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Acid-Base and Catalytic Properties of ZrO_2-SnO_2

Gong-Wei Wang, Hideshi Hattori, and Kozo Tanabe*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The acid-base properties of ZrO_2–SnO_2 with different compositions have been measured by the indicator method and the adsorption with NH_3 and CO_2 and the catalytic activities studied. The ZrO_2–SnO_2 (atomic ratio=9 : 1) catalyst which was found to have the highest acid strength and the maximum acid amount exhibited the highest activities for the isomerization of cyclopropane and the dehydration of 2-butanol. The activities of the catalysts with different compositions for the two reactions correlated with the acidic properties. On the other hand, the activities for the isomerization of 1-butene and the decomposition of diacetone alcohol (4-hydroxyl-4-methyl-2-pentanone) correlated with the basic properties. The activity for the dehydrogenation of 2-butanol was found to increase with an increase of the SnO_2 content. The active sites on the ZrO_2–SnO_2 catalysts are discussed.

Recently, many kinds of mixed oxides were reported to show acidic property on the surfaces.[1] Among them, the binary oxides consisting of the oxides of the fourth group metals in the periodic table are interesting from the view-point of the acid-base property. Namely, the acid strengths of SiO_2–TiO_2[2] and SiO_2–ZrO_2[3] are very strong and that of TiO_2–SnO_2[4] is moderate, while TiO_2–ZrO_2 has not only strong acidic property,[5] but also distinct basic property.[6] These catalysts showed interesting activities for particular reactions, respectively. However, no study has been made on the acid-base and catalytic property of ZrO_2–SnO_2, another type of the binary oxides consisting of the fourth group metal oxides. Therefore, various kinds of ZrO_2–SnO_2 with different compositions calcined at different temperatures have been prepared and the acid-base property has been characterized in the present work. The catalytic activity and selectivity for the isomerizations of cyclopropane and 1-butene, and the decompositions of 2-butanol and diacetone alcohol are also studied.

Experimental

Catalysts and Reagents. Zirconium(IV) hydroxide and tin(IV) hydroxide were prepared by adding 28% aqueous ammonia to aqueous solutions of zirconium(IV) dichloride oxide ($ZrOCl_2 \cdot 8H_2O$) and anhydrous tin(IV) chloride ($SnCl_4$), respectively. The precipitates were aged at 100 °C over a water bath for 1 h, washed with deionized water until no chloride ions were detected with a silver nitrate test solution and dried at 100 °C for 24 h. The mixtures of zirconium(IV) and tin(IV) hydroxides with different atomic ratios of Zr to Sn were prepared by coprecipitation of mixed solutions of $ZrOCl_2 \cdot 8H_2O$ and $SnCl_4$ with 28% aqueous ammonia, followed by aging, washing and drying similarly as in the cases of zirconium and tin hydroxides. Zirconium oxide, tin oxide and the binary oxides with different atomic ratios of Zr to Sn were obtained by calcining the respective hydroxides at various temperatures in air for 2 h.

1-Butene and cyclopropane were purified by passage through 4A Molecular Sieves kept at Dry Ice temperature and distilled before use. 2-Butanol and diacetone alcohol were obtained from Wako Pure Chemical Industries Ltd., the latter being purified by vacuum distillation.

Measurement of Physico-chemical Properties. Specific surface areas of the samples calcined in air at various temperatures were obtained by applying the BET equation to the adsorption isotherm of nitrogen at −196 °C. Differential thermal analysis (DTA) and thermal gravimetry (TG) were carried out simultaneously with a heating rate of 10 °C/min. X-Ray diffraction patterns were measured over the range of $2\theta = 20$—60 ° for the powdered samples which had been calcined in air at 500 °C for 2 h.

Acidic and basic properties of the samples calcined in the air at 500 °C for 3 h were measured by titrating with butylamine and benzoic acid in benzene, respectively, the indicators of different pK_a values being used.[7] Adsorbed amounts of CO_2 and NH_3 were measured by use of Cahn 200 electrobalance. The sample was outgassed at 500 °C for 2 h. After cooling to room temperature, it was exposed to about 10 Torr (1 Torr≈133.322 Pa) of CO_2 or NH_3 for 30 min, followed by outgassing at room temperature for 20 min.

Reaction Procedure. The isomerizations of 1-butene and cyclopropane were carried out in a closed recirculation reactor having a volume of about 789 ml. Prior to reaction, catalysts were outgassed at 500 °C for 2 h. A 100 Torr of 1-butene or cyclopropane was allowed to react at 100 °C for 1-butene or 300 °C for cyclopropane. The catalyst weights were 200 mg for the isomerization of 1-butene and 400 mg for the isomerization of cyclopropane. The reaction mixture was periodically withdrawn and analyzed by gas chromatography; VZ-7 was used for a 6 m chromatographic column of 4 mm o.d. copper tubing. For the dehydration of 2-butanol, a microcatalytic pulse reactor was employed. One μl of 2-butanol was passed over a 100 mg catalyst at 200 °C in a helium carrier whose flow rate was 20 ml/min. Products were first trapped in a liquid nitrogen trap and flash evaporated into a first gas chromatographic column in which PEG 20M was packed. Olefins which flowed out of the first column were trapped again and flash evaporated into a second gas chromatographic column in which VZ-7 was packed.

The decomposition of diacetone alcohol was carried out at 30±0.5 °C in a reactor of liquid phase suspension. Thirty ml of diacetone alcohol was allowed to react over a powdered catalyst calcined at various temperatures. The sample was taken out from the reactor at 10 min interval and analyzed by gas chromatography.

Activities for all reactions were expressed as initial mole conversion to the product per unit time per unit surface area or unit weight of catalyst.

Results and Discussion

Surface areas of ZrO_2, SnO_2, and the binary oxides with different compositions calcined in the air at different temperatures are given in Table 1. For all samples, the surface areas decreased monotonously with a rise

TABLE 1. SPECIFIC SURFACE AREAS /$m^2\,g^{-1}$

Catalyst composition	Pretreatment temperature/°C				
	500	650	750	850	1000
ZrO_2	47.8	22.8	16.7	6.35	3.06
ZrO_2–SnO_2 (9 : 1)	80.3	37.4	26.6	16.9	8.73
ZrO_2–SnO_2 (7 : 3)	72.6	—	—	—	—
ZrO_2–SnO_2 (1 : 1)	52.2	31.4	27.6	21.4	9.11
ZrO_2–SnO_2 (3 : 7)	59.9	—	—	—	—
ZrO_2–SnO_2 (1 : 9)	57.6	35.8	28.8	27.4	9.94
SnO_2	37.6	—	14.5	8.68	4.85

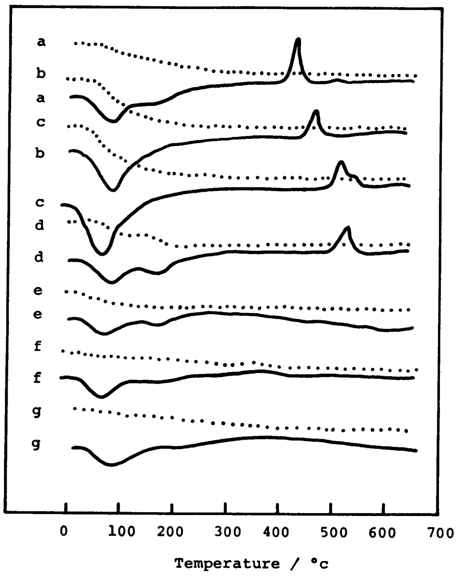

Fig. 1. DTA (——) and TG (······) diagrams of ZrO_2, SnO_2, and the binary oxides.
a: ZrO_2, b: ZrO_2–SnO_2 (9 : 1), c: ZrO_2–SnO_2 (7 : 3), d: ZrO_2–SnO_2 (1 : 1), e: ZrO_2–SnO_2 (3 : 7), f: ZrO_2–SnO_2 (1 : 9), g: SnO_2.

of the calcination temperature. The binary oxides had larger surface areas than the single component oxides when compared at the same calcination temperature. The DTA and TG curves are shown in Fig. 1. The exothermic peak for ZrO_2 was observed at about 424 °C. The exothermic peaks for the ZrO_2–SnO_2 samples with atomic ratios (Zr/Sn) of 9 : 1, 7 : 3, and 1 : 1 shifted to 459, 508, and 516 °C, respectively. However, no exothermic peaks were observed for SnO_2 and ZrO_2–SnO_2 containing more than 50% of SnO_2. X-Ray diffraction patterns of ZrO_2–SnO_2 (9 : 1) and (7 : 3) were similar to those of monoclinic ZrO_2, while those of ZrO_2–SnO_2 (3 : 7) and (1 : 9) were similar to those of tetragonal SnO_2, though the peaks for the binary oxides were broad as compared with the single component oxides. However, ZrO_2–SnO_2 (1 : 1) showed a distinct but unidentified X-ray peak at $2\theta=29.6°$ in addition to the patterns for ZrO_2 and SnO_2. The acidity and basicity distributions of the catalysts calcined at 500 °C are summarized in Table 2. The acid sites on ZrO_2 and SnO_2 are weak; $H_0=+4.0$ and $+4.8$, respectively. Among the binary oxides, ZrO_2–SnO_2 (9 : 1) showed the highest acid strength whose H_0 value was -3. The other binary oxides were weakly acidic. The strengths were in the range of $H_0=+3.3$—$+4.0$. The amount of basic sites equal to or stronger than $H_-=9.1$ decreased with an increase in SnO_2 content. In the case of ZrO_2–SnO_2 (9 : 1), the amount of basic sites is almost comparable with the amount of acid sites having $H_0\leqq+6.8$.

The amounts of NH_3 and CO_2 adsorbed on the catalysts outgassed at 500 °C for 2 h are shown in Fig. 2. The adsorbed amount of NH_3 was maximum on ZrO_2–SnO_2 (9 : 1) which showed the highest acid strength. The amount of CO_2 adsorbed decreased with an

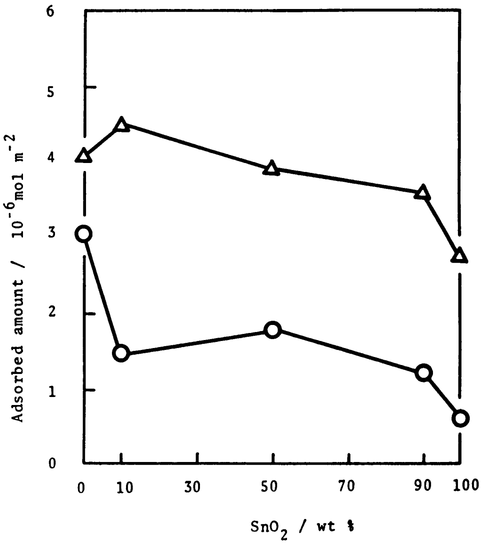

Fig. 2. Change of irreversibly adsorbed amounts of NH_3 and CO_2 with different catalyst compositions.
Temperature of adsorption and desorption: 22 °C, ○: CO_2, △: NH_3.

TABLE 2. ACIDITY AND BASICITY DISTRIBUTION OF ZrO_2–SnO_2 CALCINED AT 500 °C

Catalyst composition	Surface area $m^2\,g^{-1}$	Acidity and basicity distribution/mmol g^{-1}						
		-3.0[a]	$+1.5$[a]	$+3.3$[a]	$+4.0$[a]	$+4.8$[a]	$+6.8$[a]	$+9.1$[b]
ZrO_2	47.9	0	0	0	0.29	—	—	0.36
ZrO_2–SnO_2 (9 : 1)	80.3	0.072	0.086	0.20	0.25	—	0.28	0.31
ZrO_2–SnO_2 (7 : 3)	72.6	0	0	0	0.17	—	0.21	0.27
ZrO_2–SnO_2 (1 : 1)	52.9	0	0	0	0.12	—	0.15	0.25
ZrO_2–SnO_2 (3 : 7)	59.9	0	0	0	0.19	—	0.12	0.19
ZrO_2–SnO_2 (1 : 9)	57.6	0	0	0.053	0.12	—	0.19	0.058
SnO_2	31.6	0	0	0	0	0.13[c]	—	—

a) H_0 value. b) H_- value. c) Cited from K. Shibata, T. Kiyoura, J. Kitagawa, T. Sumiyoshi, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **46.**, 2985 (1973).

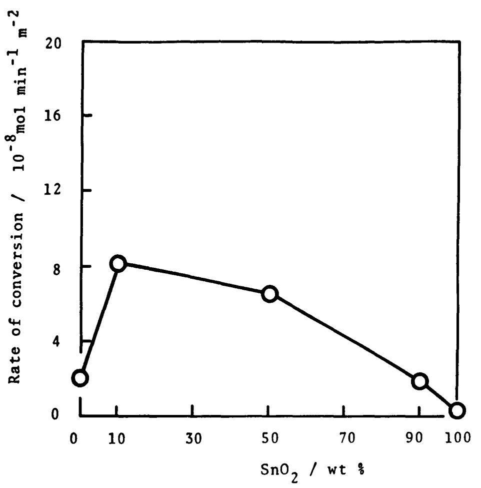

Fig. 3. Change in catalytic activity for isomerization of cyclopropane with catalyst compositions.
Reaction temperature: 300 °C.

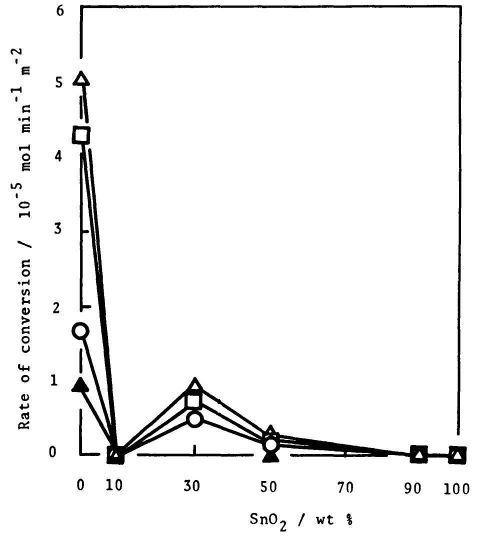

Fig. 4. Change in catalytic activity for isomerization of 1-butene with catalyst compositions.
Pretreatment temperature, ○: 500 °C, □: 750 °C, △: 850 °C, ▲: 1000 °C.

increase in SnO_2 content except ZrO_2–SnO_2 (9 : 1). The basic sites on all samples were as weak as $H_- = -9.1$.

Table 3. Distribution of products in isomerization of 1-butene in 60 min

Catalyst composition	Products distribution/%			*cis-/trans-*
	cis-2-Butene	*trans*-2-Butene	1-Butene	
ZrO_2	56.2	31.6	12.2	1.78
ZrO_2–SnO_2 (9 : 1)	0	0	100	—
ZrO_2–SnO_2 (7 : 3)	43.0	14.0	43.0	3.05
ZrO_2–SnO_2 (1 ; 1)	5.74	1.25	93.0	4.59
ZrO_2–SnO_2 (3 : 7)	0.52	0	99.5	
ZrO_2–SnO_2 (1 : 9)	0.93	0	99.1	
SnO_2	1.37	0	98.6	

The activities of the catalysts calcined at 500 °C for the isomerization of cyclopropane are plotted against the catalyst composition in Fig. 3. The activity change roughly correlates with the change of the acid amount measured by NH_3 adsorption shown in Fig. 2. The highest activity was observed over the ZrO_2–SnO_2 (9 : 1) catalyst which showed the maximum acid amount and the highest acid strength (*cf.* Table 2).

The variations in the activities for the isomerization of 1-butene as a function of SnO_2 content are shown in Fig. 4 for the catalysts calcined at different temperatures. For all catalysts, the activities increased with an increase in the calcination temperature and reached maxima when calcined at 850 °C. Further increase in the calcination temperature to 1000 °C resulted in a decrease in the activities. It is interesting to note that the ZrO_2–SnO_2 (9 : 1) catalyst showed no activity in spite of its acid sites being stronger than those of the other catalysts. The products distributions in the isomerization of 1-butene are summarized in Table 3. With all catalysts, *cis*-2-butene was predominantly formed. The predominant formation of *cis*-2-butene is generally observed in the base-catalyzed isomerization of 1-butene[8–11] in contrast with the formation of about equal amounts of *cis*-2-butene and *trans*-2-butene in the acid-catalyzed reaction.[8,12] Therefore, the isomerization is suggested to proceed by a carbanion mechanism over the all catalysts. Hence, no activity of the ZrO_2–SnO_2 (9 : 1) catalyst seems to be partly due to the small amount of basic sites as seen in Fig. 2, and partly due to the basic strength being weakened by the electron shift to the neighboring strong acid sites.

The results of the decomposition of 2-butanol are summarized in Table 4. As the content of SnO_2 increased, the dehydration to 1-butene decreased, whereas the dehydrogenation to ethyl methyl ketone increased. The highest activity for the formation of butenes was

Table 4. Catalytic activity and distribution of products in decomposition of 2-butanol

Catalyst composition	Distribution of products/%					$\frac{1\text{-}C_4'}{2\text{-}C_4'}$	$\frac{cis\text{-}}{trans\text{-}}$	Conversion
	1-Butene	*trans*-2-Butene	*cis*-2-Butene	Ketone	2-Butanol			10^{-5} mol m^{-2}
ZrO_2	2.49	—	—	0.21	97.3	—	—	0.61
ZrO_2–SnO_2 (9 : 1)	1.47	0.50	2.34	4.50	91.2	0.51	4.68	1.19
ZrO_2–SnO_2 (7 : 3)	1.27	—	—	12.7	86.1	—	—	2.10
ZrO_2–SnO_2 (1 : 1)	0.46	—	—	19.4	80.1	—	—	4.15
ZrO_2–SnO_2 (3 : 7)	—	—	—	40.1	52.3	—	—	7.59
ZrO_2–SnO_2 (1 : 9)	—	—	—	41.8	57.9	—	—	7.98
SnO_2	—	—	—	33.0	66.5	—	—	11.6

1-C_4': 1-Butene: 2-C_4': 2-butenes.

observed over ZrO_2–SnO_2 (9 : 1) which possessed the highest acidity. The dehydration activity correlates with the catalyst acidity. The butenes produced over ZrO_2, ZrO_2–SnO_2 (7 : 3) and (1 : 1) consisted exclusively of 1-butene. In the case of the ZrO_2–SnO_2 (9 : 1) catalyst, however, the formation of 2-butenes exceeded that of 1-butene. This was generally observed in the dehydrations catalyzed by strong acids.[13] It is suggested that the relatively strong acid sites which are generated on the surface of ZrO_2–SnO_2 (9 : 1) (*cf.* Table 2) are the active sites for the dehydration.

The decrease of the dehydrogenation activity with the increase of ZrO_2 content might be attributed to the decrease in the reducing property of SnO_2 on mixing of ZrO_2, since the reducing property of SnO_2 is reported to decrease on mixing of the other oxide, TiO_2.[4]

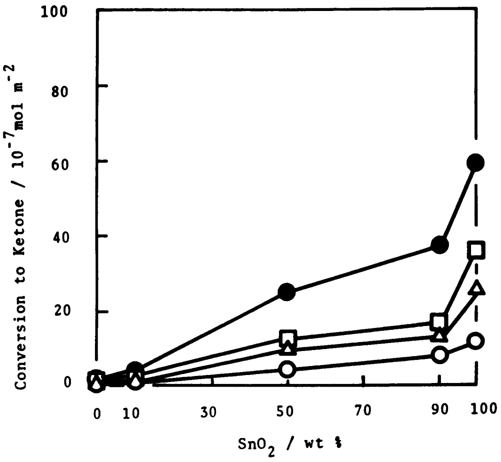

Fig. 5. Change of conversion to ketone from 2-butanol with change of pretreatment temperature of catalysts. ○: 500 °C, △: 750 °C, □: 850 °C, ●: 1000°C.

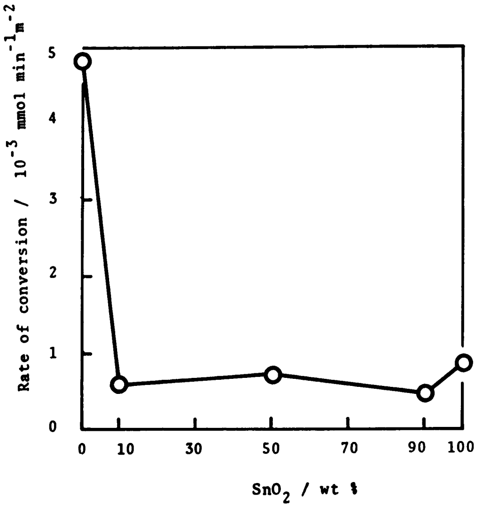

Fig. 6. Change in catalytic activity for decomposition of diacetone alcohol with catalyst compositions.

The conversion of 2-butanol to ethyl methyl ketone in the decomposition of 2-butanol over the catalysts calcined at different temperatures are plotted against the catalyst composition in Fig. 5. The formation of ethyl methyl ketone increased with a rise of the calcination temperature for all catalysts.

The activities for the decomposition of diacetone alcohol are shown in Fig. 6. The activities decreased as the content of SnO_2 increased. The activity change is roughly similar to the basicity change in Fig. 2. The little ambiguity is probably due to the difference in basic strength, though it could not be differentiated by the indicator method. Thus, the decomposition of diacetone alcohol is concluded to be controlled by both the amount and strength of the basic sites on the catalyst.

In summary, the ZrO_2–SnO_2 (9 : 1) catalyst can be classified as a solid acid catalyst having a moderate acid strength ($H_0 \leqq -3$). The acid strength is lower than that of SiO_2–TiO_2, SiO_2–ZrO_2, or TiO_2–ZrO_2 and almost equal to that of TiO_2–SnO_2. The difference in acid-base property of ZrO_2–SnO_2 from TiO_2–SnO_2 is that the ZrO_2–SnO_2 catalysts with different compositions have a definite basic property and only the ZrO_2–SnO_2 (9 : 1) showed the acid strength of $H_0 \leqq -3$. These acid-base properties reflected on the catalytic behavior.

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