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PRONOUNCED EFFECT OF SULFATE ION ON CATALYTIC ACTIVITY OF ZrO_2-SnO_2 FOR ISOMERIZATION OF CYCLOPROPANE

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The catalytic activity of ZrO_2-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 ZrO_2-SnO_2 and even higher than those of ZrO_2 and 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,[1,2] ZrO_2,[3] Fe_2O_3,[4] and SnO_2.[5] 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_0= -16.04,[3] -14.52,[2] and -8.2,[5] 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 cyclopropane which is known to be catalyzed by acids was studied.

Zirconium oxide, SnO_2, and ZrO_2-SnO_2 were prepared from aqueous solutions of $ZrOCl_2$, $SnCl_4$, and $ZrOCl_2$+$SnCl_4$, 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 SO_4^{2-} were prepared by immersing the hydroxides in solutions of $(NH_4)_2SO_4$ 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 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 ZrO_2, ZrO_2-SnO_2 of different compositions, and SnO_2 with and without the addition of 2.9 wt% 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 ZrO_2-SnO_2 (9:1), (7:3), (1:1), (3:7) and (1:9) with SO_4^{2-} at 100°C of reaction temperature were 7, 140, 9, 6, and 22 times higher than those of the catalysts without SO_4^{2-} at 300°C of reaction temperature, respectively. The activity of ZrO_2-SnO_2 (7:3) containing SO_4^{2-} was about 3 and 2 times higher than those of ZrO_2+SO_4^{2-} which was reported previously.[5] The isomerization reaction did not take place at 100°C over the catalysts without SO_4^{2-}, while the reaction rate was too

Table 1. The effect of SO_4^{2-} on catalytic activity of ZrO_2-SnO_2 for isomerization of cyclopropane.

Catalyst (atomic ratio)	Surface area $m^2\ g^{-1}$	Reaction temp. °C	Activity[a)] $10^{-5}mol\ min^{-1}g^{-1}$
ZrO_2	47.8	300	0.098 (0.21)
$ZrO_2+SO_4^{2-}$	113	100	2.48 (2.19)
ZrO_2-SnO_2(9:1)	80.3	300	0.65 (0.81)
ZrO_2-SnO_2(9:1)+SO_4^{2-}	102	100	5.80 (5.69)
ZrO_2-SnO_2(7:3)	72.6	300	0.034 (0.05)
ZrO_2-SnO_2(7:3)+SO_4^{2-}	129	100	9.06 (7.02)
ZrO_2-SnO_2(1:1)	52.2	300	0.34 (0.65)
ZrO_2-SnO_2(1:1)+SO_4^{2-}	111	100	6.66 (6.00)
ZrO_2-SnO_2(3:7)	59.8	300	0.70 (1.17)
ZrO_2-SnO_2(3:7)+SO_4^{2-}	109	100	7.29 (6.69)
ZrO_2-SnO_2(1:9)	57.6	300	0.10 (0.17)
ZrO_2-SnO_2(1:9)+SO_4^{2-}	110	100	4.14 (3.76)
SnO_2	31.6	300	0.034 (0.11)
$SnO_2+SO_4^{2-}$	84.3	100	4.25 (5.04)

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

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 ZrO_2-SnO_2+SO_4^{2-} is expected to act as an efficient catalyst for various acid-catalyzed reactions.

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