 200°C. The results are given in Table 2. Based on the conversion at 40 minutes with pyrrhotite of 24 m²/g initial surface area, a specific catalytic activity for pyrrhotite of 0.39 nmoles I/(m²hour) is calculated. X-ray diffraction data indicate that pyrrhotite is the primary material present after 20 minutes at 320°C. Assuming the only catalytically active phase present even at short reaction time is pyrrhotite, then for the 45% conversion of I in the first 20 minutes of the reaction, an average surface area of 108 m²/g can be calculated for this interval using the specific activity mentioned above. This value compares well with the observed decrease in the surface area during the first 20 minutes of reaction from ~180 m²/g

to $\sim 41 \text{ m}^2/\text{g}$ (a calculated average would be $110 \text{ m}^2/\text{g}$). Using this result along with the observation that pyrrhotite is by far the major component in the system leads to the conclusion that pyrrhotite is most likely the catalytically active phase.

The possible catalytic activity of magnetite (a major component after pretreatment of the mixture of ferrihydrite and sulfur in the presence of 9,10-DHP at 200°C for 1 hour) was studied using samples of genuine magnetite of known particle sizes (8). However, based on the observed conversion to pyrrhotite after 20 minutes at 320°C , it is unlikely that magnetite makes any important contribution to the activity under the reaction conditions reported in Table 2. The observed conversions after pretreatment at various temperatures can be explained by pyrrhotite as the catalytically active phase and by the variation of its particle size (surface area) as a function of the experimental conditions. Consequently, our present data indicate no measurable catalytic activity for the new form of pyrite-marcasite identified when the iron-sulfur system is preformed at 200°C , as described above. However, the stability at room temperature of the iron-sulfur system formed after pretreatment for 1 hour at 200°C without loss of the catalytic activity (Table 3) may be due to the fact that this complex system prevents the agglomeration of the particles.

Data by Cugini et al. (9) show that when highly dispersed FeOOH is precipitated on coal and the coal is pretreated at 275°C in presence of a sulfur compound, an active catalyst for coal liquefaction can be formed. It is likely that this catalyst is highly dispersed pyrrhotite and that coal prevents its agglomeration. However, in the absence of sulfur, other iron compounds are stable and can act as catalysts. When a low sulfur bituminous coal is liquefied in the presence of magnetite, a significant catalytic activity is observed and magnetite is observed as such at the end of reaction (8).

CONCLUSIONS

We have found that pretreatment of fine particle size (30 nm) iron oxide with sulfur in the presence of 9,10-DHP, at 200°C for one hour gives a high surface area mixture of magnetite, pyrrhotite, and a newly identified phase of marcasite-pyrite (4). We studied this system for hydrocracking reactions of compound I at various temperatures. The iron-sulfur mixture transforms at 320°C (the temperature at which we report kinetic data) into pyrrhotite. The surface area of pyrrhotite varies with the reaction time and the catalytic activity can be correlated to the surface area variation. The observed catalytic activity in the hydrocracking reaction of I is attributed under these conditions to pyrrhotite.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contribution of Dr. S. Pollack, Dr. N. Johnson and Mrs. E. Frommel from PETC for their assistance with XRD analyses and helpful discussions. Technical

discussions with prof. I. Wender, Dr. B.D. Blaustein and Dr. R.P. Warzinski are gratefully acknowledged. This work was supported in part (PAE and SCP) by appointments to the Department of Energy Fossil Fuels Energy Postgraduate Research Training Program administered by Oak Ridge Institute for Science and Education.

DISCLAIMER

Reference in the paper to any specific commercial product, process or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Catalytic Conversion of I at Various Temperatures in the Presence of Iron-Sulfur Catalysts.

Conditions: 25 mg I, ~100 mg 9,10 DHP, 10 wt% (based on I) ferrihydrite, 10 wt% (based on I) sulfur, 1h reaction time.

Reaction Temperature °C	Conversion of I, %			
	no catalyst pretreatment	pretreatment 1h at 200°C	pretreatment 1h at 250°C	pretreatment 1h at 320°C
200	0	0	0	0
250	10	9	0	0
275	31	32	10	-
300	52	54	30	10
320	79	78	48	17
350	92	92	66	38
400	94	93	87	40

Table 2. Catalytic Conversion of I at 320°C as Function of Time.

Time h	Catalytic Conversion % in presence of Pyrrhotite* ~24m ² /g	
		Catalyst from 200°C, 1h pretreatment
0.33	~ 12	45
0.5	13	57
0.66	20	65
1	17	79

* Pyrrhotite obtained after pretreatment for 1h at 320°C.

Table 3. Stability of the Iron-Sulfur System Preformed at 200 °C Reaction of I at 320°C, 1 hour.

Storage Time days	Conversion of I %
0	79
1	79
3	73