

THE ENHANCEMENT OF ACID STRENGTH AND CATALYTIC ACTIVITY OF  $\text{SnO}_2$  BY  
THE ADDITION OF SULFATE ION

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The addition of about 3 wt% of sulfate ion to  $\text{SnO}_2$  caused the enhancement in the acid strength from  $H_0 = +3.3$  to  $-8.2$ . The catalytic activity of  $\text{SnO}_2 + \text{SO}_4^{2-}$  for the isomerization of cyclopropane at  $100^\circ\text{C}$  was found to be higher than 100 times that of simple  $\text{SnO}_2$  for the same reaction at  $300^\circ\text{C}$ . The effect of sulfate ion was remarkable also for the dehydration of 2-butanol.

The activity enhancement of metal oxide catalysts by the addition of sulfate ion for acid catalyzed reactions has been recently observed for  $\text{TiO}_2$ ,<sup>1,2)</sup>  $\text{ZrO}_2$ ,<sup>3)</sup> and  $\text{Fe}_2\text{O}_3$ .<sup>4,5)</sup> The catalytic activities of the other oxides such as  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{ThO}_2$ , and  $\text{Bi}_2\text{O}_5$  are reported to be unaffected by the addition of sulfate ion.<sup>6)</sup> In the present work,  $\text{SnO}_2$  has been found to be a forth oxide whose acid strength as well as activity is enhanced by the addition of a small amount of sulfate ion.

The  $\text{SnO}_2$  catalyst was prepared by calcining  $\text{Sn}(\text{OH})_4$  in air at  $500^\circ\text{C}$  for 2.5 h. The  $\text{Sn}(\text{OH})_4$  was obtained by the hydrolysis of an aqueous 10% solution of anhydrous  $\text{SnCl}_4$  (Wako Pure Chemical Industries Ltd., guaranteed reagent) with 28% ammonia water (the final pH of solution = 8-9), followed by aging the precipitates at  $85-90^\circ\text{C}$ , washing with deionized water until no chloride ion was detected in the washing and drying at  $100^\circ\text{C}$  for 24 h. The  $\text{SnO}_2$  catalyst including  $\text{SO}_4^{2-}$  was prepared by immersing the  $\text{Sn}(\text{OH})_4$  in a solution of  $(\text{NH}_4)_2\text{SO}_4$  and evaporating it to dryness, followed by drying at  $110^\circ\text{C}$  for 24 h and then calcining at  $500^\circ\text{C}$  for 2.5 h. The content of  $\text{SO}_4^{2-}$  was 2.9 wt%. The surface areas of  $\text{SnO}_2$  and  $\text{SnO}_2 + \text{SO}_4^{2-}$  were measured by the B.E.T. method.

The acid strength of the catalysts in benzene<sup>7)</sup> or in a vacuum<sup>8)</sup> was determined by using various basic indicators. The strength measured in benzene was the same as that measured in a vacuum, though the color intensity of the acidic form indicator was less in the former than in the latter.

The isomerization of cyclopropane was carried out at 100 or 300°C by using a closed recirculation apparatus of 789 ml capacity. About 100 Torr of cyclopropane was introduced over 0.4g of catalyst evacuated at 500°C for 2 h. The decomposition of 2-butanol was carried out at 150 or 200°C by using a microcatalytic pulse reactor. About 0.1g of catalyst pretreated in a helium stream (20 ml/min) at 500°C for 2 h was used. The reaction products of both reactions were analyzed by gas chromatography.

The surface areas and the highest acid strengths of SnO<sub>2</sub> and SnO<sub>2</sub>+SO<sub>4</sub><sup>2-</sup> were 31.6 and 84.3 m<sup>2</sup>/g, and +3.3 and -8.2(H<sub>0</sub>), respectively. Namely, the addition of 2.9 wt% SO<sub>4</sub><sup>2-</sup> to SnO<sub>2</sub> caused the increase in the surface area by less than three times, and the remarkable enhancement in the acid strength by 11 units in H<sub>0</sub> scale.

The effect of SO<sub>4</sub><sup>2-</sup> on the catalytic activity for the isomerization of cyclopropane is also remarkable as shown in Table 1.

Table 1. The Effect of SO<sub>4</sub><sup>2-</sup> on Isomerization of Cyclopropane

Catalyst	Reaction temperature/°C	Rate of conversion/10 <sup>-5</sup> mol g <sup>-1</sup> min <sup>-1</sup>
SnO <sub>2</sub>	300	0.034
SnO <sub>2</sub> +SO <sub>4</sub> <sup>2-</sup>	100	4.25

The rate of conversion at 100°C over SnO<sub>2</sub>+SO<sub>4</sub><sup>2-</sup> was higher than 100 times that at 300°C over simple SnO<sub>2</sub>.

The results for the decomposition of 2-butanol are shown in Table 2.

Table 2 The Effect of  $\text{SO}_4^{2-}$  on Decomposition of 2-Butanol<sup>a)</sup>

Catalyst	Reaction temp. /°C	Conversion / %		cis-/trans- <sup>b)</sup>
		to butenes	to ethyl methyl ketone	
$\text{SnO}_2$	200	0	32.9	—
$\text{SnO}_2 + \text{SO}_4^{2-}$	150	61.1	2.2	1.35
$\text{SnO}_2 + \text{SO}_4^{2-}$	200	86.3	3.8	0.78

a) Pulse size; 1  $\mu\text{l}$  for  $\text{SnO}_2$ , 4  $\mu\text{l}$  for  $\text{SnO}_2 + \text{SO}_4^{2-}$ .

b) Ratio of cis-2-butene to trans-2-butene in produced butenes.

Over the  $\text{SnO}_2$  catalyst, the dehydrogenation of 2-butanol which is known to be catalyzed mainly by bases occurred appreciably, but the dehydration which is known to be catalyzed by acids did not take place. However, the dehydration predominated over the dehydrogenation on the addition of  $\text{SO}_4^{2-}$ . This is considered due to the enhancement of acid strength. The ratios of cis-2-butene to trans-2-butene in the butenes produced by the dehydration were 0.78-1.35. The values which are usually obtained in the dehydration of 2-butanol catalyzed by acids<sup>9)</sup> also indicate the acidic nature of  $\text{SnO}_2 + \text{SO}_4^{2-}$ .

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