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# The Reduction of Sulfuric Acid by Hydrogen on Activated Carbon Impregnated with Copper Sulfate

Akira KATAGIRI,* Kiyoshi WATANABE,† and Shiro YOSHIZAWA**

*Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606*

*** Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606*

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The reduction of sulfuric acid has been studied for the purpose of the regeneration of activated carbon, which is used as an acceptor of sulfur dioxide from exhaust gas. When activated carbon impregnated with sulfuric acid was heated in a hydrogen atmosphere, sulfuric acid was reduced to sulfur dioxide by carbon in the temperature range from 200 °C to 350 °C. When copper sulfate was added, the sulfuric acid was reduced to sulfur dioxide, mainly by hydrogen, in the temperature range from 190 °C to 270 °C. At 227 °C, for example, the rate of reduction by hydrogen was nine times greater than the rate of reduction by carbon. Copper sulfate was sufficiently effective in an amount of one-fifth of the sulfuric acid in moles, indicating that copper in some form participates in the catalytic reaction.

Activated carbon can be used as an acceptor of sulfur dioxide from exhaust gas emitted by the combustion of fossil fuels. When exhaust gas which contains sulfur dioxide, oxygen, and water vapor is passed through a column of activated carbon, the sulfur dioxide is catalytically oxidized on carbon, according to Eq. 1, to sulfuric acid, which is then accumulated in the micropores of carbon:

$$SO_2 + 1/2O_2 + H_2O \longrightarrow H_2SO_4. \qquad (1)$$

The kinetics and mechanism of this reaction have been investigated by several groups of workers.[1—10] Since the rate of the reaction decreases as the amount of sulfuric acid increases, the sulfuric acid must be removed periodically in order to recover the catalytic activity of carbon. Several methods have been proposed for this purpose. One of them is to remove the sulfuric acid as sulfur dioxide by heating it in an inert gas, where the following reaction takes place:[1,2]

$$H_2SO_4 + 1/2C \longrightarrow SO_2 + 1/2CO_2 + H_2O. \qquad (2)$$

This method has the advantage that sulfur dioxide is obtained in a concentration high enough to be used directly for a sulfuric acid plant. However, it has the disadvantage of consuming the carbon. Another method is to reduce the sulfuric acid to elemental sulfur by the following two steps:[11,12]

$$H_2SO_4 + 3H_2S \longrightarrow 4S + 4H_2O \qquad (3)$$

$$3H_2 + 3S \longrightarrow 3H_2S. \qquad (4)$$

Reactions 3 and 4 proceed at 150 °C and 540 °C respectively. In this method, 3 mol of hydrogen are needed per mol of sulfuric acid in the over-all reaction.

Another process has also been investigated, in which a copper-alumina absorbent is used as an acceptor of sulfur dioxide and is regenerated by hydrogen.[13,14] Reactions 5 and 6 occur in the absorption step at 400 °C, and Reaction 7 occurs in the regeneration step at 400 °C. In this process, 2 mol of hydrogen are needed per mol of sulfur dioxide recovered.

$$Cu + 1/2O_2 \longrightarrow CuO \qquad (5)$$

$$CuO + SO_2 + 1/2O_2 \longrightarrow CuSO_4 \qquad (6)$$

$$CuSO_4 + 2H_2 \longrightarrow Cu + SO_2 + 2H_2O \qquad (7)$$

The reduction of sulfuric acid by hydrogen (Eq. 8) is even more favorable, because only 1 mol of hydrogen is consumed per mol of sulfur dioxide recovered.

$$H_2SO_4 + H_2 \longrightarrow SO_2 + 2H_2O \qquad (8)$$

Although Reactions 2 and 8 are both thermodynamically possible, the second one can be conducted preferentially if an appropriate catalyst is used. The aim of the present work is to test the catalytic effect of copper on this reaction.

It has previously been reported[3,5] that, when Reaction 1 takes place on activated carbon at temperatures from 50 °C to 140 °C, the concentration of sulfuric acid formed is the equilibrium one which depends upon the water-vapor concentration in the gas phase. For example, 73 wt% $H_2SO_4$ is formed at 100 °C at the water-vapor concentration of 6 vol %. In such an acidic medium and in the presence of oxygen, copper would exist in the form of sulfate. Thus, copper sulfate was used as the catalyst component in this work.

## Experimental

*Apparatus and Procedure.* Granular activated carbon, which had been impregnated with sulfuric acid with or without copper sulfate, was heated in a stream of nitrogen or hydrogen at a constant or linearly increasing temperature, while the evolved gas was analyzed.

The apparatus used is shown in Fig. 1. A Pyrex tube, 23 mm in inner diameter, was used as a reactor; in it an activated carbon sample (13 g) was packed to a length of 9 cm. The reactor was placed in an electric heater. The temperature of the catalyst was controlled so as to increase at the rate of 2 °C/min using a chromel–alumel thermocouple and a temperature-programming unit. In some experiments, the temperature was kept constant. The flow rate of the gas was kept constant at 100 cm$^3$/min.

*Preparation of Samples.* Commercially available activated carbon (4 mm$\phi$ × 6 mm, cylindrical, BET surface area 1170 m$^3$/g), made from coconut shell, was used for all the experiments. The activated carbon was impregnated under reduced pressure with an aqueous sulfuric acid containing 20 g of $H_2SO_4$ per 100 cm$^3$, or with a solution containing 20 g of $H_2SO_4$ and 20 g of $CuSO_4 \cdot 5H_2O$ per 100 cm$^3$, and then dried at 100 °C for 2 h. These samples contained 0.76 mmol of $H_2SO_4$ per g of carbon and, if added, 0.15 mmol of $CuSO_4$ per g of carbon. Other samples containing

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† Present address: Research Laboratories of Osaka Soda Co., Ltd., 9 Otakasu-cho, Amagasaki 660.

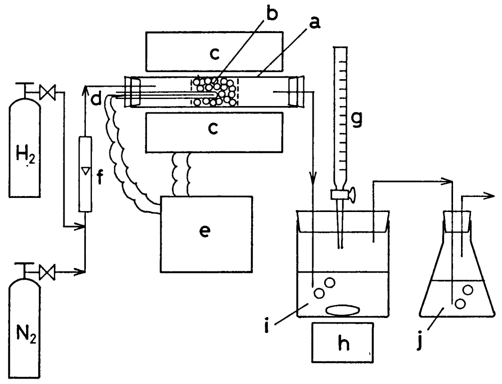

Fig. 1. Experimental apparatus.
a: Reactor (Pyrex), b: activated-carbon, c: electric heater, d: thermocouple, e: temperature-programing unit, f: flow meter, g: buret (1 mol dm$^{-3}$ NaOH), h: magnetic stirrer, i: 6 wt% $H_2O_2$ solution, j: 0.025 mol dm$^{-3}$ $Ba(OH)_2$ solution.

different amounts of copper sulfate were also prepared.

*Analysis of Evolved Gas.* The amount of sulfur dioxide evolved was measured as a function of the time, according to the method reported by Kamino *et al.*[2] The outflow gas from the reactor was passed through a 6 wt% hydrogen peroxide solution, and the solution was titrated at appropriate intervals with a standard solution of sodium hydroxide, using a mixed solution of Methyl Red and Methylene Blue as an indicator.[††]

The total amount of carbon dioxide evolved was determined as follows: after the removal of the sulfur dioxide, the outflow gas was introduced into a 0.025 mol dm$^{-3}$ barium hydroxide solution, in which carbon dioxide was absorbed. The solution was made free from barium carbonate by filtration, and then it was titrated with 0.1 mol dm$^{-3}$ hydrochloric acid. The amount of carbon dioxide absorbed was calculated from the decrease in the concentration of barium hydroxide during each run.

The formation of hydrogen sulfide was checked qualitatively by introducing the outflow gas directly into a silver nitrate solution and looking for a black precipitate of $Ag_2S$. The formation of elemental sufur was checked by visual inspection, because even a small amount of sulfur could be detected by means of a yellowish-white deposit at the outlet of the reactor. To confirm the results of the above tests, the gravimetric determination of hydrogen sulfide and elemental sulfur was also done by a method described elsewhere.[15]

## Results and Discussion

Activated carbon containing 0.76 mmol of $H_2SO_4$ per g of carbon was heated in a stream of nitrogen or hydrogen under an increasing temperature, while the amount of sulfur dioxide evolved was measured. As is shown by Curves a and b in Fig. 2, which represent the cumulative amount of sulfur dioxide as a function of the increasing temperature, the evolution of sulfur dioxide occurred in the temperature range from 200 °C to 350 °C. This temperature range is in good agreement with that reported for Reaction 2 by other workers.[1,2] Curves c and d show similar results for activated carbon containing 0.76 mmol of $H_2SO_4$ and 0.15 mmol of $CuSO_4$ per g of carbon. In the case of the nitrogen atmosphere (Curve c), the evolution of sulfur dioxide took place in almost the same temperature range as above. In the case of the hydrogen atmosphere (Curve d), the evolution of sulfur dioxide began at 190 °C and was completed at 270 °C. We supposed that Curves a, b, and c correspond to Eq. 2, and Curve d, to Eq. 8. To verify this supposition, the amounts of sulfur dioxide and carbon dioxide evolved were determined in the same runs. The results are shown in Table 1. The mole ratio of $CO_2/SO_2$ was about 0.5 in the cases in which an activated carbon sample not containing copper sulfate was heated in the hydrogen atmosphere, and in which a sample containing copper sulfate was heated in the nitrogen atmosphere. These results indicate that Reaction 2 took place almost exclusively. On the contrary, the mole ratio of $CO_2/SO_2$ was much smaller when the sample containing copper sulfate was heated in the hydrogen atmosphere, indicating that Reaction 8 took place predominantly. Hydrogen sulfide and elemental sulfur were not detected in any of the above cases.

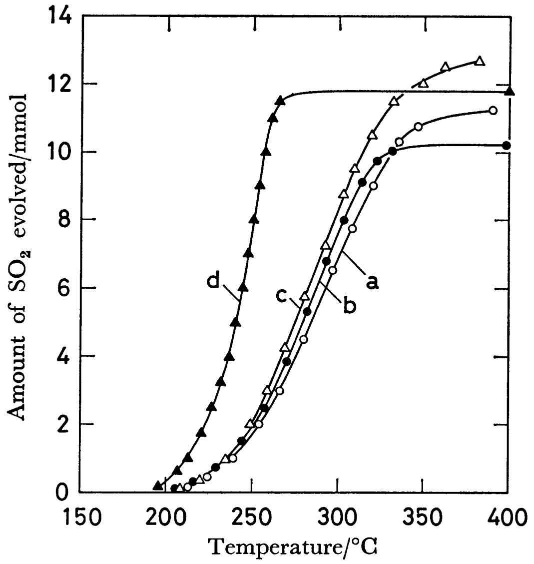

Fig. 2. Relationships between amount of $SO_2$ evolved and temperature under different conditions.
Atmosphere; ○,△: $N_2$, ●,▲: $H_2$, addition of $CuSO_4$; ○,●: None, △,▲: 0.15 mmol/g-carbon, heating rate: 2 °C/min.

Table 1. The amounts of $SO_2$ and $CO_2$ evolved

| Experimental conditions | | Evolved gases/mmol | |
|---|---|---|---|
| Atmosphere | $CuSO_4$ | $SO_2$ | $CO_2$ |
| $H_2$ | Not added | 12.0 | 5.03 |
| $N_2$ | Added[a)] | 11.6 | 5.44 |
| $H_2$ | Added[a)] | 10.0 | 1.20 |

Temperature range: Room temperature—400 °C. Heating rate: 2 °C/min. a) 0.15 mmol/g-carbon.

The amounts of carbon dioxide and sulfur dioxide

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[††] As the color of this indicator changes from purple to green at pH 5.4, neither carbon dioxide nor hydrogen sulfide, if present, affects the results of titration.

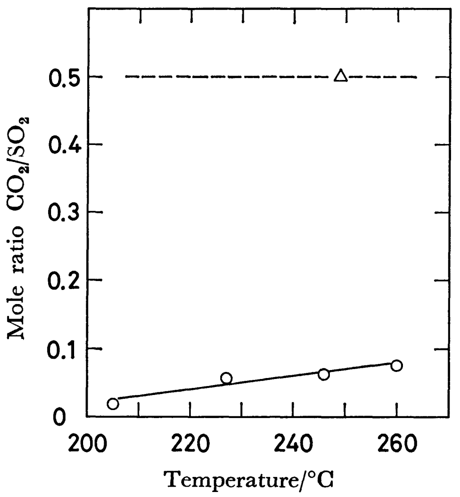

Fig. 3. Mole ratio $CO_2/SO_2$ in the evolved gas at constant temperatures (The broken line shows the mole ratio expected from Eq. 2).
Amount of $CuSO_4$ added: 0.15 mmol/g-carbon, atmosphere; △: $N_2$, ○: $H_2$.

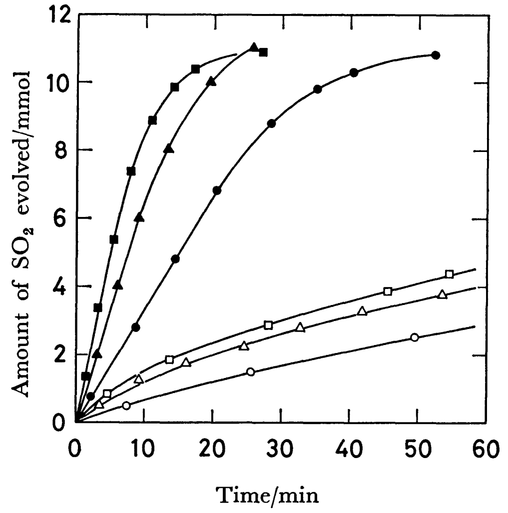

Fig. 4. Relationships between amount of $SO_2$ evolved and time at constant temperatures.
○,△,□: Without addition of $CuSO_4$, ●,▲,■: with addition of $CuSO_4$ (0.15 mmol/g-carbon), temperature; ○: 224 °C, △: 244 °C, □: 253 °C, ●: 221 °C, ▲: 244 °C, ■: 250 °C.

evolved were also measured at constant temperatures, using activated carbon samples which contained copper sulfate. Figure 3 shows the mole ratio of $CO_2/SO_2$ which was obtained when the sample was heated in the nitrogen or hydrogen atmosphere. In the case of the nitrogen atmosphere, the mole ratio was 0.5, as would be expected from Eq. 2. The mole ratio was much smaller in the case of the hydrogen atmosphere, but increased slightly with an increase in the temperature. This indicates that the rate of Reaction 2 increases more rapidly with an increase in the temperature than that of Reaction 8. Since the reduction of sulfuric acid is considered to proceed only according to Eqs. 2 and 8, of the total amount of sulfuric acid the fraction which is reduced by carbon

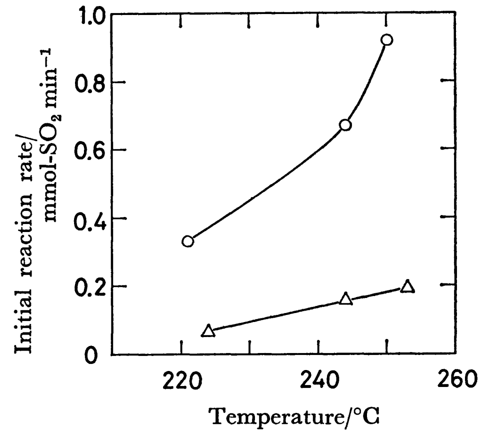

Fig. 5. Initial reaction rates with and without addition of $CuSO_4$.
△: Without addition of $CuSO_4$, □: with addition of $CuSO_4$.

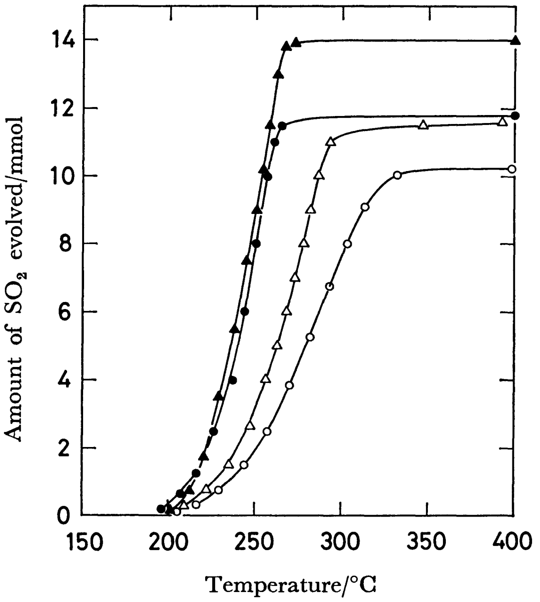

Fig. 6. Relations between amount of $SO_2$ evolved and temperature for different amounts of $CuSO_4$ added. Amount of $CuSO_4$ added (mmol/g-carbon); ○: 0, △: 0.015, ●: 0.15, ▲: 0.52, heating rate: 2 °C/min.

is simply twice the mole ratio of $CO_2/SO_2$. At 227 °C, for example, the contribution of Reaction 2 to the total amount of sulfuric acid reduced was 10%, and that of Reaction 8 was 90%.

The rate of reduction of sulfuric acid was also studied at constant temperatures. Figure 4 shows the cumulative amount of sulfur dioxide, which was evolved at constant temperatures, as a function of the time. Figure 5 shows the initial reaction rate, which was determined from the initial slope of the curve in Fig. 4. The rate of the evolution of sulfur dioxide was much higher in the presence of copper sulfate than in its absence at the same temperatures. The Arrhenius plot of the initial reaction rate gives the apparent activation energies of 83 kJ/mol in the absence of copper sulfate and 73 kJ/mol in its presence. These values are regarded as approximately corresponding to Reactions 2 and 8 respectively, and they indicate that the contribution of Reaction 2 should increase as the temperature increases. This conclusion is consistent with the result that the mole ratio of $CO_2/SO_2$ increases with an increase in the temperature, as is shown by the solid line in Fig. 3. Judging from the values of the activation energy, the transport processes are not the rate-determining steps in either reaction.

The effect of the amount of copper sulfate was also studied, using activated carbon impregnated with a constant amount of sulfuric acid, but with different amounts of copper sulfate. It may be seen from Fig. 6 that the addition of 0.15 mmol-$CuSO_4$/g-carbon is sufficient for Reaction 8 to occur under these conditions. This amount of copper sulfate is about one-fifth that of the sulfuric acid in moles. Therefore, it is supported that copper in some state has a cataytic effect on Reaction 8.

## Concluding Remarks

It was found that sulfuric acid is reduced by hydrogen on activated carbon with copper sulfate at temperatures from 190 °C to 270 °C. A succeeding paper will describe metals other than copper as catalysts, and will discuss the catalytic mechanisms.

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