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THE ENHANCEMENT OF ACID STRENGTH AND CATALYTIC ACTIVITY OF SnO_2 BY THE ADDITION OF SULFATE ION

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The addition of about 3 wt% of sulfate ion to SnO_2 caused the enhancement in the acid strength from H_0=+3.3 to -8.2. The catalytic activity of $SnO_2+SO_4^{2-}$ for the isomerization of cyclopropane at 100°C was found to be higher than 100 times that of simple SnO_2 for the same reaction at 300°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 TiO_2,[1,2] ZrO_2,[3] and Fe_2O_3.[4,5] The catalytic activities of the other oxides such as MgO, CaO, CuO, ZnO, CdO, Al_2O_3, La_2O_3, MnO_2, ThO_2, and Bi_2O_5 are reported to be unaffected by the addition of sulfate ion.[6] In the present work, 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 SnO_2 catalyst was prepared by calcining $Sn(OH)_4$ in air at 500°C for 2.5 h. The $Sn(OH)_4$ was obtained by the hydrolysis of an aqueous 10% solution of anhydrous $SnCl_4$ (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°C, washing with deionized water until no chloride ion was detected in the washing and drying at 100°C for 24 h. The SnO_2 catalyst including SO_4^{2-} was prepared by immersing the $Sn(OH)_4$ in a solution of $(NH_4)_2SO_4$ and evaporating it to dryness, followed by drying at 110°C for 24 h and then calcining at 500°C for 2.5 h. The content of SO_4^{2-} was 2.9 wt%. The surface areas of SnO_2 and $SnO_2+SO_4^{2-}$ were measured by the B.E.T. method.

The acid strength of the catalysts in benzene[7)] or in a vacuum[8)] 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_2 and $SnO_2+SO_4^{2-}$ were 31.6 and 84.3 m^2/g, and +3.3 and -8.2(H_0), respectively. Namely, the addition of 2.9 wt% SO_4^{2-} to SnO_2 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_0 scale.

The effect of SO_4^{2-} on the catalytic activity for the isomerization of cyclopropane is also remarkable as shown in Table 1.

Table 1. The Effect of SO_4^{2-} on Isomerization of Cyclopropane

Catalyst	Reaction temperature/°C	Rate of conversion/10^{-5} mol g^{-1} min^{-1}
SnO_2	300	0.034
$SnO_2+SO_4^{2-}$	100	4.25

The rate of conversion at 100°C over $SnO_2+SO_4^{2-}$ was higher than 100 times that at 300°C over simple SnO_2.

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

Table 2 The Effect of SO_4^{2-} on Decomposition of 2-Butanol[a)]

Catalyst	Reaction temp. /°C	Conversion / %		cis-/trans-[b)]
		to butenes	to ethyl methyl ketone	
SnO_2	200	0	32.9	——
$SnO_2 + SO_4^{2-}$	150	61.1	2.2	1.35
$SnO_2 + SO_4^{2-}$	200	86.3	3.8	0.78

a) Pulse size; 1 μl for SnO_2, 4 μl for $SnO_2 + SO_4^{2-}$.

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

Over the 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 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[9)] also indicate the acidic nature of $SnO_2+SO_4^{2-}$.

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