PRONOUNCED EFFECT OF SULFATE ION ON CATALYTIC ACTIVITY OF ZrO<sub>2</sub>-SnO<sub>2</sub> FOR ISOMERIZATION OF CYCLOPROPANE

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The catalytic activity of  $\text{ZrO}_2-\text{SnO}_2$  containing 3 wt% of sulfate ion for the isomerization of cyclopropane has been found to be pronouncedly higher than that of a pure  $\text{ZrO}_2-\text{SnO}_2$  and even higher than those of  $\text{ZrO}_2$  and  $\text{SnO}_2$  which contain 3 wt% of sulfate ion.

The enhancement of catalytic activities for acid-catalyzed reactions on the addition of  $SO_4^{2-}$  has been reported for certain metal oxides such as  $TiO_2$ , <sup>1,2)</sup>  $ZrO_2$ , <sup>3)</sup>  $Fe_2O_3$ , <sup>4)</sup> and  $SnO_2$ . <sup>5)</sup> The high catalytic activities are considered to be due to the generation of strong acid sites on the addition of  $SO_4^{2-}$ . In fact, the acid strengths of  $ZrO_2+SO_4^{2-}$ ,  $TiO_2+SO_4^{2-}$ , and  $SnO_2+SO_4^{2-}$  were estimated to be H<sub>0</sub>= -16.04, <sup>3)</sup> -14.52, <sup>2)</sup> and -8.2, <sup>5)</sup> respectively, according to the indicator method. Thus, the former two are called solid super acids. In the present work, the effect of  $SO_4^{2-}$  on the catalytic activity of  $ZrO_2-SnO_2$  for the isomerization of cyclo-propane which is known to be catalyzed by acids was studied.

Zirconium oxide,  $\text{SnO}_2$ , and  $\text{ZrO}_2-\text{SnO}_2$  were prepared from aqueous solutions of  $\text{ZrOCl}_2$ ,  $\text{SnCl}_4$ , and  $\text{ZrOCl}_2+\text{SnCl}_4$ , respectively, by precipitation with ammonia water, followed by washing with deionized water and drying at 100°C for 24 h and then calcining at 500°C for 2.5 h. The oxides including  $\text{SO}_4^{2-}$  were prepared by immersing the hydroxides in solutions of  $(\text{NH}_4)_2\text{SO}_4$  and evaporating them to dryness, followed by drying at 110°C for 24 h and calcining at 500°C for 2.5 h. The content of  $\text{SO}_4^{2-}$  was 2.9 wt%. The surface areas were measured by the B.E.T. method.

The isomerization of cyclopropane was carried out at 100 or 300°C by using a closed recirculation apparatus of 789 ml capacity. About 10 Torr cyclopropane was introduced over 0.4 g of catalyst evacuated at 500°C for 2 h. The reaction product was analyzed by gas chromatography.

The catalytic activities of  $\text{ZrO}_2$ ,  $\text{ZrO}_2-\text{SnO}_2$  of different compositions, and  $\text{SnO}_2$  with and without the addition of 2.9 wt%  $\text{SO}_4^{2-}$  are shown in Table 1, where the surface areas of the catalysts are also given. The activities per unit surface area of  $\text{ZrO}_2-\text{SnO}_2$  (9:1), (7:3), (1:1), (3:7) and (1:9) with  $\text{SO}_4^{2-}$  at 100°C of reaction temperature were 7, 140, 9, 6, and 22 times higher than those of the catalysts without  $\text{SO}_4^{2-}$  at 300°C of reaction temperature, respectively. The activity of  $\text{ZrO}_2-\text{SnO}_2$  (7:3) containing  $\text{SO}_4^{2-}$  was about 3 and 2 times higher than those of  $\text{ZrO}_2+$   $\text{SO}_4^{2-}$  which was reported previously.<sup>5</sup> The isomerization reaction did not take place at 100°C over the catalysts without  $\text{SO}_4^{2-}$ , while the reaction rate was too

Catalyst (atomic ratio)	Surface area m <sup>2</sup> g <sup>-1</sup>	Reaction temp. °C	Activity <sup>a)</sup> 10 <sup>-5</sup> mol min <sup>-1</sup> g <sup>-1</sup>		
Zr0,	47.8	300	0.098 (0.21)		
$2ro_2^{+}so_4^{2-}$	113	100	2.48 (2.19)		
$2rO_{2}^{-}SnO_{2}^{-}(9:1)$	80.3	300	0.65 (0.81)		
$2rO_{2}^{2}-SnO_{2}^{2}(9:1)+SO_{4}^{2}$	102	100	5.80 (5.69)		
$2rO_{2} - SnO_{2}(7:3)$	72.6	300	0.034 (0.05)		
$2rO_{2}^{2}-SnO_{2}^{2}(7:3)+SO_{4}^{2}$	129	100	9.06 (7.02)		
Zr0Sn0_(1:1)	52.2	300	0.34 (0.65)		
$2r0_{2}^{2}-Sn0_{2}^{2}(1:1)+S0_{4}^{2}$	111	100	6.66 (6.00)		
$2rO_{2} - SnO_{2}(3:7)$	59.8	300	0.70 (1.17)		
$2rO_{2}^{-}-SnO_{2}^{-}(3:7)+SO_{4}^{2-}$	109	100	7.29 (6.69)		
Zr0 <sub>2</sub> -Sn0 <sub>2</sub> (1:9)	57.6	300	0.10 (0.17)		
$2ro_{2}^{2}-SnO_{2}^{2}(1:9)+SO_{4}^{2}$	110	100	4.14 (3.76)		
SnO <sub>2</sub>	31.6	300	0.034 (0.11)		
$\operatorname{SnO}_{2}^{2} + \operatorname{SO}_{4}^{2-}$	84.3	100	4.25 (5.04)		

Table l.	The effect of	$so_4^{2-}$	on catalytic	activity	of	Zr02-Sn02	for
	isomerization	of c	yclopropane.				

a) The figures in parentheses are the activity per unit surface area  $(10^{-7} \text{ mol min}^{-1}\text{m}^{-2})$ .

high to measure at 300°C over the catalysts with  $SO_4^{2-}$ . It is noted that the acid strength of  $ZrO_2-SnO_2+SO_4^{2-}$  could not be measured by the indicator method, because the basic indicators which are used for the measurement of super acidity gave the colors different from those of the conjugated acids on the catalyst surface.

In conclusion, it should be emphasized that  $2rO_2-SnO_2+SO_4^{2-}$  is expected to act as an efficient catalyst for various acid-catalyzed reactions.

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## References

 K. Tanabe, M. Itoh, K. Morishige, and H. Hattori, "Preparation of Catalyst", ed by B. Delmon, P. A. Jacobs, and G. Poncelet, Elsevier, Amsterdam (1976), p. 65.

2) M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., 1979, 1148.

- 3) M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., 1980, 851.
- 4) K. Tanabe, A. Kayo, and T. Yamaguchi, J. Chem. Soc., Chem. Commun., <u>1981</u>, 602.
- 5) G. Wang, H. Hattori, and K. Tanabe, Chem. Lett., 1983, 277.

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