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The Study of Thermochemical Hydrogen Preparation. III.[1] An Oxygen-evolving Step through the Thermal Splitting of Sulfuric Acid

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The thermal decomposition of sulfuric acid is used as a step in the oxygen evolution in some thermochemical water-splitting cycles. The catalytic activity of metal oxides was studied in an attempt to find some suitable catalysts for sulfuric acid decomposition. The catalytic activity of SiO_2, Al_2O_3, ZnO, CuO, NiO, CoO, Fe_2O_3, MnO, Cr_2O_3, V_2O_5, TiO_2 was measured at high temperatures (800—870 °C) and at atmospheric pressure. Iron(III) oxide was found to have the highest activity as a catalyst. Low catalytic activity was observed for the oxides (Al_2O_3, ZnO, NiO, CoO, MnO) which change to their sulfates under the present reaction conditions. Since the reaction conditions were very severe (more than 800 °C and in the presence of steam), a rapid decrease in both the specific surface area and the catalytic activity was observed. In order to avoid these disadvantages and in order to prepare practically useful catalysts, iron(III) oxide was pelletized and sintered (1000 °C, 6 h). Upon this procedure, this catalyst showed an almost constant activity for 120 hours' reaction.

Among the many thermochemical water-splitting cycles[2–5] proposed thus far, the following cycle is thought to be one of the most promising ones. The most difficult problem of this cycle is, though, how to separate the hydroiodic acid from the sulfuric acid in Reaction 1:

$$I_2 + 2H_2O + SO_2 \longrightarrow H_2SO_4 + 2HI, \qquad (1)$$

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

$$2HI \longrightarrow H_2 + I_2. \qquad (3)$$

Three solutions have been proposed for this problem by the present authors[1] and by others.[6–10]

The most simple solution is to omit Reaction 3 and to replace Reaction 1 by a Reaction 4 evolving hydrogen by electrolysis.[1,6–8,10] In this case, the electric power will be reduced to one-third of that needed in the electrolysis of water:

$$2H_2O + SO_2 \xrightarrow{\text{electrolysis}} H_2SO_4 + H_2. \qquad (4)$$

Another solution was proposed by Russel *et al.*[9] They tried to separate hydroiodic acid from sulfuric acid by adding a large amount of iodine to the reaction mixture of Reaction 1, and then to separate it into two liquid phases.

The present authors showed the possibility of performing Reaction 1 as a cell reaction using a cation-exchange membrane, which serves as a diaphragm and a separator of hydroiodic acid and sulfuric acid at the same time.[1]

In every case, Reaction 2 serves as an oxygen-evolving reaction. The decomposition of sulfur trioxide seemed feasible when studied by Spewock *et al.*;[8] however, the composition of the catalyst has not been reported:

$$SO_3 \longrightarrow SO_2 + 1/2O_2. \qquad (5)$$

Moreover, there exists a difference between Reactions 2 and 5; that is, steam is also present in Reaction 2 and not in Reaction 5. Thus, in the latter case, one more process step will be needed before Reaction 5 — the dehydration of sulfuric acid.

In this paper, the catalytic activities of various metal oxides have been studied for Reaction 2.

Experimental

The experimental system is shown in Fig. 1. To find out the most suitable chemical species for use as the catalyst for Reaction 2, the reaction vessel, C, was used. The same volume ($2.8\ \text{cm}\phi \times 0.4\ \text{cm} = 2.5\ \text{ml}$) of powder oxides of Si, Al, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, and Ti were put in the reaction vessel, C. These oxides were all guaranteed reagents and were commercially available. The 60 wt% sulfuric acid was used as a reactant, as the concentration of sulfuric acid yielded in Reaction 1 could be expected to be 60 wt% on the basis of another experiment.[1] The sulfuric acid was introduced into the reaction vessel, C, which was kept at 820 ± 10 °C or 860 ± 10 °C, by the use of a microfeeder at the rate of 0.85 ± 0.04 ml/min. The reaction mixture, consisting of unreacted gaseous sulfuric acid, sulfur dioxide, and oxygen, was then cooled to room temperature at the cold trap, and the unreacted sulfuric acid was condensed out. The sulfur dioxide and oxygen gas mixture was washed with a sodium hydroxide solution, in which the sulfur dioxide was absorbed almost completely (less than 0.1 %); the amount of oxygen evolved per unit of time was measured by means of a conventional gas meter.

The decomposition of sulfuric acid with the sintered iron(III) oxide catalyst was carried out by the use of the same

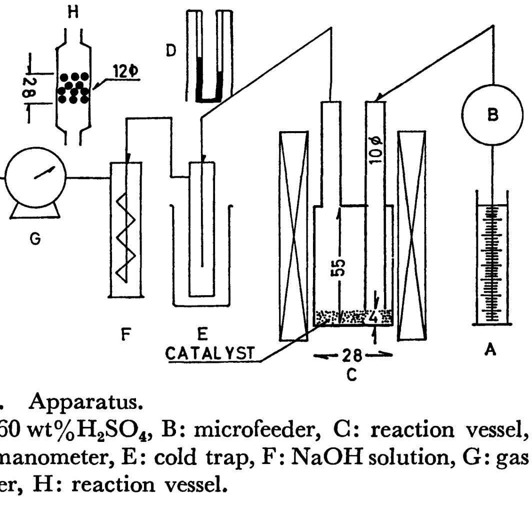

Fig. 1. Apparatus.
A: 60 wt%H_2SO_4, B: microfeeder, C: reaction vessel, D: manometer, E: cold trap, F: NaOH solution, G: gas meter, H: reaction vessel.

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apparatus as in Fig. 1, except that the reaction vessel, C, was replaced by the vessel, H, as may be seen in the figure. The volume of the catalyst bed was 1.2 cm$\phi \times 2.8$ cm$=3.2$ ml. The iron(III) oxide catalyst was prepared as follows: iron(III) oxide powder was pressed at 5 tons/cm^2 into cylindrical pellets 4 cm in diameter and 1 cm in height. These pellets were sintered at 1000 °C for 6 h, and then crushed. Particles of 2—4 mm were used as the catalysts. The other procedure was almost the same as has been described above, except for the feeding rate of sulfuric acid.

Results and Discussion

Some typical results on the iron(III) oxide powder catalyst are shown in Fig. 2, where the amount of oxygen evolved per unit of time is plotted against the time. The rapid increase and decrease in the reaction rate observed at the initial stage at 820 °C was due to the time lag, during which the evolved sulfur dioxide and oxygen replaced the air in the experimental system. As may be seen in Fig. 2, the amount of oxygen evolved per unit of time gradually decreased with the reaction time at 860 °C. Such a tendency was observed with almost all kinds of chemical species the catalytic activity of which was examined.

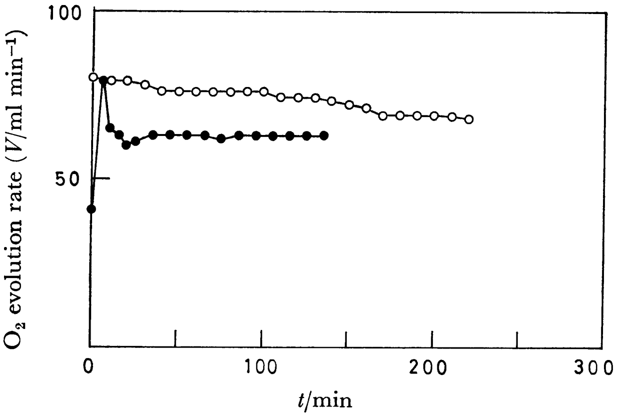

Fig. 2. The change of catalytic activity of Fe_2O_3 with time.
● 820 °C, ○ 865 °C.

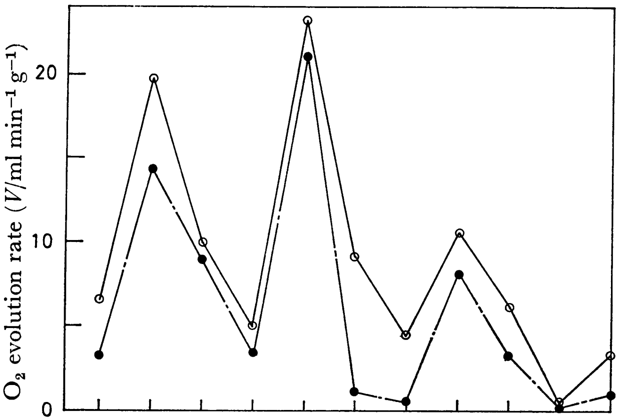

Fig. 3. The comparison of activity per unit weight of various oxides.
● 820±10 °C, ○ 860±10 °C.

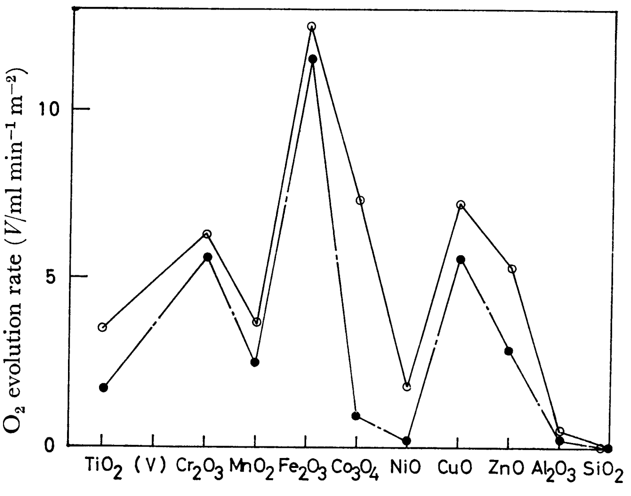

Fig. 4. The comparison of activity per specific surface area of various oxides.
● 820±10 °C, ○ 860±10 °C.

In Figs. 3 and 4, the amount of oxygen evolved per unit of time is plotted against the metal oxides used as catalysts. The ordinates of Figs. 3 and 4 are the amount of oxygen evolved per unit of time per unit of weight of the catalyst and the amount of oxygen evolved per unit of time per unit of the specific surface area, respectively. In Fig. 4, the value for vanadium(V) oxide is omitted because vanadium(V) oxide is a liquid at these reaction temperatures. Here, the amount of oxygen evolved per unit of time 4—5 h after the initiation of the reaction was chosen as the representative value of the amount of oxygen evolved per unit of time for each oxide. As may be seen from these results, iron(III) oxide has the highest activity among the oxides used.

Table 1. The crystal structure and specific surface area of catalysts

Catalyst		Surface area S/m^2 g^{-1}	
Original	Used	Original	Used
TiO_2	rutile≫ anatase	2.50	1.86
V_2O_5	V_2O_5	—	fused
Cr_2O_3	eskolaite	3.10	1.58
MnO_2	$MnSO_4$	31.8	1.43
Fe_2O_3	Fe_2O_3	9.21	1.85
Fe_3O_4	Fe_2O_3	—	—
SiO_2(am)	SiO_2(am)	655.0	95.5
Co_3O_4	Co_3O_4, CoO α-$CoSO_4$	0.88	1.24
CoO	Co_3O_4, CoO α-$CoSO_4$	—	—
NiO	NiO $NiSO_4$	0.42	2.48
CuO	CuO≫ CuO(SO_4)	1.84	1.48
ZnO	$ZnSO_4$ $Zn_5O_2(SO_4)_3$ $Zn_3O_2(SO_4)_2$	5.26	1.15
α-Al_2O_3	α-Al_2O_3 $Al_2(SO_4)_3$	6.20	1.41

As may be seen in Table 1, the speicfic surface area and the crystal structure of the catalysts used changed during the reaction. The specific surface area decreased except in the cases of cobalt(II) oxide and nickel(II) oxide. This fact and the gradual decrease in the amount of oxygen evolved per unit of time are noteworthy for the practical preparation of catalysts.

The oxides of Al, Zn, Ni, Co, and Mn, which were found as sulfates after the reaction (Table 1), showed low catalytic activity, as can be seen in Figs. 3 and 4. Among the active oxides (V, Cr, Cu, and Fe), iron(III) oxide was chosen as a candidate for catalyst for practical use, considering the cost of the catalyst and the environmental safety.

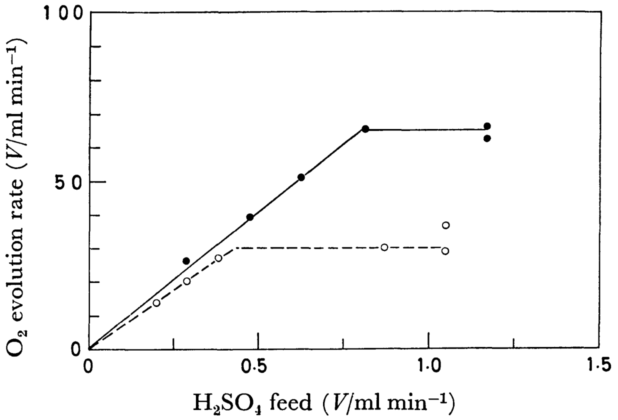

Fig. 5. The dependence of oxygen evolution rate upon the feeding rate of H_2SO_4.
○ 800 °C, ● 850 °C.

Five g of well-sintered particles of iron(III) oxide were used for each reaction, having been placed in the reaction vessel, H, shown in Fig. 1. In Fig. 5, the amount of oxygen evolved per unit of time *vs.* the feeding rate of the sulfuric acid is plotted. A linear dependence of the amount of oxygen evolved per unit of time on the feeding rate below 0.5 or 0.8 ml/min at 800 °C or 850 °C was observed. These results indicate that the space velocities based on the sulfur dioxide and oxygen gas produced are 560 ml/ml-catalyst-h (800 °C) and 1200 ml/ml-catalyst-h (850 °C). Their conversion were 69 and 79% respectively. On the basis of these results, the feeding rates of sulfuric acid at 1.1 ml/min (800 °C) and 1.3 ml/min (850 °C) were chosen as the feeding rates for the following experiments.

In Fig. 6, the results of the long-time examination of the stability of catalyst at 800 °C and 850 °C are shown. In each case, an increase of activity was observed around 25 hours' reaction. After that increase, the iron(III) oxide catalyst showed a constant activity up to 120 h. The specific surface area of the catalysts used were compared with those of the original ones; the results are summarized in Table 2. At 800 °C, an increase in the specific surface area was observed with the catalyst which was used for 28 hours' reaction (open square in Fig. 6); then the specific surface area of the catalyst remained substantially constant up to 120 h (solid square in Fig. 6). At 850 °C, the specific surface area still increased from 28 hours' reaction up to 120 h.

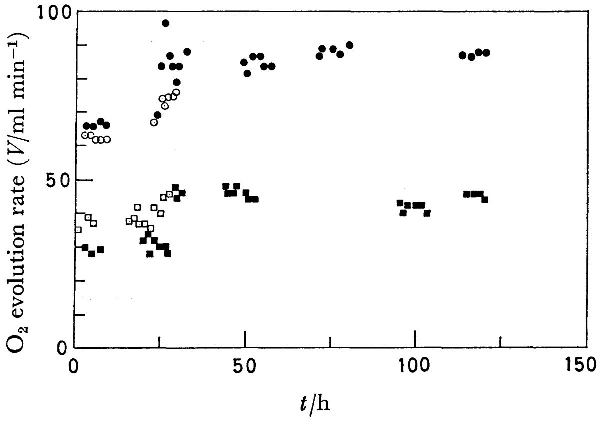

Fig. 6. The change of catalytic activity of sintered Fe_2O_3 with time.
□,■ 800 °C, ○,● 850 °C.

Table 2. The specific surface area of ferric oxide catalysts

	Surface area S/m^2 (5 g)$^{-1}$		
	Original	Used 28 h	Used 120 h
850 °C	2.20	3.09	6.41
800 °C	2.20	2.80	2.74

No sulfate species were observed by means of X-ray diffractometry. However, it was observed that a few particles changed color from violet to red and that the crushing strength of the pellets was lowered in spite of the fact that their shape did not change at all.

From these results, the authors concluded that, from a practical stand point, the well-sintered iron(III) oxide catalyst has a high possibility of being utilized in the sulfuric acid thermal splitting reaction. The next problem may be whether this catalyst can be applied for a long term or not (for example, one year's operation), because of the necessary reaction conditions of a high temperature and the presence of steam. Silica or alumina would not be proper for a catalyst support, as they are not stable enough under the reaction conditions described above, as is shown in Table 1.

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