

The Acidic Properties of $\text{TiO}_2\text{-SiO}_2$ and Its Catalytic Activities for the Amination of Phenol, the Hydration of Ethylene and the Isomerization of Butene

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The generation of strong acid sites was observed on the binary oxide, $\text{TiO}_2\text{-SiO}_2$, which was obtained by a coprecipitation method. The acidity and acid strength of the mixed oxide of a certain composition were estimated to be higher than those of $\text{SiO}_2\text{-Al}_2\text{O}_3$ containing 20 wt% of Al_2O_3 by *n*-butylamine titration and by the adsorption of basic molecules on the surface. The acidity depended both on pre-treating temperature and the catalyst composition. The highest acidity per unit weight of catalyst was observed when $\text{TiO}_2\text{-SiO}_2$ (mole ratio = 1) was heated at 500°C.

The binary oxide showed high catalytic activity and selectivity for the amination of phenol with ammonia to produce aniline, but low activity and selectivity for the hydration of ethylene. The isomerizations of butenes were also catalyzed; the products ratio of *cis*-/*trans*-2-butene was 1-2. The catalytic action for three reactions is well interpreted in terms of the acidic property.

The mechanism of the generation of acid sites by mixing TiO_2 with SiO_2 is discussed.

INTRODUCTION

Some kinds of binary oxides represented by $\text{SiO}_2\text{-Al}_2\text{O}_3$ are well known to possess acid sites on the surface. The general mechanism of acidity generation, however, was uncertain. In order to find out a general rule of the generation of acid sites, many varieties of combinations of two oxides were prepared and subjected to acidity measurement by Shibata *et al.* (1). Among those mixed oxides, $\text{TiO}_2\text{-SiO}_2$ showed the highest acid strength. It was briefly reported that the mixed oxide was highly active for the amination of phenol with ammonia (2).

The oxidizing and reducing properties together with the structural nature of $\text{TiO}_2\text{-SiO}_2$ have been investigated by several workers (3-5). However, the correlation between the catalytic activity and the acidic or redox property has not been investigated.

In the present work, the acidic properties of a series of $\text{TiO}_2\text{-SiO}_2$ having different molar ratio of Ti/Si and their relations to the catalytic activities have been studied. The mechanism of acidity generation by mixing TiO_2 with SiO_2 is discussed.

EXPERIMENTAL METHODS

Catalyst Preparation

$\text{TiO}_2\text{-SiO}_2$ with different molar ratios of Ti to Si were prepared by coprecipitation of the mixed solution of ethyl orthosilicate and titanium tetrachloride with aqueous ammonia. The precipitate was aged over water bath for 1 hr, washed with distilled water until no chloride ion was detected and dried at 100°C for 20 hr. TiO_2 and SiO_2 were prepared by hydrolysis of titanium tetrachloride and ethyl orthosilicate, respectively, followed by washing and drying as above.

Two kinds of $\text{SiO}_2\text{-Al}_2\text{O}_3$ were used for comparison. $\text{SiO}_2\text{-Al}_2\text{O}_3$ (I) was prepared from alcoholic solution of ethyl orthosilicate and aluminum isopropoxide by coprecipitation with water, the alumina content being 20 wt%. $\text{SiO}_2\text{-Al}_2\text{O}_3$ (II) was commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$, N631 (L), from Nikki Chemical Co. whose alumina content was 15 wt%.

X-Ray Analysis and DTA-TGA

Measurement

X-Ray diffraction patterns were measured in the range of $2\theta = 20\text{-}70^\circ$ for the powdered samples which had been calcined for 3 hr in air at various temperatures.

DTA and TGA measurements were carried out simultaneously in air, heating rate being $20^\circ\text{C}/\text{min}$.

Acidic Property Measurement

Acidic property was measured both by the titration with *n*-butylamine in benzene and by the adsorption of basic molecules in gas phase. Titration was carried out for the catalysts calcined in air for 3 hr at 200, 350, 500, and 650°C by using indicators of different $\text{p}K_a$ according to the Benesi's method (6, 7). The indicators used are *p*-dimethylaminoazobenzene ($\text{p}K_a = +3.3$), benzeneazodiphenylamine ($\text{p}K_a = +1.5$), dicinnamylacetone ($\text{p}K_a = -3.0$), benzalacetophenone ($\text{p}K_a = -5.6$), and anthraquinone ($\text{p}K_a = -8.2$). Adsorption in gas phase was carried out as follows. Catalyst previously calcined in air at 550°C for 2 hr was put in a sample holder hanging from microbalance and evacuated at 450°C for 6 hr. After cooling to 100°C , the sample was exposed to basic gas such as ammonia, pyridine or *n*-butylamine under a pressure of about 10 Torr (1 Torr = 133.3 N m^{-2}). The sample was evacuated at this temperature until no change in weight was observed (usually it took more than 1 hr) and the amount of basic molecules retained on the surface was determined. The sample was slowly heated up to 150°C under vacuum and kept at the temperature more than 1 hr and the weight of the sample was measured. This

kind of procedure was repeated by raising the temperature stepwise by an increment of 50°C up to 450°C .

Reaction Procedures

Synthesis of aniline from phenol and ammonia was carried out at 450°C with a flow reactor. Catalyst of 16-30 mesh was pretreated by 450°C under nitrogen stream for 3 hr. The reaction mixture of phenol and ammonia (molar ratio, 1:9) was passed through catalyst bed with contact time of 1358 g min/mol and the liquid products were trapped at 0°C . The analysis was carried out at 110°C on a $2 \text{ m} \times 4 \text{ mm}$ chromatographic column containing silicone DC 500 on Shimalite.

Hydration of ethylene was done in a closed circulation system at 220°C . The reaction system had a water vaporizer which contained 3 ml of water thermostated at 24°C . Ethylene (670 Torr) was bubbled through the vaporizer to keep the vapor pressure of water constant (23 Torr) and passed through a catalyst bed. The entire reaction system was wrapped with a tape heater to prevent the water vapor from condensation. The catalyst which had been calcined at 450°C in air for 3 hr was evacuated at reaction temperature for 30 min before use. The reaction mixture in liquid phase was taken out by a syringe and subjected to gas chromatographic analysis. A 2-m column packed with polyethylene glycol 6000 on Celite 545 and thermostated at 100°C was used.

Isomerization reaction of 1-butene or *cis*-2-butene was also carried out in a closed circulation system at 200°C . Catalyst calcined at 450°C in air for 3 hr was put in a reactor and evacuated at reaction temperature for 2 hr. In poisoning experiment, the catalyst which had been evacuated at reaction temperature was exposed to NH_3 at 20°C for 10 min and evacuated. Then, it was heated to 200°C and evacuated for 30 min. For analysis of the butenes, a 5-m column packed with 30% dimethyl fluoride on alumina and thermostated at 0°C was used.

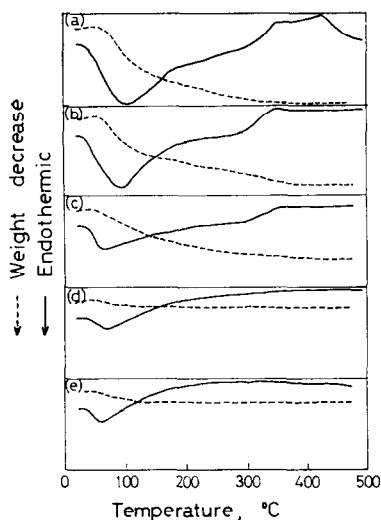


FIG. 1. DTA (—) and TGA (---) curves: (a) TiO_2 , (b) $\text{TiO}_2\text{-SiO}_2$ (9:1), (c) $\text{TiO}_2\text{-SiO}_2$ (1:1), (d) $\text{TiO}_2\text{-SiO}_2$ (1:9), (e) SiO_2 .

RESULTS

DTA and TGA curves are shown in Fig. 1. The endothermic peaks appearing at 50–100°C for all samples are ascribed to the desorption of physically adsorbed water molecule. Corresponding sharp decreases in weight were observed. Gradual decrease in weight continued up to 400°C. This is considered to be due to the dehydration of surface OH groups. TiO_2 , $\text{TiO}_2\text{-SiO}_2$ (9:1) and $\text{TiO}_2\text{-SiO}_2$ (1:1) showed exothermic peaks around 350°C. Since any corresponding weight decrease was not observed, the exothermic peaks in this range could be assigned to be the structural changes. The peak intensities were in the order of TiO_2 , $\text{TiO}_2\text{-SiO}_2$ (9:1) and $\text{TiO}_2\text{-SiO}_2$ (1:1). No distinct peak could be observed for $\text{TiO}_2\text{-SiO}_2$ (1:9). Besides this peak an additional peak was observed around 420°C only for TiO_2 .

From the X-ray diffraction pattern, TiO_2 calcined at each temperature was assigned to be anatase. The peak intensity was increased by calcining TiO_2 at 350°C or higher. This suggests that the crystallization progresses around 350°C in accordance with the DTA observation. Addition of SiO_2 to TiO_2 resulted in decrease in peak

TABLE 1
SPECIFIC SURFACE AREAS OF $\text{SiO}_2\text{-TiO}_2$
CALCINED AT VARIOUS TEMPERATURES

Calcination temp (°C)	Surface area of $\text{TiO}_2\text{-SiO}_2$ (m^2/g)				
	$\text{TiO}_2\text{-SiO}_2$				
	TiO_2	9:1 ^a	1:1 ^a	1:9 ^a	SiO_2
200		342	374	274	
350	169	326	379	294	220
500	85	245	338	292	227
650		133	237	255	

^a Mole ratio.

intensity. The peak height of $\text{TiO}_2\text{-SiO}_2$ (9:1) was less than one half of that of TiO_2 . $\text{TiO}_2\text{-SiO}_2$ (1:1) and (1:9) showed only broad and weak diffraction lines.

Specific surface areas are listed in Table 1. As the ratio of TiO_2 to SiO_2 became higher, remarkable decrease in surface area was observed when calcined at high temperature. This also suggests that the crystallization occurred more easily on the sample which was rich in TiO_2 .

Acidities at various acid strengths of the catalysts having different molar ratio of Si to Ti calcined at 500°C are shown in Fig. 2 together with the specific surface areas. Although both of single component

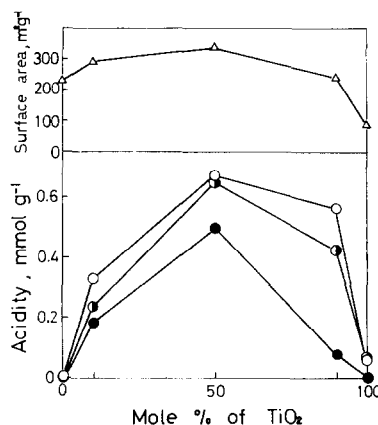


FIG. 2. Surface areas and acidities of $\text{TiO}_2\text{-SiO}_2$ of different compositions calcined at 500°C: (Δ) specific surface area, (\circ) acidity at $\text{H}_0 \leq 3.3$, (\bullet) $\text{H}_0 \leq 1.5$, (\bullet) $\text{H}_0 \leq -3.0$.

oxides, SiO_2 and TiO_2 , showed little acidity, mixing of the two oxides resulted in remarkable increase in acidity. This increase was not caused only by the increase in surface area. The maximum acidity at $\text{Ho} \leq 1.5$ was 0.62 mmol/g for $\text{TiO}_2\text{-SiO}_2$ (1:1), which is larger than 0.42 mmol/g for $\text{SiO}_2\text{-Al}_2\text{O}_3$ (I) or 0.25 mmol/g for $\text{SiO}_2\text{-Al}_2\text{O}_3$ (II). The acidities at higher acid strength of $\text{Ho} \leq -5.6$ and -8.2 could not be measured by titration method. It was difficult to determine the end point of the titration, since the color of the acidic forms of indicators of $\text{p}K_a = -5.6$ and -8.2 is clear yellow and the color of $\text{TiO}_2\text{-SiO}_2$ (1:1 and 9:1) is the same tone (light yellow). However, it is certain that the catalysts have a high acid strength of $\text{Ho} \leq -8.2$, since the color of the catalysts turned clear yellow with both the indicators. The observed acidity also depends on calcination temperature as shown in Fig. 3. Acidities per unit area are shown in Fig. 3 because it would reflect the qualitative change of surface property more clearly. As the ratio of TiO_2 to SiO_2 increased, the temperature which gave the maximum acidity became higher, i.e., 350, 500 and $>650^\circ\text{C}$ for $\text{TiO}_2\text{-SiO}_2$ (1:9), and $\text{TiO}_2\text{-SiO}_2$ (1:1) and $\text{TiO}_2\text{-SiO}_2$ (9:1), respectively. The amounts of ammonia, *n*-butylamine and pyridine remained on the surface of $\text{TiO}_2\text{-SiO}_2$ (1:1) after evacuating at various temperatures are shown in Fig. 4, where that of $\text{SiO}_2\text{-}$

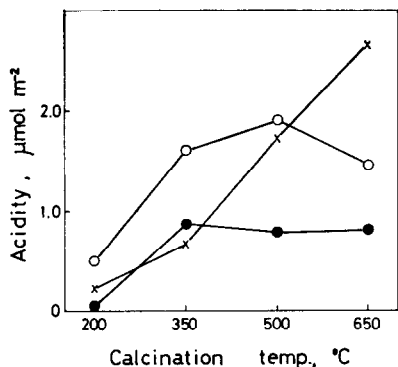


Fig. 3. Acidity per unit surface area at $\text{Ho} \leq 1.5$ of $\text{TiO}_2\text{-SiO}_2$ calcined at various temperatures: (●) $\text{TiO}_2\text{-SiO}_2$ (1:9), (○) $\text{TiO}_2\text{-SiO}_2$ (1:1), (×) $\text{TiO}_2\text{-SiO}_2$ (9:1).

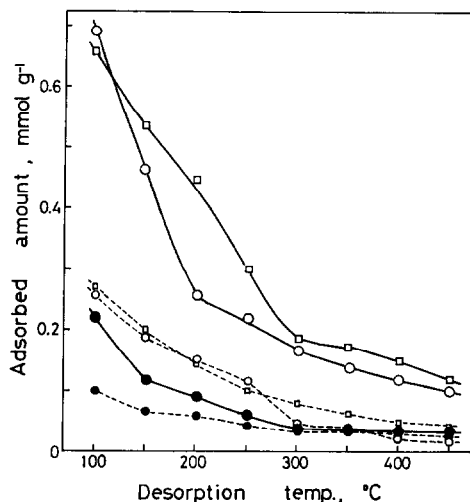


Fig. 4. Amounts of ammonia, *n*-butylamine and pyridine remained on catalyst surface after evacuating at various temperatures: (—) $\text{TiO}_2\text{-SiO}_2$ (1:1), (---) $\text{SiO}_2\text{-Al}_2\text{O}_3$ (I), (□) ammonia, (○) *n*-butylamine, (●) pyridine.

Al_2O_3 (I) is also shown for comparison. The fact that the amounts of basic molecules retained on $\text{TiO}_2\text{-SiO}_2$ (1:1) were larger than those on $\text{SiO}_2\text{-Al}_2\text{O}_3$ (I) at all temperatures (Fig. 4) suggests that the $\text{TiO}_2\text{-SiO}_2$ possesses higher acidity and acid strength than $\text{SiO}_2\text{-Al}_2\text{O}_3$ (I).

In the synthesis of aniline, the activity decreased very quickly in the first 30 min followed by slow degradation. The conversions of phenol to aniline at reaction time of 60 min over mixed oxides are shown in Fig. 5. $\text{TiO}_2\text{-SiO}_2$ (9:1) showed

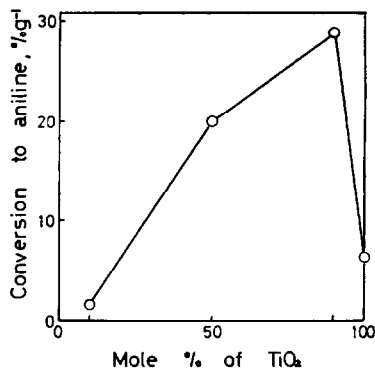


Fig. 5. Conversions of phenol to aniline at reaction time of 60 min over $\text{TiO}_2\text{-SiO}_2$.

a maximum activity of 29% g⁻¹ which was higher than 22% g⁻¹ for SiO₂-Al₂O₃ (II). Besides the higher activity, TiO₂-SiO₂ showed higher selectivity than SiO₂-Al₂O₃ (II). For instance, the formation of diphenylamine was 0.8% for TiO₂-SiO₂ which was smaller than 1.3% for SiO₂-Al₂O₃ (II).

In contrast to the high activity for the synthesis of aniline, TiO₂-SiO₂ showed poor activity and selectivity for the hydration of ethylene; the results are listed in Table 2. During the reaction, pressure decrease which was considered to be due to polymerization was observed. Relatively large amount of acetaldehyde was also formed.

For the isomerization of 1-butene, TiO₂ itself is active. However, remarkable changes in activity and selectivity were observed by mixing of TiO₂ and SiO₂ as shown in Fig. 6. TiO₂ showed little activity for the isomerization of *cis*-2-butene. Although the selectivity could not be determined over TiO₂ because of its low activity, remarkable increase in activity by mixing SiO₂ was observed (Fig. 7). The decrease in activity to one half of original activity by poisoning with NH₃ over TiO₂-SiO₂ (9:1) suggests that the active sites for this reaction are acidic sites.

DISCUSSION

All results can be explained in terms of the generation of acid sites on the binary oxides

TABLE 2
ACTIVITY AND SELECTIVITY FOR
HYDRATION OF ETHYLENE

Mole ratio TiO ₂ -SiO ₂	Calcina- tion temp (°C)	Initial rate (10 ⁻⁴ vol% min ⁻¹ g ⁻¹)	By-products	
			CH ₃ CHO ^a	Poly- mer ^b
1:9	450	0.5	0	3
1:1	450	1.1	0.22	11
9:1	450	0.8	tr	19
SiO ₂ -Al ₂ O ₃ ^c	400	3.7	0.16	10

^a Peak height ratio in gas chromatogram of acetaldehyde to ethanol after 3 hr.

^b Pressure decrease (Torr g⁻¹) after 3 hr.

^c Cited from Ref. (11).

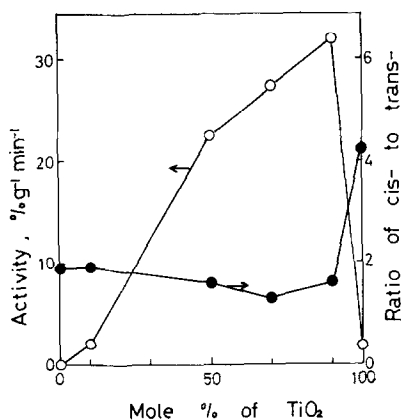


FIG. 6. Isomerization of 1-butene: (○) activity; conversion percentage per 1 min and 1 g of catalyst, (●) selectivity; the ratio of *cis*- to *trans*-2-butene obtained by extrapolation to zero conversion.

which is caused by mixing of two oxides.

Many kinds of combinations of two oxides were reported to generate acid sites on the surface (1, 9). The combination of TiO₂ and SiO₂ generated the very strong acid sites and the very high acidity as well, which were evidenced by acidity measurements.

In the case of the amination of phenol, it is known that only the catalyst having acid site of $H_0 \leq -3.0$ is active and the stronger the acid sites, the higher the activity (10). Consequently, the high activity of TiO₂-SiO₂ is due to the strong

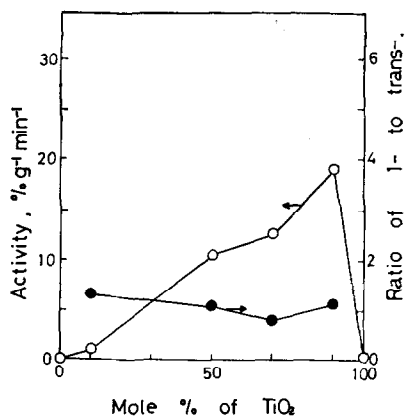


FIG. 7. Isomerization of *cis*-2-butene: (○) activity, (●) selectivity.

acid sites which are formed by mixing TiO_2 with SiO_2 , as revealed by the acidity measurement using a gas adsorption method. The higher acidity of $\text{TiO}_2\text{-SiO}_2$ (9:1) than that of $\text{TiO}_2\text{-SiO}_2$ (1:1) is considered to be caused by the existence of the stronger acid sites or larger number of the strong acid sites of $\text{H}_0 < -5.6$.

For the hydration of ethylene, however, very strong acid sites on $\text{TiO}_2\text{-SiO}_2$ cause the formation of aldehyde and polymer to decrease the activity for ethanol formation. This is in agreement with the conclusion that effective acid strength for the formation of ethanol is in the range of $-8.2 \leq \text{H}_0 \leq -3$ (11).

For the isomerization of butenes, active sites could be ascribed to acid sites in mixed oxides because of great increase in activity as well as acidity by mixing of two oxides and of poisoning effect with NH_3 . The ratios of *cis*- to *trans*-2-butene from 1-butene were around 1.5 for the mixed oxides. The selectivity value is typical for acid-catalyzed isomerization which proceeds via butyl-carbonium ion as an intermediate (12). On the other hand, much higher values were reported for base-catalyzed isomerization where π -allyl carbanion was considered to be intermediate (13-16). The value of 4.2 over TiO_2 suggests that the isomerization proceeds mainly via π -allyl carbanion intermediate, though the acidic mechanism cannot be excluded (17).

The mechanism of the generation of acid sites by mixing of two oxides has been proposed by Tanabe *et al.* (18). It can be well applied to $\text{TiO}_2\text{-SiO}_2$ system. The coordination numbers of Ti^{4+} and Si^{4+} in each oxide are 6 and 4, those of O^{2-} being 3 and 2, respectively. According to the above mechanism (18), the coordination numbers of the positive elements should be maintained to 6 and 4, respectively, even when mixed and those of all oxygens should be 3 or 2 according as whether the major component oxide in $\text{TiO}_2\text{-SiO}_2$ is TiO_2 or SiO_2 . Hence, for the $\text{TiO}_2\text{-SiO}_2$ whose major component oxide is TiO_2 , four positive charges of silicon atom are distributed to four bonds, i.e., a positive charge is distributed to each bond, while two negative charges of oxygen

atom are distributed to three bonds, i.e., $-2/3$ of valence unit is distributed to each bond. The difference in charge for one bond is $+1 - 2/3 = +1/3$ and for all bonds, the valence units of $+1/3 \times 4 = +4/3$ is excess. For the $\text{TiO}_2\text{-SiO}_2$ whose major component oxide is SiO_2 , it is similarly calculated that the valence unit of $(+4/6 - 1) \times 6 = -2$ is excess. In any case, $\text{TiO}_2\text{-SiO}_2$ should exhibit acidic property because of the excess of positive or negative charge according to a hypothesis proposed by Tanabe *et al.* (18), though it should not show any acidic property according to Thomas' hypothesis (19). According to the above mechanism, the structure of $\text{TiO}_2\text{-SiO}_2$ is considered to have little crystallinity or to be amorphous. This is evidenced by the fact that X-ray diffraction lines of each oxide become weak by mixing of two oxides.

The high acid strength of $\text{TiO}_2\text{-SiO}_2$ is considered to be due to the high electronegativities of both Ti^{4+} and Si^{4+} ions, since a general rule that the acid strengths of various binary oxides increase with the algebraically averaged electronegativities of metal ions is established (1).

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