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The Reduction of Sulfuric Acid by Hydrogen on Various Metal-Carbon Catalysts

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The reduction of sulfuric acid, which is formed on the activated carbon catalyst in the course of removing sulfur dioxide from exhaust gas, was investigated. The platinum, palladium, silver, and copper on activated carbon were found to be catalytically active in the reduction of sulfuric acid by hydrogen, while manganese, iron, cobalt, nickel, and zinc were found to be inactive. The copper–carbon catalyst is favorable, because sulfuric acid was reduced selectively to sulfur dioxide on it at temperatures from 190 °C to 270 °C. On the platinum–carbon catalyst, the reduction occurred at a relatively low temperature (140 °C to 200 °C), but hydrogen sulfide and elemental sulfur were formed in addition to sulfur dioxide. It is concluded from thermodynamic calculations that catalytically active metals were in the metallic state on activated carbon under the present reaction conditions. An electrochemical mechanism is proposed for the reaction.

In the course of removing sulfur dioxide from exhaust gas by using the activated carbon catalyst, sulfuric acid is formed and accumulated on the catalyst. As a method for removing the sulfuric acid and regenerating the catalyst, Reaction 1 seems to be suitable,

$$H_2SO_4 + H_2 \longrightarrow SO_2 + 2H_2O \quad (1)$$

because the sulfur dioxide obtained can be used directly for sulfuric acid production. However, other side reactions such as Reactions 2, 3, and 4, may possibly occur. For example, the standard Gibbs energy change, ΔG°, for reactions 1, 2, 3, and 4 at 500 K

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

$$H_2SO_4 + 3H_2 \longrightarrow S + 4H_2O \quad (3)$$

$$H_2SO_4 + 4H_2 \longrightarrow H_2S + 4H_2O \quad (4)$$

are −133.0 kJ/mol, −110.8 kJ/mol, −271.5 kJ/mol, and −311.8 kJ/mol respectively.[1] It was reported in a previous paper[2] that, when copper sulfate was added, Reaction 1 took place on activated carbon, with only a small consumption of carbon due to Reaction 2. It was suggested that copper in a certain state exerts a catalytic effect on Reaction 1 selectively. In the present paper, experimental results on several metals other than copper as a catalyst component are described, and a possible mechanism of the catalysis is discussed.

Experimental

Apparatus and Procedure. Granular catalysts were heated in a stream of hydrogen under the condition of a linearly increasing temperature, and the gas thus evolved was analyzed. The apparatus used was described in the previous paper.[2] A Pyrex tube 23 mmϕ in inner diameter was used as the reactor, in which catalyst was packed to a length of *ca.* 9 cm. The amount of catalyst packed in was *ca.* 13 g in the case of activated carbon and *ca.* 15 g or 20 g in the case of activated alumina. The catalyst temperature was controlled so that it increased at the rate of 2 °C/min. The flow rate of hydrogen was held constant at 100 cm^3/min. Under these conditions it was easy to follow the amount of sulfur dioxide evolved, and the linearity of the temperature with the time was relatively good.

Preparation of Catalysts. Commercial activated carbon (4 mmϕ × 6 mm cylindrical) made from coconut shell was used for these experiments. The activated carbon was impregnated with aqueous sulfuric acid, together with or after the addition of each metal component, and then dried at 100 °C for 2 h. Manganese, iron, cobalt, nickel, copper, and zinc were added to the carbon by impregnating it with a mixed solution of sulfuric acid and the respective sulfates. Platinum, palladium, and silver were added to the carbon in advance by impregnating it with aqueous solutions of hexachloroplatinic(IV) acid, palladium(II) chloride, and silver nitrate respectively, and by then heating it in a hydrogen atmosphere at 400 °C, where these salts were reduced to metals. The content of the metal or the metal ion was controlled so as to be *ca.* 9 mg/g carbon in all cases. In the case of the copper–carbon catalyst, this amount was sufficient as a catalyst component.[2] The amount of sulfuric acid was *ca.* 0.8 mmol/g carbon. This amount was chosen on the basis of the practical data in a pilot-plant test performed by Kamino *et al.*,[3] where 0.7—1.6 N m^3 of sulfur dioxide was adsorbed by 57 kg of activated carbon per hour.

Activated alumina (3 mmϕ spherical) was also used in place of activated carbon. In this case, the metal content was *ca.* 8 mg/g alumina, and the amount of sulfuric acid impregnated was *ca.* 0.7 mmol/g alumina.

Analysis of Gas Evolved. The amount of sulfur dioxide in the outflow gas from the reactor was determined by passing the gas through a hydrogen peroxide solution and by titrating the solution at appropriate intervals with a sodium hydroxide solution.[2] The total amounts of hydrogen sulfide and of elemental sulfur evolved were determined gravimetrically in the other runs, as follows: the outflow gas from the reactor was introduced directly into an acidic solution of silver nitrate, in which silver sulfite, silver sulfide, and elemental sulfur were precipitated. After the filtration of these precipitates, the silver sulfite was removed by washing with an aqueous ammonia solution, and then the elemental sulfur was dissolved in carbon disulfide. The weight of the remaining silver sulfide was measured, from which the amount of hydrogen sulfide evolved was calculated. Since solid sulfur was also deposited at the outlet of the reactor, it was dissolved in carbon disulfide and the solution thus obtained was put together with the former one. After the evapolation of the solvent, the weight of the solid sulfur was measured.

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Results and Discussion

Activated carbons containing sulfuric acid and various metals or metal sulfates were heated in a stream of hydrogen under the condition of an increasing temperature, while the amount of sulfur dioxide evolved was followed. The results are shown in Fig. 1. When platinum, silver, palladium, or copper was added to activated carbon, the evolution of sulfur dioxide was observed in a lower temperature range than in the case of simple activated cabon. These metals are considered to catalyze Reaction 1. In the cases of platinum–, silver–, and palladium–carbon catalysts, the contribution of Reaction 2 must be smaller, if there is any at all, than in the case of the copper–carbon catalyst, because the rate of this reaction depends upon the temperature, but not upon the presence of metal.[2] When manganese, iron, cobalt, nickel, or zinc was added, the evolution of sulfur dioxide was observed in the same temperature range as in the case of simple activated carbon. In these cases, it was likely that not Reaction 1, but Reaction 2 took place exclusively. A comparison of the total amount of sulfur dioxide evolved was rather difficult because of the poor reproducibility of the initial amount of sulfuric acid impregnated. However, the curve for the platinum–carbon catalyst in Fig. 1 differs apparently from the others, indicating that sulfur dioxide was not the only product. In fact, a yellow deposit was observed at the outlet of the reactor in this case.

In order to see whether carbon in itself plays any role in Reaction 1, similar experiments were carried out by using activated alumina in place of activated carbon. Figure 2 shows the results on copper–alumina and copper–carbon catalysts, as well as on simple activated alumina and activated carbon. The evolution of sulfur dioxide took place on the copper–alumina catalyst in a temperature range *ca.* 100 °C higher than in the case of the copper–carbon catalyst. This fact indicates that carbon also participates in the catalysis in Reaction 1. A similar result was obtained for the platinum–alumina catalyst, where the evolution of sulfur dioxide occurred mainly in the temperature range from 300 °C to 450° C. Incidentally, the total amount of sulfur dioxide evolved was almost the same in Fig. 2, although the initial amount of sulfuric acid on the alumina catalysts was about 1.3 times larger than that on the carbon catalysts.

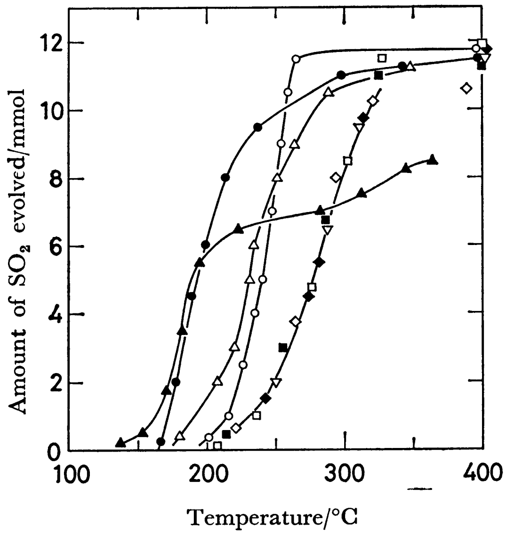

Fig. 1. Relations between amount of sulfur dioxide evolved and temperature for various metal-carbon catalysts.
Metal or metal sulfate added; ▽: $MnSO_4$, □: $FeSO_4$, ■: $CoSO_4$, ◇: $NiSO_4$, ○: $CuSO_4$, ◆: $ZnSO_4$, ●: Ag, △: Pd, ▲: Pt. Weight of packed catalyst: 13 g.

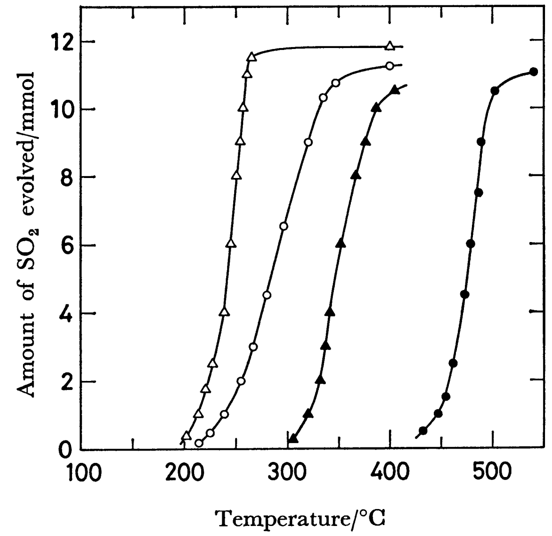

Fig. 2. Relations between amount of sulfur dioxide evolved and temperature for copper–alumina (▲), copper–carbon (△), simple alumina (●), and simple carbon (○) catalysts. Weight of packed catalyst ▲,●: 20 g, △,○: 13 g.

Since it is possible that sulfuric acid is reduced by hydrogen to elemental sulfur and further to hydrogen sulfide, the amounts of these products were determined in the cases of the platinum–, silver–, and copper–carbon catalysts and the copper–alumina catalyst. As is shown in Table 1, a considerable amount of hydrogen sulfide was formed on the platinum–carbon catalyst, together with a small amount of elemental sulfur. On the silver–carbon catalyst, a small amount of hydrogen sulfide was formed. To the contrary, neither of these products was detected in the case of the copper–carbon catalyst. Considerable amounts

TABLE 1. THE AMOUNTS OF SO_2, S, AND H_2S EVOLVED

Catalyst	Weight of packed catalyst	Evolved gases/mmol		
	g	SO_2	S	H_2S
Platinum-carbon[a]	13	8.5	0.3	3.5
Silver-carbon[a]	13	10.0	0.0	0.2
Copper-carbon[a]	13	10.5	0.0	0.0
Copper-alumina[b]	15	6.0	0.8	4.1

Temperature range: a) Room temperature to 400 °C. b) Room temperature to 500 °C. Heating rate: 2 °C/min.

of hydrogen sulfide and elemental sulfur were formed on the copper–alumina catalyst, which is used in commercial plants of the flue-gas desulfurization process (Shell Process).[4,5] This catalyst seems to be suitable for the purpose of recovering elemental sulfur in combination with the Claus process.

In order to infer the actual state of each metal component under the reaction conditions, the standard Gibbs energy change, ΔG°, for Reaction 5 was calculated from the thermodynamic data.[1]

$$M_{2/n}SO_4 + H_2 \longrightarrow (2/n)M + H_2SO_4 \tag{5}$$

Here, "n" indicates the ionic valence of the metal, M. As is shown in Table 2, the values of ΔG° calculated for silver and copper have a negative sign. This suggests that these metals exist in the metallic state under the present reaction conditions. There is no doubt that platinum and palladium are also in the metallic state, though the necessary data are not available. The other metals in Table 2 have positive values of ΔG°, indicating that these metals exist as sulfates. It is probable that catalytically active metals are in the metallic state, while inactive metals are in the ionic state.

TABLE 2. THE STANDARD GIBBS ENERGY CHANGE, ΔG° (kJ/mol), FOR REACTION 5

$M_{2/n}SO_4$	Temperature/K			
	300	400	500	600
$MnSO_4$	267.4	272.2	276.2	280.2
$FeSO_4$	135.1	141.3	146.6	152.0
$CoSO_4$	70.9	76.5	82.0	88.0
$NiSO_4$	87.4	91.4	95.2	99.5
$CuSO_4$	−29.1	−24.7	−21.2	−17.5
$ZnSO_4$	182.7	188.3	193.2	198.3
Ag_2SO_4	−71.5	−63.1	−55.5	−47.8

It may be noted in Fig. 1 that, when the added metal has a lower hydrogen overvoltage, the evolution of sulfur dioxide takes place in the lower temperature range. Thus, the sequence of hydrogen overvoltage at 25 °C,[6] $Pt<Pd<Ag<Cu$, agrees substantially with the sequence of the temperature range in which the reaction occurs, $Pt<Ag<Pd<Cu$.[††] Considering that the hydrogen overvoltage is a measure of the electrocatalytic activity of metal in the hydrogen-evolution reaction, and that sulfuric acid is a liquid electrolyte at temperatures below 337 °C, the following electrochemical mechanism is proposed for Reaction 1:

$$H_2 \longrightarrow 2H^+ + 2e^- \tag{6}$$

$$H_2SO_4 + 2H^+ + 2e^- \longrightarrow SO_2 + 2H_2O. \tag{7}$$

Thus, the anodic reaction Eq. 6, proceeds on metal, and the cathodic reaction, Eq. 7, on cabon. Reaction 7 is the reverse of that proposed in the catalytic oxidation of sulfur dioxide on activated carbon.[7,8] When the added metal has a low hydrogen overvoltage, Reaction 6 is catalyzed by the metal: therefore, the total reaction, Eq. 1, can occur at a relatively low temperature. In contrast, alumina has no electric conductivity; therefore, Reaction 7 cannot proceed on alumina. Probably, then the catalytic reduction of sulfuric acid on the copper- or platinum–alumina catalyst occurs by another mechanism.

The standard electromotive force of the hypothetical cell composed of Reactions 6 and 7 is calculated as 0.689 V at 500 K. If the overvoltage for Reaction 6 on the catalyst surface is greater than 0.689 V at 500 K, it is impossible for these reactions to occur at this temperature. This is the case with the simple activated carbon. Thus, one of the present authors has previously investigated the kinetics of Reaction 6 at various electrodes in the eutectic melt of lithium chloride and potassium chloride in relation to the hydrogen–chlorine fuel cell;[9] he found that the overvoltage at the carbon electrode was greater than 0.84 V at 773 K. At the temperature of 500 K, the overvoltage must be much greater. This may be the reason why Reaction 1 does not take place on the simple activated carbon.

It has been reported that sulfur dioxide, hydrogen sulfide, and elemental sulfur were produced in the electrolysis of concentrated sulfuric acid at moderately high temperatures, and that the distribution of the products depended strongly on the temperature.[10,11] Besides, the kinetics and mechanism of the electrode reaction are possibly dependent on the electrode potential. In the catalytic reduction of sulfuric acid in the present work, also, it is probable that the distribution of the products is determined by the reaction temperature and the local potential on the catalyst surface, both of which are dependent on the electrocatalytic activity of the metal added.

Conclusion

It is concluded that the copper–carbon catalyst is the best for the purpose of recovering sulfur dioxide from the reduction of sulfuric acid by hydrogen. This catalyst is not likely to be poisoned by sulfide formation, because copper on carbon may become ionic in the oxidizing atmosphere in the step of sulfuric-acid formation, and then be reduced to metal in the reduction step, cyclically.

References

1) I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag (1973).

2) A. Katagiri, K. Watanabe, and S. Yoshizawa, *Bull. Chem. Soc. Jpn.*, **54**, 1 (1981).

3) Y. Kamino, S. Onitsuka, K. Yasuda, and S. Inoue, *Bull. Jpn. Petrol. Inst.*, **14**, 135 (1972).

4) D. H. McCrea, A. J. Forney, and J. G. Myers, *J. Air Pollution Control Assoc.*, **20**, 819 (1970).

5) F. M. Dautzenberg, J. E. Nader, and A. J. J. van Ginneken, *Chem. Eng. Prog.*, **67**[8], 86 (1971).

6) N. Kameyama, "Denkikagaku No Riron Oyobi Ōyō," Maruzen (1963), Vol. 1.

7) A. Katagiri, Z. Takehara, and S. Yoshizawa, *Denki Kagaku*, **41**, 430 (1973).

8) A. Katagiri, C. Inazumi, Z. Takehara, and S. Yoshizawa, *Nippon Kagaku Kaishi*, **1975**, 1471.

9) S. Yoshizawa, Z. Takehara, and H. Katsuya, *Denki Kagaku*, **32**, 519 (1964).

10) H. Hoffmann, *Z. Elektrochem.*, **27**, 442 (1921).

11) F. Beck, *Electrochim. Acta*, **17**, 2317 (1972).

[††] Palladium seems to be out of order in these two sequences. This may be ascribed either to the specific temperature dependency of its activity, or to the discrepancy of the mechanisms of hydrogen-electrode reaction on it at low and high temperatures.