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Chemisorption of Sulfur on Thermally Decomposed Copper and Iron Sulfides

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The chemisorption of sulfur on thermally decomposed copper and iron sulfides was studied and its application to the desulfurization process of heavy oil was attemped. Thermal decomposition of sulfides was carried out by calcining CuS and FeS_2 at 200—800 °C under 10^{-3} mmHg and with 5 °C/min. Sulfur was adsorbed on the calcined sulfides in toluene. Thermally decomposed copper sulfide (Cu/S: 1—2) easily chemisorbs free sulfur in toluene below 100 °C, but not iron sulfide (Fe/S: 1—0.5). The relationship between sulfur affinity and the structure of partially decomposed sulfide was discussed in terms of the kinetics of initial chemisorption of sulfur and the sulfur adsorption coefficient calculated from the ratio of the adsorbed sulfur to the sulfur required to reform starting CuS and FeS_2. The partially decomposed copper sulfide ($Cu_{1-2}S$) easily chemisorbs free sulfur in heavy oil. Chemisorption might be applied to the desulfurization of heavy oil.

The colloidal or dissolved sulfur in solvent is gradually oxidized by air, forming sulfur oxides. In industry, the sulfur oxides not only cause the corrosion of steel container or pipe line, but also produce substances harmful to human life. Active carbon or zeolite is used as an adsorbent of sulfur. The adsorption mechanisms of sulfur on active carbon and zeolite are explained by the physical trapping or van der Waals bonding. It is supposed that the thermally decomposed sulfides which partially release sulfur in a vacuum have the defect of sulfur atoms in crystal lattice. Such sulfides are expected to be strong adsorbents of sulfur reforming the chemical bonding of sulfur in defective positions of the crystal.

The partially decomposed sulfide in a vacuum generally has a skelton structure and is active to the reverse reaction, that is, adsorption. The thermal decomposition processes and phase diagrams of CuS and FeS_2 were discussed by Samsonov and Drozdova,[1] and the formation energies of CuS and FeS_2 were reported by Richardson and Jeffes.[2] However, no report seems to have appeared on the thermal decomposition of these sulfides in a vacuum and the chemisorption of sulfur. The relation between the sulfur release from starting sulfide and the chemisorption of sulfur is of interest as regards the development of new sulfur adsorbent.

The major sulfur compounds contained in heavy oil are mercaptan, disulfide and aromatic sulfide as thiophen. These sulfur compounds have analogy to H_2S in the redox-reaction. H_2S is easily oxidized by SO_2 even at room temperature, forming free sulfur. Sulfur compounds in heavy oil are also oxidized by SO_2 gas to sulfur at relatively high temperature or high pressure. Such free sulfur can be easily removed by adsorption on metal sulfide decomposed thermally in a vacuum.

In order to obtain a strong sulfur adsorbent, it is necessary to study the relationship between the various degree of decomposition of sulfide in a vacuum and the rate of chemisorption of sulfur.

Experimental

Preparations of Samples. The mode of the thermal decomposition of CuS and FeS_2 in a vacuum largely depends on the conditions of the preparation of starting materials. A distinct difference was observed between two kinds of CuS precipitated in alkaline and acidic solutions respectively, as regards the decomposition temperature in a vacuum. However, the two kinds of CuS have the same crystal structure.

Precipitation of starting materials was carried out as follows. FeS_2 was prepared by the dry method of Titarenko.[3] CuS was prepared by a wet method. An aqueous solution of Na_2S was added slowly to 10% aq solution of $Cu(NO_3)_2$ with stirring at 25 °C. The resulting precipitate (CuS) was aged on a hot plate for two hours with bubbling of nitrogen gas, filtered, and washed with ethanol, carbon disulfide, and then acetone. The product was kept to dry in a vacuum dessicator.

Thermal Decomposition. Proper calcination temperatures were selected from the results of TG-DTA. The starting FeS_2 or CuS was set in a quartz container in furmace, degassed slowly, and heated at a heating rate of 5 °C/min, under 10^{-3} mmHg, as in the case of TG-DTA. After the desired temperature of the container had been reached, the furnace was removed immediately and the container was cooled from outside with a fan. The samples calcined at various temperatures were subjected to elemental analysis, X-ray powder diffraction, and determination of specific surface area. The data of TG-DTA and specific surface area are shown in Figs. 1 and 2, and the X-ray powder patterns at various temperatures in Figs. 3 and 4. The preferable sulfur adsorbents selected according to the data of sulfur release and crystal structures are given in Table 1.

Elemental Analysis (Determination of Metal/S). In the Lunge method, the sample is dissolved in aqua regia on a steam bath. In order to suppress the formation of insoluble free sulfur, $KClO_3$ or Br_2 is added to the solution as an exhaustive oxidizing agent. In the present experiment, however, the sample was dissolved in nitric acid instead of aqua regia. After the evolution of H_2 gas had ceased, the solution was subjected to centrifugation and the insoluble residue separated was put into a glass tube, the liquid phase being kept for the subsequent procedure. A small amount of nitric acid centrifuged was added to the glass tube and sealed. The sealed tube was set in a micro-autoclave of inner volume of 25 ml. The outside of the tube was filled with water to prevent the breakdown of the glass tube. The autoclave was heated at 250 °C for a few minutes and cooled quickly. After the glass tube had been opened, the contents were added to the solution which had been centrifuged. The combined solution was treated according to a process similar to the Lunge method. Fe^{3+} was determined by colorimetry.[4]

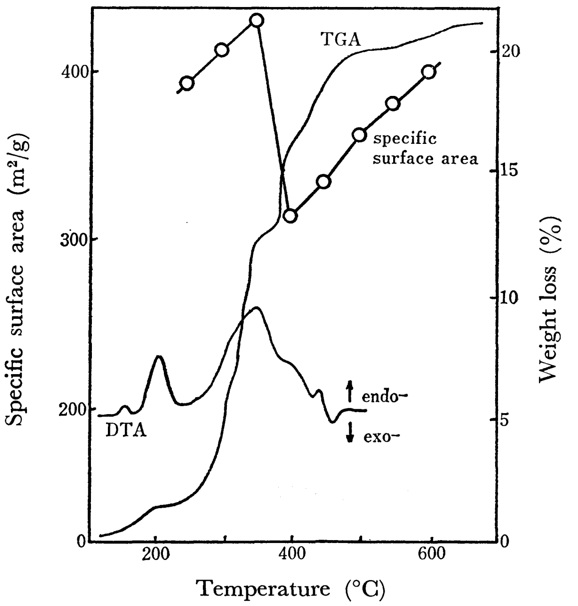

Fig. 1. Thermal decomposition pattern of CuS.

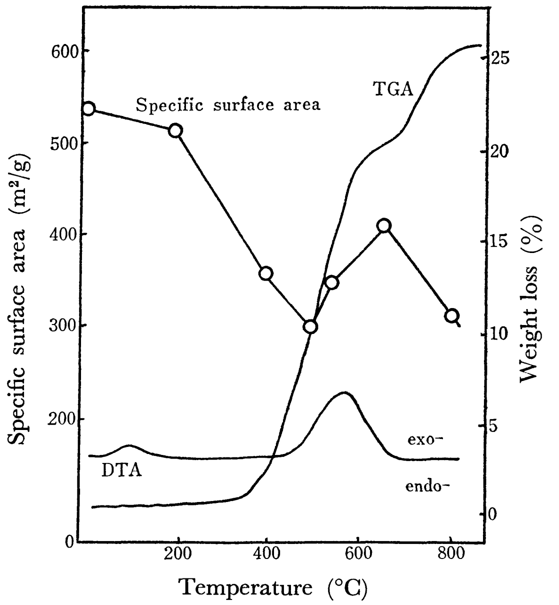

Fig. 2. Thermal decomposition pattern of FeS_2.

Sulfur Adsorption Procedure. The kinetics and quantities of sulfur adsorption were measured as follows.

The thermally decomposed iron sulfide adsorbed no sulfur in toluene under 100 °C. However, it reacted with sulfur vapor in a sealed glass tube at 200—260 °C.

A half gram of the decomposed iron sulfide was put into a glass tube with 0.5 g of sulfur (in excess), the tube then being sealed in a vacuum. This was heated in an electric furnace. After cooling, iron sulfide was washed with ethanol, acetone, and then CS_2, and dried in a vacuum oven. The quantity of the adsorbed sulfur was determined from the weight change and elemental analysis. The crystal structure was identified by means of X-ray diffraction.

The sulfur adsorption on active carbon was carried out as follows. Active carbon (animal charcoal) washed with 20% H_2SO_4 and 5 M NaOH solution was dried, and 1.000 g of the dried active carbon was added to 10 ml of toluene saturated with sulfur. Adsorption was carried out as in the case of copper sulfide.

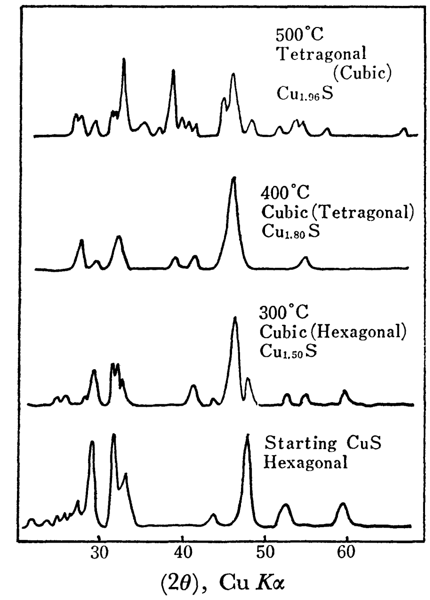

Fig. 3. X-Ray profiles of $Cu_{1-2}S$ at various calcined temperatures.

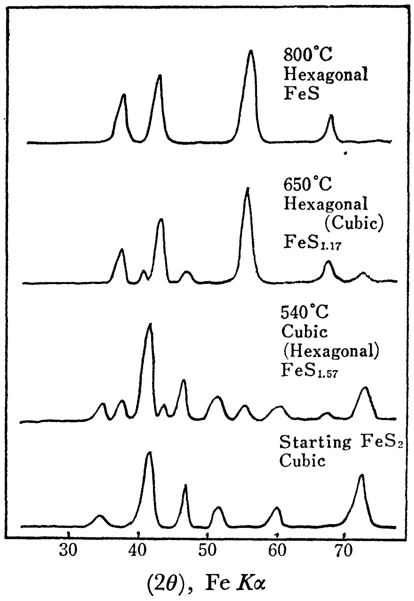

Fig. 4. X-Ray profiles of FeS_{1-2} at various calcined temperatures.

Application Procedure to Desulfurization Process of Heavy Oil. A B-class heavy oil (sulfur content 1.42%) was used as a starting material. The SO_2 gas of 2 kg/cm² and B-class heavy oil of 3 ml were introduced in a micro-autoclave shown in Fig. 5, and heated with stirring in a revolving furnace (Fig. 6) at 300 °C for 15 min. A half gram of thermally decomposed copper sulfide obtained by calcination of CuS in a vacuum at 500 °C for 90 min was added to the resulting heavy oil of 1.5 ml. The mixture was warmed on a water bath at 80 °C with stirring for 60 min. Heavy oil was separated from copper sulfide by filtration. The sulfur content of the heavy oil was determined by JIS K-2541, the desulfurization ratio being calculated. In order to confirm the chemisorption of sulfur, *viz.*, the formation of CuS ($Cu_2S+S=2CuS$), the crystal structure of the resulting copper sulfide was examined by means of X-ray diffraction.

TABLE 1. RATIOS OF METAL/SULFUR AND STRUCTURE AT VARIOUS CALCINED TEMPERATURES FOR SULFUR ADSORPTION

Calcined temp (°C)	Cu/S	Structure
100	1.00	hexagonal
250	1.20	hexagonal, (cubic)[a]
300	1.50	cubic, hexagonal
400	1.80	cubic
500	1.96	cubic, tetragonal
Calcined temp (°C)	**Fe/S**	**Structure**
100	0.50	cubic
540	0.64	cubic, (hexagonal)[a]
650	0.85	hexagonal, (cubic)[a]
800	1.02	hexagonal

a) ( ) is a meaning of small content.

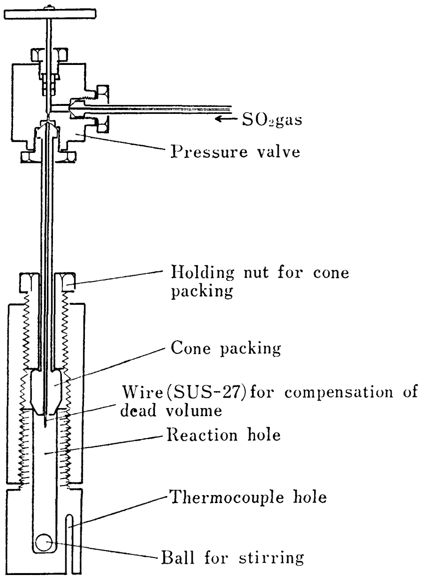

Fig. 5. Cross sectional view of micro-autoclave.

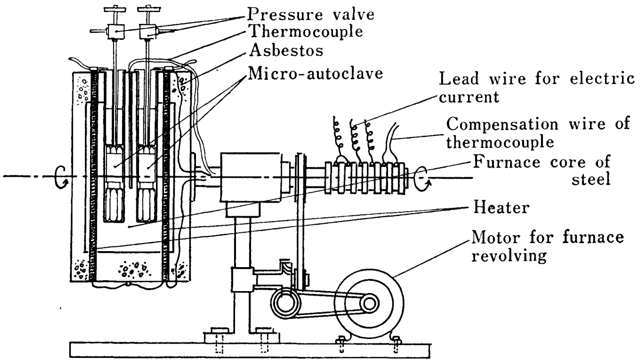

Fig. 6. Schema of revolving furnace.

Results and Discussion

The decomposition of CuS at 200—500 °C in a vacuum (Fig. 1) does not proceed linearly with the rise in temperature because of the existence of metastable state in the temperature range 380—400 °C. The crystal structure in the temperature range is cubic $Cu_{1.80}S$ (Fig. 3). On the other hand, the decomposition of FeS_2 is the constant release of sulfur in vacuum calcination (Figs. 2 and 4).

The ratios of metal/sulfur and the structures of decomposed sulfides at various temperatures are given in Table 1.

Transformation of Structure with Sulfur Chemisorption. The crystal structures of partially decomposed sulfides vary with sulfur adsorption (Figs. 7 and 8). The figures show that the process of sulfur chemisorption is opposite that of thermal decomposition in a vacuum. The tetragonal $Cu_{1.96}S$ calcined at 500 °C adsorbs sulfur 100 °C, forming hexagonal CuS through cubic $Cu_{1.80}S$. The X-ray profiles of Figs. 7 and 8 for the final product adsorbed sulfur show that the half value width of the X-ray peaks is about twice that of the starting CuS before thermal decomposition, and the crystalline size of the final product of copper sulfide is smaller than that of the starting materials. The results suggest that the starting CuS particles break in a vacuum at high temperature, new CuS particles being formed.

In the case of iron sulfide the chemisorption of sulfur occurs at high temperature above 200 °C, proceeding continuously.

Sulfur Adsorption Coefficient. The sulfur adsorption coefficient was calculated by means of the equation

$$K = (S_2/S_1) \times 100,$$

where K is adsorption coefficient, S_1 the amount of sulfur required to form starting sulfides CuS and FeS_2, and S_2 the amount of the adsorbed sulfur estimated from weight change and mole ratio of sulfur/metal by chemical analysis.

These coefficients increase with rise in adsorption temperature (Figs. 9 and 10). These data and results of X-ray anlysis (Figs. 7 and 8) show that the sulfur adsorption cause $Cu_{1.80}S$ or CuS. The adsorption is the reverse of the thermal decomposition of sulfide in a vacuum. Sulfur release is very small in copper sulfide calcined at 200 °C, and the sulfur adsorption coefficient (approximately 90% even at room temperature) is large as shown in Fig. 9. This suggests that the number of the empty site which can adsorb sulfur is small. However, the sample has a strong affinity to sulfur.

All the curves of adsorption coefficient for the samples calcined at above 300 °C are of similar form. This suggests that the mechanisms of sulfur adsorption at 400 and 500 °C are similar.

The adsorption temperatures of thermally decomposed copper sulfides are relatively lower than those of iron sulfides (Figs. 9 and 10). These results agree with those in which the formation energies for CuS and FeS_2 are −66.5 and +32 kcal/mol, respectively. The formation energy of CuS is endothermic, but that of FeS_2 is exothermic. The formation of CuS from $Cu_{1-2}S$ (released sulfur partially) occurs at relatively low temperature.

Activation Energies on Sulfur Adsorption. In general, the specific surface area is estimated by means of powder activity. In this experiment the copper

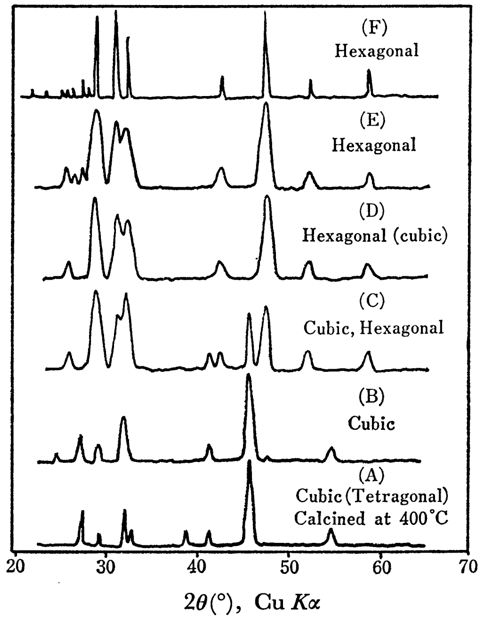

Fig. 7. X-Ray profiles of $Cu_{1-2}S$ at various sulfur adsorption temperatures of starting $Cu_{1.80}S$.
Adsorption time: 60 min, solvent: toluene.
A: Starting $Cu_{1.80}S$(calcined at 400 °C), B: adsorption temperature 25 °C, C: adsorption temperature 50 °C, D: adsorption temperature 75 °C, E: adsorption temperature 100 °C, F: $Cu_{1.00}S$(before thermal decomposition).

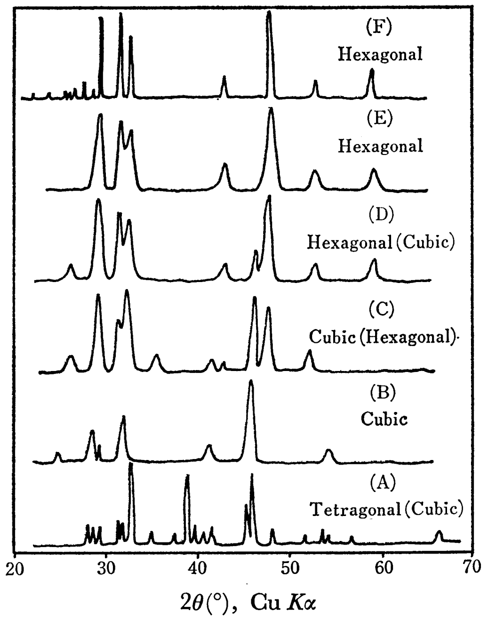

Fig. 8. X-Ray profiles of $Cu_{1-2}S$ at various sulfur adsorption temperatures of starting $Cu_{1.96}S$.
Adsorption time: 60 min, solvent: toluene.
A: Starting $Cu_{1.96}S$(calcined at 500 °C), B: adsorption temperature 25 °C, C: adsorption temperature 50 °C, D: adsorption temperature 75 °C, E: adsorption temperature 100 °C, F: $Cu_{1.00}S$(before thermal decomposition).

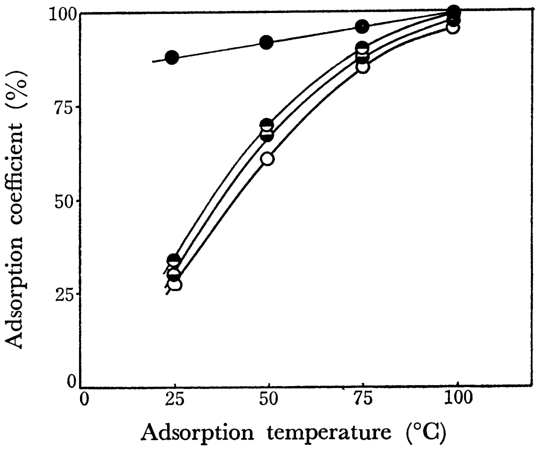

Fig. 9. Adsorption coefficient at various adsorption temperature (Comparison between different calcination temperature about $Cu_{1-2}S$).
Calcination temperature, ●: 250 °C, ◓: 300 °C, ◒: 400 °C, ○: 500 °C.

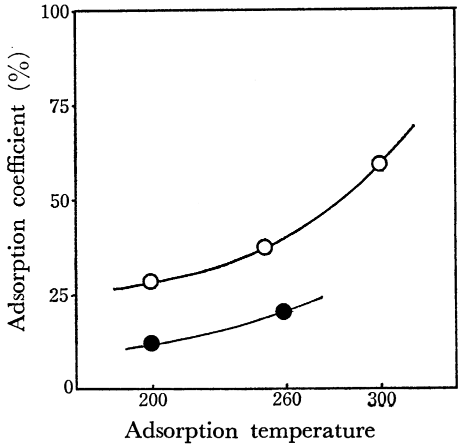

Fig. 10. Comparison of sulfur adsorption coefficient of FeS_{1-2} between different calcination temperature of 540 (○) and 800 °C (●).

sulfide sample calcined at 400 °C gave the same adsorption coefficient as the one at 500 °C, but their crystal structures differ. Activation energies for sulfur adsorption were calculated from the adsorption kinetics of copper sulfides calcined at 400 and 500 °C and of iron sulfides calcined at 540 and 800 °C. The Arrhenius plots of sulfur adsorption on copper and iron sulfides are shown in Figs. 11 and 12, respectively. The activation energies of copper sulfides are 12.7 and 9.7 kcal/mol for the two calcination temperatures. The results show that the sample calcined at 400 °C is more stable than the one calcined at 500 °C. This suggests that the thermally decomposed sample which is more stable on thermal decomposition is less active for the reverse reaction, that is, sulfur adsorption. The specific surface area is an important factor for the facility of sulfur adsorption. The crystal strain or distortion seems to influence the sulfur adsorption. In order to estimate the effect of the surface area on reactivity, the activity of partially decomposed sulfide was defined as the product of unit formula weight per specific surface area and reciprocal of activation energy. The values estimated for copper sulfides calcined at 400 and 500 °C are 1.73×10^{-6} and 1.83×10^{-6} mol^2/kcal·m^2, respectively. This suggests

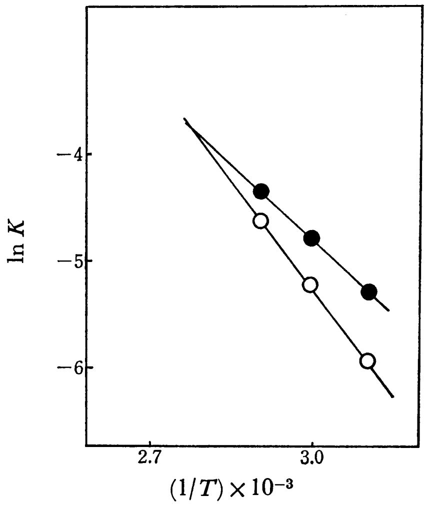

Fig. 11. Arrhenius plots of sulfur adsorption rates of $Cu_{1.80}S$, (○, calcined at 400 °C) and $Cu_{1.96}S$, (●, calcined at 500 °C).

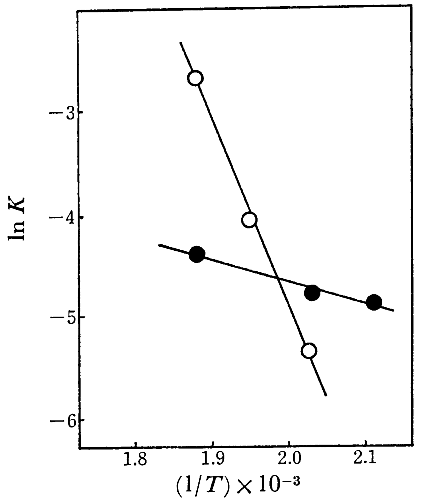

Fig. 12. Arrhenius plots of sulfur adsorption rates of $Fe_{0.64}S$ (○, calcined at 540 °C) and $Fe_{1.02}S$ (●, calcined at 800 °C).

that the sample calcined at 400 °C (cubic $Cu_{1.80}S$) is more stable than that calcined at 500 °C (mixed structure of cubic and tetragonal). Arrhenius plots of sulfur adsorption on iron sulfides calcined at 540 and 800 °C are shown in Fig. 12. The activation energies are 36.9 and 4.3 kcal/mol, respectively. This suggests that different adsorption mechanisms exits for the two species of iron sulfides. The sample calcined at 800 °C, in which the number of empty sites for bonding sulfur is large, has a low activation energy for the sulfur adsorption. This suggests that the diffusion of sulfur vapor is the rate-determing step in the adsorption kinetics.

Comparison with Active Carbon Used. The sulfur adsorbed on active carbon was washed out completely with CS_2. The amount of adsorbed sulfur was negligible. In the case of thermally decomposed copper sulfides the bond between sulfur and copper is chemical, but not that between sulfur and carbon.

Table 2. COMPARISON OF DESULFURIZATION PERCENTAGE BETWEEN TWO DIFFERENT TREATMENTS OF B-CLASS HEAVY OIL BEING OXIDIZED WITH SO_2 GAS IN AUTOCLAVE

Treatment	Sulfur content (%)	Desulfurization percentage
No treatment	1.61	−13.4
Washing out with 5% H_2O_2	1.25	+12.0
Adsorption by $Cu_{1.96}S$	1.13	+20.4

Table 3. BLANK TEST WITHOUT SO_2 GAS TREATMENT

Treatment	Sulfur content (%)
No treatment (starting B-class heavy oil)	1.42
Washing out with 5% H_2O_2	1.24
Adsorption by $Cu_{1.96}S$ at atmospheric pressure	1.43
Adsorption by $Cu_{1.96}S$ with heating in micro-autoclave	1.37

Sulfur Adsorption in Heavy Oil on Thermally Decomposed Sulfide. A comparison of the sulfur contents and the desulfurization percentage of heavy oil by different treatment is given in Table 2. The heavy oil oxidized only with SO_2 has a higher sulfur content 1.61%, its desulfurization percentage being negative (−13.4%). The heavy oil washed with 5% H_2O_2 shows a 1.25% sulfur content decrease, the desulfurization percentage increasing by 12%. Asdorption on thermally decomposed copper sulfide ($Cu_{1.96}S$) gave the lowest sulfur content (1.13%) and the highest desulfurization percentage (20.4%). Results of a blank test without SO_2 gas treatment are given in Table 3. Adsorption by $Cu_{1.96}S$ as an adsorbent indicates 1.43% sulfur, almost the same value as in the case of no treatment. A comparison of the data given in Tables 2 and 3 shows the obvious effect of SO_2 on desulfurization. However, at 300 °C in an autoclave the sulfur content shows a slight decrease (Table 3). In copper sulfide after adsorption treatment partial existence of Cu(II)S was observed by means of X-ray diffraction (Table 2). It seems that the thermally decomposed copper sulfide does not react with sulfur compounds in heavy oil, but reacts with the free sulfur formed by SO_2 oxidation in heavy oil. The desulfurization percentage 20% is low for practical use. However, a higher percentage is expected by selection of temperature, pressure, mixing mole ratio, and by repetition of SO_2 oxidation and adsorption.

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