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Acidic Property and Catalytic Activity of TiO_2·ZnO

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A new type of mixed metal oxide TiO_2·ZnO was prepared by either heterogeneous or homogeneous co-precipitation and the acidic property was measured by *n*-butylamine titration and by observation of infrared spectra of adsorbed pyridine. It was found that TiO_2·ZnO containing about 7 or 57% of ZnO shows a very large acid amount of 0.5—0.9 mmol/g and a fairly high acid strength of $H_0 \leqq -3$, the acid sites being both Brönsted and Lewis type and the acid sites of high strength created by heterogeneous precipitation. The catalytic activity and selectivity of TiO_2·ZnO were found very high for the hydration reaction of ethylene. The catalyst was active also for the alkylation of phenol by methanol and gave only monoalkylated products.

Metal oxides such as SiO_2·Al_2O_3, SiO_2·MgO, SiO_2·ZrO_2, Al_2O_3·B_2O_3, and Al_2O_3·MgO are known to be solid acid catalysts, each of which contains either SiO_2 or Al_2O_3, both essential constituents of natural clay minerals. The oxides have been extensively used as useful catalysts for various acid-catalyzed reactions in the field of petroleum chemistry. However, not much work has been done on other combinations of oxides, which might show surface acidity and catalytic acitvity, and we have initiated a systematic study on mixed metal oxides which do not contain any clay mineral component. The present paper reports the acidic property and catalytic activity of TiO_2·ZnO, a new combination of metal oxides. Each of TiO_2 and ZnO was previously reported to have only weak acidic property,[1,2] but the combination shows large acid amount and high acid strength as well as high catalytic activity.

Experimental

Preparation of Catalysts. Titanium oxide, zinc oxide, and TiO_2·ZnO of various compositons were prepared respectively by heating titanic acid, zinc hydroxide and the mixtures in air at 200—500° for 3 hr. Titanic acid, zinc oxide and their mixtures were prepared as follows.

1) Titanic Acid; 62.6 m*l* of $TiCl_4$ was dissolved into 120 m*l* of distilled water cooled by ice. To this was added 240 m*l* of distilled water in which 3 m*l* of concd. HCl and 156 g of $(NH_4)_2SO_4$ had been dissolved. The solution was boiled on a water bath for 1 hr and 110 m*l* of 28% ammonia water was added to form the precipitate of titanic acid H_4TiO_4, pH of the solution being 6.67. After the solution had been heated further for 1 hr, the precipitate was filtered off and washed thoroughly with distilled water until no anions of chloride and sulfate were detected in the washing. The precipitate was dried at 90° for 1—2 days.

2) Zinc Hydroxide: A precipitate was formed by adding 56 m*l* of 28% ammonia water into 100 m*l* of water containing 46.9 g of $ZnCl_2$, the final pH of the solution being found to be 6.27. The precipitate was washed and dried as in 1).

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[1] K. Tanabe and M. Katayama, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **7**, 106 (1959).

[2] K. Tanabe and T. Yamaguchi, *ibid.*, **11**, 179 (1964).

Table 1. Conditions for preparation of co-precipitated mixtures 2 and 3

	Co-precipitated mixture 2	Co-precipitated mixture 3
Solution I	137 g $ZnCl_2$ dissolved in 100 m*l* H_2O	261 g $ZnCl_2$ dissolved in 100 m*l* H_2O
Solution II	4 m*l* conc. HCl+210 g $(NH_4)_2SO_4$ in 322 m*l* H_2O	0.4 m*l* conc. HCl+21.0 g $(NH_4)_2SO_4$ in 32 m*l* H_2O
Solution III	84 m*l* $TiCl_4$ in 161 m*l* cooled H_2O	8.4 m*l* $TiCl_4$ in 16.1 m*l* cooled H_2O
Aqueous NH_3	198 m*l*	270 m*l*
Final pH	6.02	7.04

3) Co-precipitated Mixtures 1,2,3,4, and 5 of Titanic Acids and Zinc Hydroxides: Co-precipitated mixture 1 was prepared as follows. 14.0 g of $ZnCl_2$ was dissolved in 30 m*l* of water. 398 g of $(NH_4)_2SO_4$ and 7.6 m*l* of concd. HCl were dissolved in 600 m*l* of water. These were added to 160 m*l* of a solution prepared by dissolving $TiCl_4$ in 306 m*l* of water cooled by ice. The solution was heated on a water bath for 1 hr and 337 m*l* of 28% ammonia water was added to form co-precipitates of the mixture, the final pH of the solution being 7.08. After the solution was heated further for 1 hr, the precipitate was filtered off and washed thoroughly with distilled water until no anions of chloride and sulfate were detected in the washing. It was then dried at 90° for 1—2 days. Weight% of ZnO in the calcined mixture was calculated to be 6.7.

Co-precipitated mixtures 2 and 3 were prepared by adding 28% ammonia water to mixtures of solutions I, II, and III heated on a water bath for 1 hr (see Table 1), and by treating the co-precipitated mixture in a similar way to that for 1. Weight % of ZnO in 2 and 3 was 57.4 and 96.2, respectively.

Co-precipitated mixture 4 was prepared as follows. A cooled solution prepared by dissolving 10 m*l* concd. HCl and 150 g of $(NH_4)_2SO_4$ in 300 m*l* H_2O was added to a cooled mixture of two solutions, one 15.07 g $ZnCl_2$ in 50 m*l* H_2O and the other 69 m*l* $TiCl_4$ in 132 m*l* H_2O. After stirring 150 m*l* of ammonia was added and the solution was then treated in a similar way to that for 1. The final pH of the solution was 7.3. Weight % of ZnO was 15.2.

In the preparation of co-precipitated mixtures 1—3, two thirds of the added ammonia was poured at once and the remaining portion dropwise until the pH of the solution became approximately 7. For 4, all the ammonia was added gradually. The concentration of ammonium hydroxide ion differs locally during the formation of precipitates, *i.e.*, precipitates are formed in a heterogeneous concentration of hydroxide ion. Co-precipitated mixture 5 was prepared by homogeneous precipitation using urea instead of ammonia.[3] By this method, precipitates are formed from homogeneous solution of hydroxide ion, since urea decomposes to give ammonium hydroxide at elevated temperatures according to the formulas.

$$(NH_2)_2CO + H_2O \rightleftharpoons 2NH_3 + CO_2$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

Two solutions, one prepared by dissolving 26.9 m*l* $TiCl_4$ in 51 m*l* H_2O, and the other 5.3 g $ZnCl_2$ in 25 m*l* H_2O, were put into a 5 *l* beaker and the solution was diluted with water to make the volume 5 *l*. 97.2 g of urea was then added and the solution was stirred, the pH being 2. When the solution was heated at 95—98°C for 10—20 min, a fine colloidal and elastic precipitate was formed gradually. The solution was heated further for 2—3 hr until the pH of the solution became approximately 7. The precipitate was filtered off, washed with water until no anions of chloride and sulfate were detected in the washing and then dried at 120—150°C for 1—2 days. The weight % of ZnO was 13.9. All reagents used were of guaranteed grade from Wako Pure Chemical Co.

X-Ray Diffraction. The powder pattern of each specimen was obtained with an X-ray diffractometer ADG-301 DIFF PET, Toshiba electric Co. with filtered Cu$K\alpha$ radiation. The specimen was scanned between 10 and 65° (2θ).

Measurement of Surface Area and Acidic Property. Surface areas of TiO_2, ZnO, and No. 1 and 3 samples of $TiO_2 \cdot ZnO$ which were calcined at 200—500° were determined by applying the BET method to the adsorption isotherm of nitrogen at −196°.

The acid amounts and strengths of catalysts were measured by titrating the 100—200 mesh powder suspended in benzene with 0.1 N *n*-butylamine benzene solution, using neutral red ($pK_a=6.8$), methyl red (4.8), 4-phenylazo-1-naphthylamine (4.0), *p*-dimethylaminoazobenzene (3.3), benzeneazodiphenylamine (1.5), dicinnamalacetone (−3.0) or benzalacetophenone (−5.6) as indicators.

The Brönsted and Lewis acidity was determined by observing the infrared spectra of pyridine adsorbed on catalyst surface. The catalyst was heat-treated in a glass tube at various temperatures for 3 hr in air and the glass tube was sealed off. Immediately after the tube had been opened, it was connected to a vacuum apparatus and evacuated to 10^{-5} mmHg for 30 min at room temperature. Pyridine (about 2 mmHg) was then introduced and adsorbed for 10 min. After removing the excess of pyridine by evacuating at 100°C for 30 min, 3 mg of the sample was mixed with 200 mg of KBr powder and pressed into tablets of 12 mm diameter using a pressure of approximately 40000 psi. The spectrum in the 1400—1600 cm^{-1} region was measured using a Hitachi EPI-2 infrared spectrophotometer.

Measurement of Catalytic Activity. Hydration of ethylene was carried out by circulating a mixture of ethylene and water vapor (molar ratio:20) through 2 g of $TiO_2 \cdot ZnO$ catalyst at 200°C. The ethanol formed was analyzed with a gas chromatograph using a column of silicon DC 550 on celite.

Alkylation of phenol by methanol was carried out by means of the usual flow method at 400°C. The products were analyzed by a gas chromatograph using a column of polyethylene glycol on celite.

Results and Discussion

Acidic Properties and Structures. Acid amounts at various acid strengths of TiO_2, ZnO, and samples 1—3 of $TiO_2 \cdot ZnO$ calcined at various temperatures are given in Tables 2 and 3. Titanium oxides calcined at 400—500°C and zinc oxide at 400°C showed an acid strength of $H_0 \leqq +1.5$, which was never observed in their commercial products calcined at any temperature.[1,2] The effects of ZnO content on the acidities of $TiO_2 \cdot ZnO$ calcined at 300 and 400°C are shown in Figs. 1 and

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[3] H. H. Willard and N. K. Tang, *J. Amer. Chem. Soc.*, **59**, 1190 (1937).

Table 2. Acidic property of TiO_2 and ZnO

	Calcination temp., °C	Acid amount, mmol/g					
		$H_0 \leqq 6.0$	$H_0 \leqq 4.8$	$H_0 \leqq 4.0$	$H_0 \leqq 3.3$	$H_0 \leqq 1.5$	$H_0 \leqq -3$
TiO_2	300	—	0.056	—	0.029	0	
	400	—	0.056	—	0.038	0.028	0
	500	—	0.061	—	0.058	0.032	0
	600	—	0.037	—	0.017	0	
ZnO	200	0.37	0.29	0.005	0		
	300	2.07	1.71	—	0.15	0	
	400	2.29	1.81	—	0.52	0.22	0
	500	0.024	0.018	—	0.017	0	

Table 3. Acidic property of $TiO_2 \cdot ZnO$

No. of sample (wt % of ZnO)	Calcination temp., °C	Acid amount, mmol/g				
		$H_0 \leqq 4.8$	$H_0 \leqq 3.3$	$H_0 \leqq 1.5$	$H_0 \leqq -3$	$H_0 \leqq -5.6$
No. 1 (7)	200	0.76	0.86	0.83	0.73	0.5—0.4[a)]
	300	0.95	1.04	1.04	0.92	
	400	0.64	0.70	0.65	0.57	
	500	0.56	0.59	0.58	0.54	
No. 2 (57)	200	0.39	0.89	0.89	0.84	
	300	0.42	0.93	0.90	0.85	
	400	0.24	0.57	0.53	0.48	
	500	0.28	0.68	0.63	0.50	
No. 3 (96)	200	0.48	0.02	0		
	300	0.95	0.34	0.003	0	
	400	1.72	1.44	1.42	0	
	500	1.35	1.24	1.07	0	

a) End point of titration was not clear. Anthraquinone of $pK_a = -8.2$ did not show its acidic color on the surface.

we see that the acid amounts at various acid strengths become large when $TiO_2 \cdot ZnO$ contains about 7 or 57% of ZnO. The acidities of the mixed oxides containing about 96% of ZnO are small when they are calcined at 300°C, but their acid amounts at $H_0 \leqq 3.3$ and 1.5 increase greatly when calcined at 400°C. In both cases of Figs. 1 and 2, fairly strong acid sites of $H_0 \leqq -3.0$ appear only when about 7 or 57% of ZnO is contained in the catalyst. This fact and a comparison of the specific surface areas of $TiO_2 \cdot ZnO$ containing 7% of ZnO with those of TiO_2 alone (Fig. 3) indicate that the observed large amount and high strength of acid sites of $TiO_2 \cdot ZnO$ are not due to the increase of specific surface area. Since the actual amount of surface acid in a given H_0 range is given by the difference between acid amounts at pK_a's of the two indicators bracketing that H_0 range, it may be said that the characteristic of acidity distribution of $TiO_2 \cdot ZnO$ containing about 7 or 57% of ZnO calcined at 200—500°C is a fairly large acid amount in the range of acid strength, $H_0 \leqq -3.0$ (in some cases, $H_0 \leqq -5.6$), and of $TiO_2 \cdot ZnO$ containing about 96% of ZnO calcined at above 400°C is a very large acid amount in the range of acid strength, $-3.0 < H_0 \leqq 1.5$ (Figs. 1—2 and Table 3).

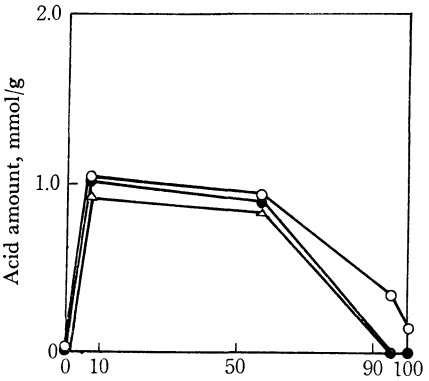

Fig. 1. Acid amounts at various acid strengths of $TiO_2 \cdot ZnO$ calcined at 300°C *vs.* wt% of ZnO.
(-○-): $H_0 \leqq 3.3$, (-●-): $H_0 \leqq 1.5$, (-△-): $H_0 \leqq -3.0$

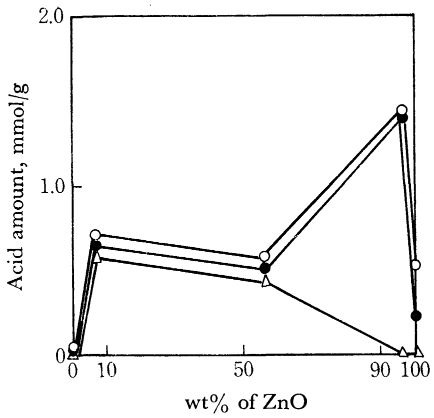

Fig. 2. Acid amounts at various acid strengths of $TiO_2 \cdot ZnO$ calcined at 400°C *vs.* wt% of ZnO.
(-○-): $H_0 \leqq 3.3$, (-●-): $H_0 \leqq 1.5$, (-△-): $H_0 \leqq -3.0$

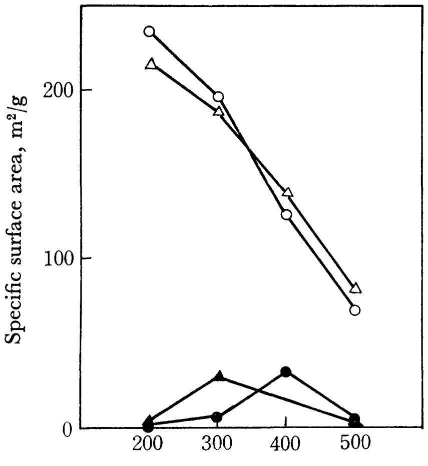

Fig. 3. Change in surface area of TiO_2 (-△-), ZnO (-▲-) sample 1 (-○-), and sample 3 (-●-) on calcination temperature.

The effects of calcination temperature on the acidities are given in Tables 2 and 3. The maximum acid amount of sample 1 was observed when calcined at 300°C and that of 3 at 400°C. The acidity change in 2 is shown in Fig. 4. It should be noted that methyl red behaves anomalously on the surface of $TiO_2 \cdot ZnO$ (57% ZnO); the acid amounts measured by using methyl red of $pK_a = 4.8$ were found in all cases to be

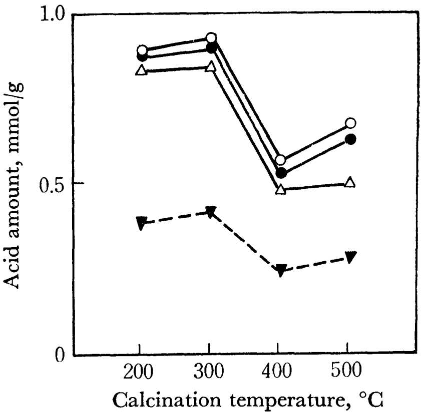

Fig. 4. Dependence of acid amount of sample 2 on temperature.
(-○-): $H_0 \leqq 3.3$, (-●-): $H_0 \leqq 1.5$, (-△-): $H_0 \leqq -3.0$, (--▼--): $H_0 \leqq 4.8$

lower than those measured by indicators having lower values of pK_a, as is shown by a dotted line in Fig. 4.

The acidity of 4 containing 15% of ZnO prepared by a slightly modified method is compared with that of 5 containing the same amount of ZnO prepared by using urea where acid amount was plotted against acid strength (Fig. 5). The acid strength of 4 is higher than that of 5, the latter having no acid sites of $H_0 \leqq -3.0$. However, the acid amount in the range of $-3 < H_0 \leqq 6.8$ is found much larger in 5 than in 4, about 0.6 mmol/g and 0.02 mmol/g, respectively. Thus, it might be said that the heterogeneous precipitation method using aqueous ammonia creates strong acid and the homogeneous method using urea relatively weak acid sites.

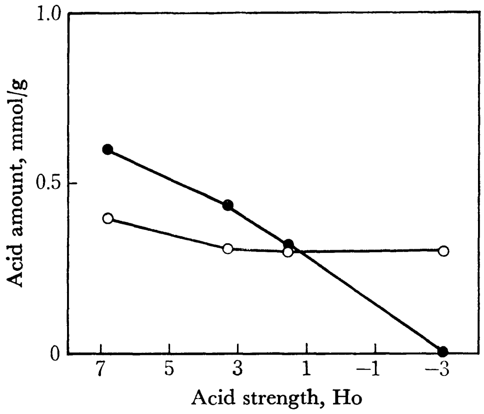

Fig. 5. Comparison of acidic property of $TiO_2 \cdot ZnO$ prepared by heterogeneous precipitation method sample 4 (-○-) with that by homogeneous precipitation method sample 5 (-●-).

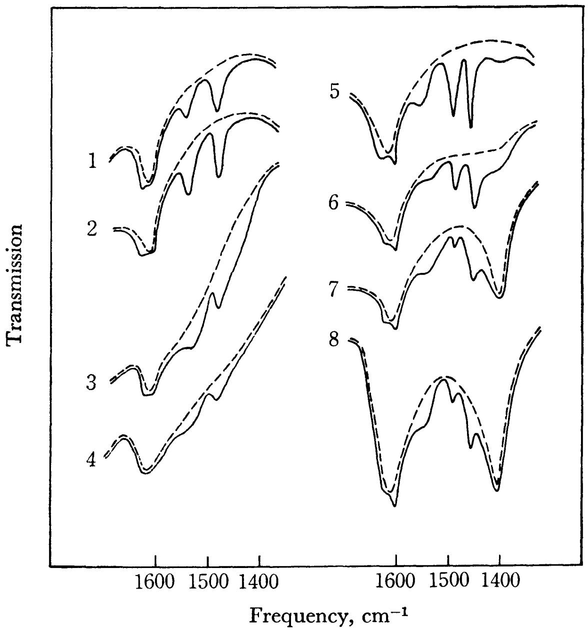

Fig. 6. Infrared spectra of pyridine adsorbed on TiO_2 (1—4) and sample 1 (5—8) calcined at various temperatures. Calcined temperatures are 500 (1,5), 400 (2,6), 300 (3,7), and 200°C (4,8)

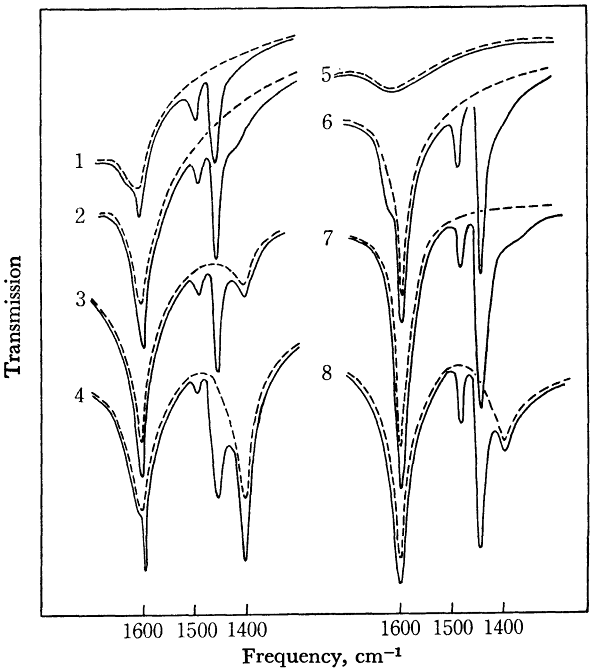

Fig. 7. Infrared spectra of pyridine adsorbed on sample 3 (1—4) and ZnO (5—8) calcined at various temperatures. Calcined temperatures are 500 (1,5), 400 (2,6), 300 (3,7), and 200°C (4,8)

The infrared spectra of pyridine adsorbed on $TiO_2 \cdot ZnO$ and samples 1 and 3 of $TiO_2 \cdot ZnO$ calcined at 200—500°C are shown in Figs. 6 and 7. Since it is known that the band of coordinately bonded pyridine appears at 1445—1460 cm^{-1} on the surface of various solid acids, and that of pyridinium ion at around 1530—1540 cm^{-1},[4-8] the band near 1540 cm^{-1} in Fig. 6 has been assigned to the band due to pyridinium ion formed on Brönsted acid site and that at 1450 cm^{-1} in Figs. 6 and 7 due to coordinately bonded pyridine on Lewis acid site. Thus, TiO_2 has only Brönsted acid

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4) E. P. Parry, *J. Catalysis*, **2**, 371 (1963).

5) M. R. Basila, T. R. Kantner, and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964).

6) J. W. Ward, *J. Catalysis*, **9**, 225 (1967).

7) B. V. Liengme and W. K. Hall, *Trans. Faraday Soc.*, **62**, 3229 (1966).

8) H. Hattori and T. Shiba, *J. Catalysis*, **12**, 111 (1968).

sites and ZnO only Lewis acid sites, though the latter disappear when calcined at 500°C. Sample 1 of $TiO_2 \cdot ZnO$ has both Brönsted and Lewis acid sites, while 3 has only Lewis acid sites. The Lewis acid sites of both samples do exist even when calcined at 500°C.

The band at 1485 cm^{-1} appears commonly on both Brönsted and Lewis acid sites. The bands near 1600 cm^{-1} observed in all samples before adsorption of pyridine are considered due to the adsorbed water molecules and/or coordinately bonded ammonia which are retained even after calcination. The bands near 1400 cm^{-1} observed in 1 and 3 and ZnO calcined below 400, 300, and 200°C, respectively, are those of the ammonium ion retained after calcination at relatively low temperature. The infrared spectra of ammonium sulfate used for the preparation of oxides give only the band at 1400 cm^{-1}, but TiO_2 prepared by using ammonium sulfate shows no band. This indicates that ammonium sulfate is not retained on the surface and therefore does not cause the observed acidic property.

A survey of the structure of $TiO_2 \cdot ZnO$ by X-ray diffraction shows that sample 2 is entirely amorphous. Sample 1 showed only a pattern of the rutile type and sample 3 only a pattern of hexagonal ZnO, no pattern of the spinel structure being found. However, the structure of acid sites of $TiO_2 \cdot ZnO$ is not clear at present.

Catalytic Activity. Since $TiO_2 \cdot ZnO$ containing about 7% of ZnO (sample 1) was found to show fairly high acidity, its catalytic activity was tested for the hydration reaction of ethylene and the alkylation of phenol with methanol which are known to be catalyzed by the usual solid acids. Hydration reaction of ethylene over sample 1 of $TiO_2 \cdot ZnO$ calcined at 400°C, was carried out at 200°C. The result is shown in Fig. 8, where the catalytic activities of nickel sulfate calcined at 300°C[9] and phosphoric acid mounted on celite[9] for the reaction under the same reaction conditions are also shown for comparison. The activity of the new $TiO_2 \cdot ZnO$ catalyst is higher than that of nickel sulfate and solid phosphoric acid which are well-known catalysts for olefin hydration. Since the acid strength of acid sites effective for ethylene hydration is reported to be $H_0 \leqq -3$ in the case of various metal sulfate catalysts,[9] the observed high activity of $TiO_2 \cdot ZnO$ catalyst is considered to be due to the fact that the catalyst has a large acid amount at $H_0 \leqq -3$ as shown in Table 3.

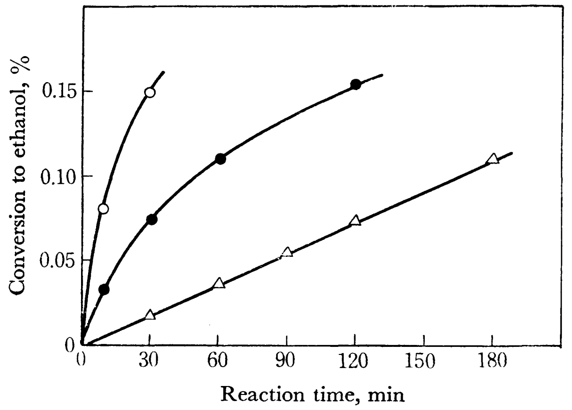

Fig. 8. Hydration of ethylene catalyzed by solid acids.
(-○-) Catalyst: 2 g of sample 1 calcined at 400°C, Reaction temp.: 200°C
(-●-) Catalyst: 2 g of $NiSO_4$ calcined at 300°C, Reaction temp.: 220°C
(-△-) Catalyst: 17 g of H_3PO_4 on celite, Reaction temp.: 220°C

The selectivity of this catalyst was also high, only ethyl alcohol being formed, although diethyl ether or acetaldehyde is usually formed when the catalysts of high acid strength ($H_0 \leqq -8.2$) such as $SiO_2 \cdot Al_2O_3$ and $Al_2O_3 \cdot B_2O_3$ are used.[9]

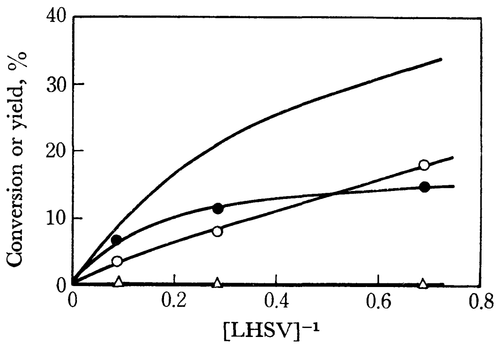

Fig. 9. Alkylation of phenol by methanol catalyzed by $TiO_2 \cdot ZnO$.
Reaction temp.: 400°C, total conversion (——), yield of *o*-cresol (-●-), *m*- and *p*-cresol (-○-), anisol (-△-)

The activity and selectivity of sample 1 of $TiO_2 \cdot ZnO$ for alkylation of phenol with methanol are shown in Fig. 9. The conversion was about 33% at $LHSV^{-1}$ 0.7 and only monoalkylated phenols were obtained. The cause of selectivity and reaction kinetics are being studied in comparison with various known acidic catalysts.

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[9] M. Nitta, I. Isa, I. Matsuzaki, and K. Tanabe, *J. Japan Petroleum Inst.*, **14**, 779 (1971).