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## ACID PROPERTY OF TITANIA-ZIRCONIA

By

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### Abstract

The acidity distribution of  $\text{TiO}_2\text{-ZrO}_2$  catalysts with various amounts of  $\text{ZrO}_2$  content was measured by *n*-butylamine titration using Hammett indicators. It was found that the acid amount and acid strength of  $\text{TiO}_2\text{-ZrO}_2$  with a molar ratio of 1:1 are largest and highest. The acid amounts were 0.34, 0.57 and 0.65 mmo/g at  $H_0 = -8.2, -5.6, -3.0$  and  $+4.0$  respectively. The mixed oxides which show such a remarkable acid property were found to be amorphous by means of D.T.A., X-ray analysis and surface area measurement. The catalysts were prepared by thermal decomposition of co-precipitated mixtures which were made by two different methods; by the addition of ammonia and by the addition of urea. The acid strengths of the catalysts did not depend on the method of preparation of the co-precipitate, but the acid amount was higher in the sample precipitated by urea than in the sample precipitated by ammonia.

### Introduction

There are a number of reports concerning the acid properties of solid catalysts and the correlations between catalytic activity and surface acidity. Silica-alumina was most extensively studied and recently some other mixed metal oxides<sup>1,2)</sup> were also studied. Silica-zirconia<sup>3,4)</sup> and silica-titania<sup>4,5)</sup> were reported to be solid acids which can act as cracking catalysts. Titania-zirconia is expected to show acid property, but acidity distribution of this combination of the oxides has not been reported yet. Therefore, we attempted to measure the acid properties of the mixed oxides by usual amine titration method. Effects of the chemical composition, the method of preparation and the crystal structure on the acid property were also studied.

### Experimental

*Preparation of oxide samples:*  $\text{TiO}_2\text{-ZrO}_2$  samples were prepared by thermal decomposition of co-precipitated titanium and zirconium hydroxides in air at  $500^\circ\text{C}$  for 3 hrs. The co-precipitated mixture was prepared by two different

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methods; (1) by the addition of ammonia to a mixed aqueous solution of titanium tetrachloride and zirconium oxychloride, and (2) by heating and stirring the mixture of aqueous solution of titanium tetrachloride, zirconium oxychloride and excess amount of urea on water bath. In latter case, about 10 hours were required to obtain complete precipitation with urea. It was also necessary to keep the total concentration of titanium tetrachloride and zirconium oxychloride in the mother liquor below 0.05 mol/l. The precipitate obtained by urea was homogeneous in nature and reproducible compared with that obtained by ammonia. The co-precipitate was washed thoroughly to remove adherent chloride ion by adding a small amount of ammonium carbonate to prevent peptization. Before calcination, the precipitate was dried in air at 110°C for 30 hrs.

*Acidity measurement:* Acidity of  $\text{TiO}_2\text{-ZrO}_2$  was measured according to JOHNSON's procedure.<sup>6)</sup> The Hammett indicators used were anthraquinone ( $\text{pK}_a = -8.2$ ), benzalacetophenone ( $-5.6$ ), dicinnamalacetone ( $-3.0$ ), benzenazodiphenylamine ( $+1.5$ ) and phenylazonaphthylamine ( $+4.0$ ).

*X-ray diffraction:* X-ray powder diffraction diagrams were recorded by X-ray diffractometer (Geigerflex). As a X-ray radiation source, vanadium filtered  $\text{Cu-K}_\alpha$  was used.

*D.T.A.* Differential thermal analysis diagram was recorded at a heating rate of 10°C/min.

*Surface area:* Surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at  $-196^\circ\text{C}$ .

## Results and Discussion

### *DTA of titanic acid, zirconium hydroxide and co-precipitated mixtures*

The various steps of the thermal decomposition of the precipitates before calcination were studied by D.T.A. The results are shown in Fig. 1. These diagrams were obtained using the samples precipitated by urea. Essentially the same diagrams were recorded for the samples precipitated by ammonia.

The thermal decomposition of pure titanic acid occurred with loss of water at around 100°C, followed by the dehydration of all the remaining water and the formation of amorphous titania at around 180°C. The crystallization of amorphous titania occurred above 300°C with exothermic peak around 310°C. The thermal decomposition of pure zirconium hydroxide occurred with loss of water at around 100~200°C and amorphous zirconia was formed. The strong exothermic peak around 410°C is due to the crystallization of zirconia.

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**Fig. 1.** DTA Diagram of Hydrogel.

- 1)  $\text{TiO}_2$ , 2)  $\text{TiO}_2/\text{ZrO}_2=85/15$ , 3) 60/40, 4) 50/50,  
5) 25/75, 6)  $\text{ZrO}_2$ .

D.T.A. diagram of the co-precipitated hydrogel mixture was different from that of each single component hydrogel. The remarkable endothermic peaks were observed around  $100^\circ\text{C}$ , but any exothermic peak around  $310^\circ$  or  $410^\circ\text{C}$  was not observed. This indicates that the co-precipitated mixture remains as an amorphous state even after calcination at  $500^\circ\text{C}$ . Measurement of surface area and X-ray diffraction diagram of calcined samples also support this presumption.

*X-ray analysis*

The X-ray powder diffraction diagrams of the studied samples are shown in Fig. 2. These samples were prepared by calcination of the precipitate in air at  $500^\circ\text{C}$  for 3 hrs. The precipitated samples before calcination gave only broad line and was assumed to be amorphous. Pure titania sample gave

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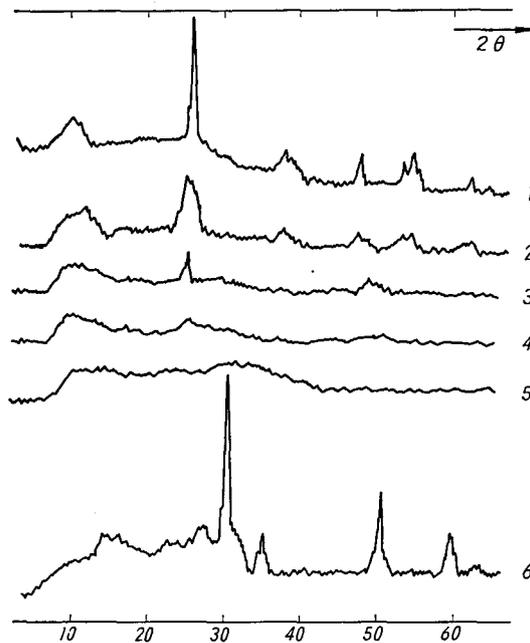


Fig. 2. X-ray Powder Diffraction Diagram.

- 1)  $\text{TiO}_2$ , 2)  $\text{TiO}_2/\text{ZrO}_2=85/15$ , 3)  $60/40$ , 4)  $55/50$ ,  
5)  $25/75$ , 6)  $\text{ZrO}_2$ .

strong diffraction lines indicating rutile crystal. Pure zirconia also gave strong diffraction lines indicating monoclinic structure, whereas the diffraction diagrams of  $\text{TiO}_2\text{-ZrO}_2$  gave only diffused line or only weak diffraction lines.

Most of the co-precipitated mixtures were amorphous as judged by X-ray diffraction. In the mixed state, titania and zirconia prevent each other their crystal growth and sintering. The X-ray diagrams of the samples precipitated by ammonia were quite the same as those of the samples precipitated by urea.

#### *Specific surface area*

The specific surface areas of calcined samples are listed in Table 1. Specific surface area of pure titania or zirconia is relatively small compared with those of the mixed oxides. This results indicating that the mixtures are amorphous agree with the results obtained by X-ray diffraction measurement. As shown in the Table, the surface area of the oxides does not depend on the method of preparation of the precipitates. Values of  $S_1$  and  $S_2$  agreed with each other within the limit of experimental error of the BET method.

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TABLE 1. Specific surface area of calcined samples

Composite	Molar ratio (%)	S <sub>1</sub> , m <sup>2</sup> /g	S <sub>2</sub> , m <sup>2</sup> /g
TiO <sub>2</sub>	100	37	40
ZrO <sub>2</sub> /TiO <sub>2</sub>	15/85	145	
ZrO <sub>2</sub> /TiO <sub>2</sub>	40/60	210	190
ZrO <sub>2</sub> /TiO <sub>2</sub>	50/50	250	230
ZrO <sub>2</sub> /TiO <sub>2</sub>	75/25	200	
ZrO <sub>2</sub>	100	70	72

S<sub>1</sub>: for the samples precipitated by urea.

S<sub>2</sub>: for those precipitated by ammonia.

*Acidic Property*

The *n*-butylamine titers, at  $H_0 \leq -5.6, -3.0$  and  $+4.0$ , plotted as a function of molar ratio of TiO<sub>2</sub>-ZrO<sub>2</sub> are shown in Fig. 3. Maximum acid amount at any acid strengths were observed for the sample with the molar ratio of 1 : 1. Also in the case of SiO<sub>2</sub>-ZrO<sub>2</sub> catalyst, a maximum acid amount was observed when the molar ratio was 1 : 1.<sup>4)</sup> Table 2 shows the total

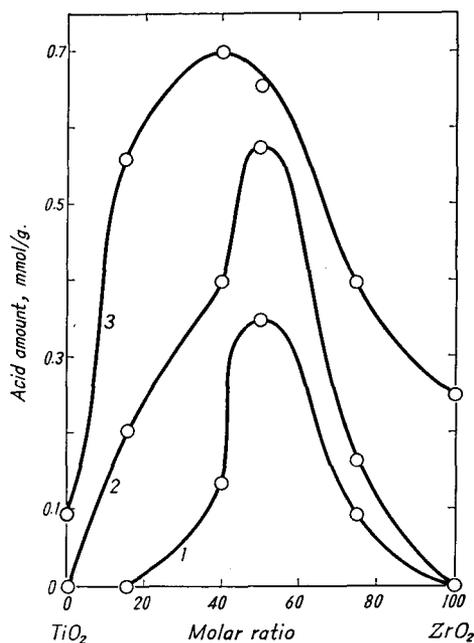


Fig. 3. Acidity of TiO<sub>2</sub>-ZrO<sub>2</sub> at Various Composition.

1)  $H_0 = -5.6$ , 2)  $-3.0$ , 3)  $+4.0$

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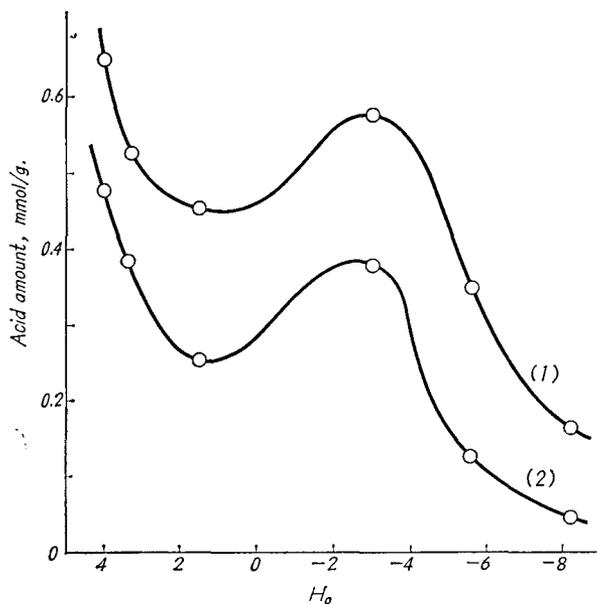
acidities (acid amounts at  $H_0 \leq +4.0$ ) of  $TiO_2-ZrO_2$ .TABLE 2. Total acidity at  $H_0 \leq +4.0$  of  $TiO_2-ZrO_2$ 

Composite	Molar ratio	Total acidity*)		Total acidity**)	
		mmo/g	mmol/m <sup>2</sup>	mmol/g	mmol/m <sup>2</sup>
$TiO_2$	100	0.09	0.0024	0.08	0.0021
$ZrO_2/TiO_2$	15/85	0.55	0.0038		
$ZrO_2/TiO_2$	40/60	0.70	0.0033	0.50	0.0026
$ZrO_2/TiO_2$	50/50	0.65	0.0026	0.48	0.0021
$ZrO_2/TiO_2$	75/25	0.40	0.0020		
$ZrO_2$	100	0.27	0.0039	0.30	0.0042

\*) for the sample prepared by precipitation with urea.

\*\*) for the sample prepared by precipitation with ammonia.

The low total acidity of titania seems mainly due to the small surface area. The total acidity expressed in mmol/g of  $TiO_2-ZrO_2$  prepared by urea changes from 0.09 to 0.70, whereas that in mmol/m<sup>2</sup> gives practically constant value over the wide range of molar ratio. The total acidity of the sample prepared by urea is higher than that by ammonia.

Fig. 4. *n*-Butylamine titer vs.  $H_0$ .1)  $TiO_2-ZrO_2$  precipitated by urea, 2)  $TiO_2-ZrO_2$  precipitated by  $NH_3$ .

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Since a sample with the molar ratio of 1:1 was found to have strong acid sites as low as below  $H_0 \leq -8.2$ , the acidity distribution of the sample was measured by using a complete set of Hammett indicators. The results are shown in Fig. 4, where acid amount is plotted against acid strength. As seen in the figure, the acid amount of the sample prepared by using urea is higher than that by using ammonia, the shape of the curves resembling each other. The results are different from those in the case of  $TiO_2-ZnO$ ,<sup>7)</sup> where strong acid sites were created by the precipitation with ammonia, but not by the precipitation with urea. The acid amounts at  $H_0 \leq +1.5$  are lower than those at  $H_0 \leq -3$ , despite that the former values should be higher than the latter ones. This unusual but interesting results were checked again by using freshly prepared indicators, but the test gave the same results. This seems to suggest the unusual surface property of  $TiO_2-ZrO_2$ .

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