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# Nature of Acid Sites on $TiO_2$, and Their Reactions with OH and $NH_2$ Groups of 3-Amino-1-propanol, 1-Propanol, and 1-Propylamine

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The IR spectra for pyridine adsorbed on the surfaces of $TiO_2$ (SA) (anatase type), prepared from titanium tetraisopropoxide, showed the existence of only Lewis acid sites which were not converted to the Brönsted type by the addition of water. However, $TiO_2$ (SB) (anatase type), prepared by the hydrolysis of titanium oxide sulfate, showed both Lewis and Brönsted acidities. The Lewis acidity of SB was converted to the Brönsted type by the introduction of water vapor. The 3-amino-1-propanol compound interacted with both Lewis and Brönsted acid sites on the $TiO_2$ surfaces in a manner similar to propylamine rather than to 1-propanol. However, in the case of SA, interactions between OH groups of the amino alcohol and surface OH groups seemed to take place to some extent. The mode of the surface reaction of $TiO_2$ differes markedly from that of $SiO_2$ which has no surface acidity. A linear relationship between the amount of surface OH groups on SB and the amount of the reaction of 3-amino-1-propanol at 235 °C in an autoclave was observed. The formation of oriented and closely packed layers of adsorbed molecules was observed for all the combination of SB and 3-amino-1-propanol, in which some condensation (mainly dimerization) seemed to be promoted by acid sites on SB.

Recently, the acid-base properties of the $TiO_2$ surfaces have become the object of practical attention because of their wide use for catalysts[1] and ion exchangers.[2] Accordingly, extensive studies of the reactivity of $TiO_2$ surfaces have been carried out to learn their specific properties.[3] It has been shown that hydroxyl groups and metal ions on the $TiO_2$ surfaces are active sites for chemisorption, and the interactions of these sites with alcohol[4,5] and amines[6] have been studied. However, the reactions of amino alcohols with the $TiO_2$ surfaces have not been investigated. It would be of great interest to know which of the groups, OH or $NH_2$, interact preferentially with active sites on the $TiO_2$ surfaces. Furtheremore, it is worthwhile to clarify the difference in mode of interaction between an amino alcohol with two functional groups and an alkylamines or alcohol, each of which has a single functional group.

In the present investigation, the interactions of OH and $NH_2$ groups in 3-amino-1-propanol with the surfaces of $TiO_2$ were studied by comparing the infrared spectra of the adsorbed molecules with those of 1-propanol and propylamine. The infrared spectra of pyridine adsorbed on $TiO_2$ were first examined in order to know the nature of acid sites which would interact with $NH_2$ or OH groups in organic reagents. For a further study of the reactivities of OH and $NH_2$ groups, the reactions of 3-amino-1-propanol, 1-propanol, and propylamine with $TiO_2$ surfaces were carried out in an autoclave. The reactions of other amino alcohols with various types of structures were also tested for comparative purposes.

## Experimental

*Materials.* The $TiO_2$ samples were used to see the effect of the solid acidity on the surface reaction. The first of the samples was prepared by the hydrolysis of titanium tetraisopropoxide (Wako Pure Chemical Co.), followed by repeated washing with deionized water. The product contained no significant traces of sulfate or chloride ions. The sample was designated as SA. The other sample (SB) was prepared using an intermediate product from the sulfuric acid process, supplied by the Sakai Chemical Co. Even after repeated washing with deionized water, SB has a considerable amount of combined sulfate ions, possibly in the form of titanium oxide sulfate. Before use, both SA and SB were heat-treated at 500 °C for 3 h. The X-ray analysis showed that both crystalline forms of SA and SB are anatase after the heat-treatment.

The organic reagents used were of a special or reagent grade from the Wako Pure Chemical Co. The propylamine was dried over solid KOH, and the other reagents, over 4A molecular sieve. Immediately before adsorption, the reagents were purified by repeating a freeze-pump-thaw cycles. The water used was distilled from an aqueous solution of $KMnO_4$.

*IR Absorption Experiment.* The infrared spectra of the organic reagents adsorbed on $TiO_2$ were measured in an *in situ* cell equipped with NaCl windows. The $TiO_2$ samples were ground and fabricated into discs of 20 mm in diameter. The discs were heat-treated at 500 °C before insertion in the cell. Immediately before adsorption, the discs were further treated at 250 °C for 12 more hours under evacuation at pressure of $10^{-4}$ mmHg.† Oxygen treatment was done by introducing $O_2$ into the cell, followed by heat-treatment at 250 °C for 0.5 h to burn out any organic contaminants on the $TiO_2$ surface. Adsorption was carried out by bringing the saturated vapor of organic reagents into contact with the $TiO_2$ in the cell for 0.5 h at room temperature or at 250 °C. The infrared spectra were measured after evacuation at 120 °C for 0.5 h and then cooling to room temperature. IR transmission through SA was almost zero in the wavenumber range from 2800 to 4000 $cm^{-1}$, probably because of the reflection of the rays due to the large particle size of the $TiO_2$ sample. Therefore, the infrared spectra were measured in the range below 1750 $cm^{-1}$, since most of the essential bands for this study are in the lower-wavenumber region.

*Reaction Procedure.* SA or SB (5 g) was treated with a large excess of organic reagents (about 100 m mol) diluted with hexane (30 ml) in an autoclave having a volume of 100 ml. The reactions were carried out for 1 h at 235 °C (the critical temperature of hexane) with vigorous stirring. The products were washed with hexane and then with acetone, followed by drying under evacuation at about 100 °C.

*Chemical Analysis, DTA, TG, and Measurements of Surface Area and Acid-Base Amount.* The carbon and nitrogen

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† 1 mmHg≈133.322 Pa.

contents of the products were determined by the Pregl-Dumas method.[7)] The specific surface areas were determined by the BET method using $N_2$ at −195 °C. The solid acidities were determined by titration with butylamine, using Methyl Red ($pK_a = +4.8$) as the indicator.[8)] The amount of surface OH groups was determined by a modification of Boehm's method[9)]. To ascertain the thermal-decomposition or decomposition temperature, DTA and TG were carried out using a Thermoflex (Rigaku Denki Co.) by heating the sample (20 mg) at a rate of 5 °C/min in an air flow.

## Results and Discussion

*Crystal Forms, $SO_4^{2-}$ Content, and Surface Properties of Samples.* As is shown in Table 1, the surface areas and amounts of the surface OH groups of SB were close to those of SA when both samples were treated at 500 °C. However, the acid amount on SB was more than ten times that on SA. The large acidity of SB is probably due to sulfate ions which diffused to the surface during the heat treatment.[10)] The crystal forms of SA and SB were both anatase, and SB contained a considerable amount of sulfate ions.

*IR Spectra of Pyridine Adsorbed on $TiO_2$.* The infrared spectra of pyridine adsorbed on SA evacuated at room temperature showed adsorption bands at 1145, 1220, 1442, 1485, 1575, and 1603 cm$^{-1}$ (Fig. 1b). Except for the band at 1142 cm$^{-1}$ the bands almost coincide with those observed on rutile by Parfitt *et al.*[11)] and are assignable to Lewis-acid sites. Unlike the other bands, the band at 1145 cm$^{-1}$ became appreciably weaker under evacuation at 250 °C. Taking into account the fact that a weak shoulder at about 1140 cm$^{-1}$ was assigned to weakly coordinated pyridine,[11)] this band at 1142 cm$^{-1}$ may also be attributable to weak Lewis acid sites. The band is clearly detectable in this study because the sample (anatase type) was heat-treated at a temperature not so high as the rutile. On exposure to water at room temperature, the bands attributed to Lewis acid sites became weaker, but the bands characteristic of Brönsted acid sites such as that at 1540 cm$^{-1}$ [12)] did not become apparent. These facts indicate that there is no conversion of Lewis acid to Börnsted acid with the addition of water to SA, much as with the result observed when water was added to the rutile sample.[11)]

On the other hand, the spectra of pyridine adsorbed on SB showed an absorption band at 1537 cm$^{-1}$ besides the bands attributed to Lewis-acid sites at 1445 and 1575 cm$^{-1}$ (Fig. 2). The band at 1537 cm$^{-1}$ may be taken as the principal band due to Brönsted acid sites.[13)] Upon heating up to 250 °C, this band became considerably weaker in contrast to that of the band characteristic of Lewis acid sites at 1575 cm$^{-1}$, which became more distinct. With the addition of water vapor, the band due to Lewis acid sites almost disappeared, while the bands due to Brönsted acid sites became more prominent. Such a conversion of Lewis to Brönsted acid sites occasioned by the addition of water vapor has also been observed for other metal oxides[12)] and for $SiO_2$–$Al_2O_3$,[13)] but it was not observed in the case of SA, as has just been described. The band at 1375 cm$^{-1}$ observed in the spectrum of SB is ascribed to –O–$SO_2$–O– groups, which should be found at 1330—1450 cm$^{-1}$.[14)] The

Table 1. Surface properties of $TiO_2$ samples[a)]

| | SA[b)] | SB[c)] |
|---|---|---|
| Crystal form[d)] | Anatase | Anatase |
| $SO_4^{2-}$ content/wt% | Trace | 4.7 |
| Surface area/m$^2$ g$^{-1}$ | 95 | 93 |
| Amount of surface OH groups/mmol g$^{-1}$ | 0.55 | 0.58 |
| Acid amount ($H_0 \leq 4.8$)/mmol g$^{-1}$ | 0.02 | 0.35 |

a) Calcined at 500 °C. b) Prepared by the hydrolysis of titanium isopropoxide. c) Prepared by the sulfuric acid process. d) Incompletely crystallized.

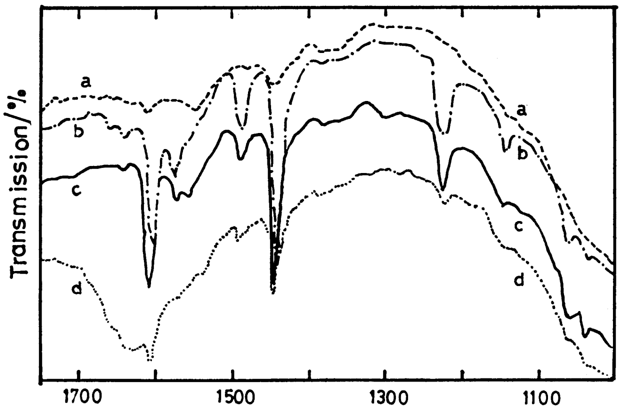


Fig. 1. IR spectra of pyridine adsorbed on SA.
(a) Initial surface, (b) exposed to pyridine at room temperature, evacuated at room temperature, (c) evacuated at 250 °C, (d) then, exposed to $H_2O$ at room temperature, evacuated at room temperature.

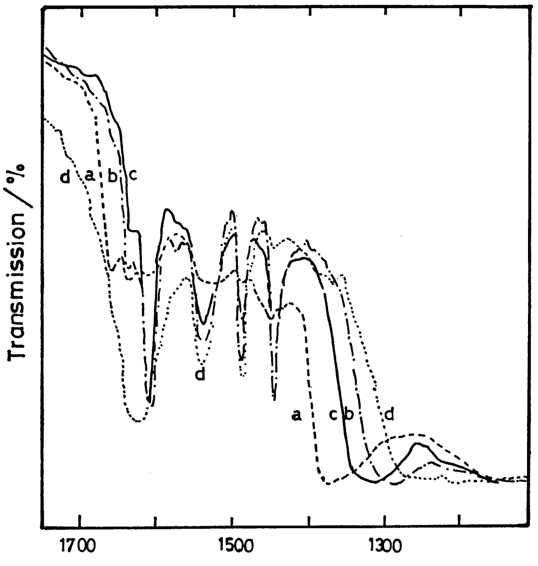
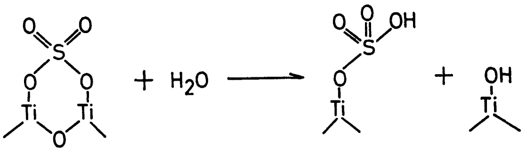


Fig. 2. IR spectra of pyridine adsorbed on SB.
(a), (b), (c), and (d) are the same as in Fig. 1.

groups may withdraw electrons from adjacent OH groups and make them Brönsted acids. Upon the addition of water vapor, the band at 1375 $cm^{-1}$ was noticeably shifted to a lower-wave number region. Since the absorption bands due to $-SO_3H$ groups should be generally found at 1150—1260 $cm^{-1}$,[14] the –O–S–O– bond on the surface might be broken by the attack of water, as is shown below;



Also, this conversion, accompanied by the addition of water, should contribute to an increase in the Brönsted acidity.

*IR Spectra of 3-Amino-1-propanol, 1-Propanol, and Propylamine Which Were Adsorbed on $TiO_2$.* The spectra of 3-amino-1-propanol adsorbed on SA are given in Fig. 3. The spectra of 1-propanol and propylamine are given in Figs. 4 and 5 respectively for comparative purposes. The band at about 1600 $cm^{-1}$ in the spectrum of liquid 3-amino-1-propanol (shown by Fig. 3, curve(d)) is shifted to near 1580 $cm^{-1}$ (curves (b) and (c)) by the adsorption. Such a shift is also seen in the spectra of propylamine adsorbed on SA. Since a similar shift has been observed in the infrared spectrum of methylamine on alumina,[15] which is a typical Lewis acid, the band-shift observed here is considered to be due to the coordination of unshared electron pairs on the N atoms with Lewis acid sites or with exposed Ti ions on the surface. The shoulder at about 1650 $cm^{-1}$ due to C=C bands in the spectra of 1-propanol adsorbed on SA (shown in Fig. 4, curves (b) and (c)) is not observed in the spectra of adsorbed 3-amino-1-propanol (Fig. 3). This fact indicates that the $\beta$-elimination of $H_2O$ or $NH_3$ from the adsorbed molecules seems improbable for 3-amino-1-propanol.

Unlike the spectra of propylamine adsorbed on SA, three absorption bands, at about 1430, 1390, and 1245 $cm^{-1}$, are found in the spectra of the amino alcohol adsorbed on SA, and they become more marked on heating to 250 °C. The first band is also found in the spectrum of free amino alcohol (Fig. 3, curve (d)). The second band can be assigned to the C–O bond in titanium alkoxide by reference to the observation that a strong band has been found at 1385 $cm^{-1}$ in the spectrum of aluminium ethoxide and in that of ethanol adsorbed on alumina.[16] The last band, at about 1245 $cm^{-1}$, was not found in the spectra of 1-propanol and propylamine, which were adsorbed on $TiO_2$ (SA and SB). The band is in the range of bands due to C–O stretching vibration (1000—1300 $cm^{-1}$ [17]) and is especially assignable to the epoxy ring (strong absorption, near 1250 $cm^{-1}$ [18]). The band in the C–N stretching vibration region (1120—1150 $cm^{-1}$) is broader and is shifted to a range lower than that found in the spectrum of propylamine adsorbed on SA at 250 °C. (Fig. 5(c)). Thus, it is

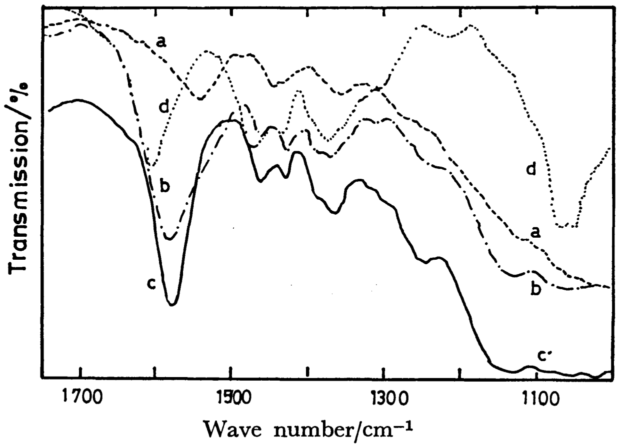


Fig. 3. IR spectra of 3-amino-1-propanol adsorbed on SA.
(a) Initial surface, (b) exposed to 3-amino-1-propanol at room temperature, (c) heated with 3-amino-1-propanol vapor at 250 °C, evacuated at 120 °C, (d) spectrum of 3-amino-1-propanol (liquid).

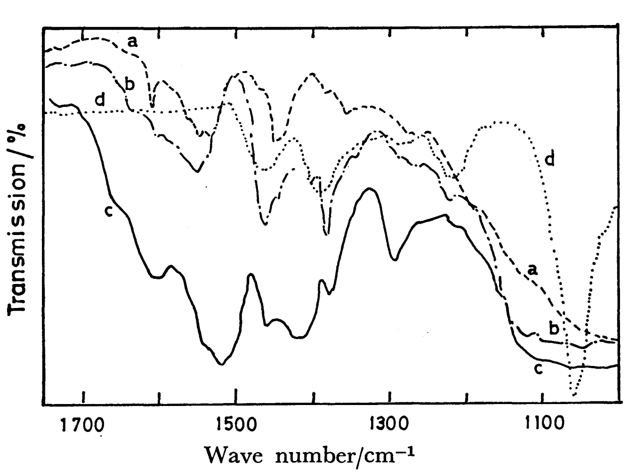


Fig. 4. IR spectra of 1-propanol adsorbed on SA. (a) Initial surface, (b) exposed to 1-propanol at room temperature, evacuated at room temperature, (c) heated with 1-propanol vapor at 250 °C, evacuated at 120 °C, (d) 1-propanol (gas).

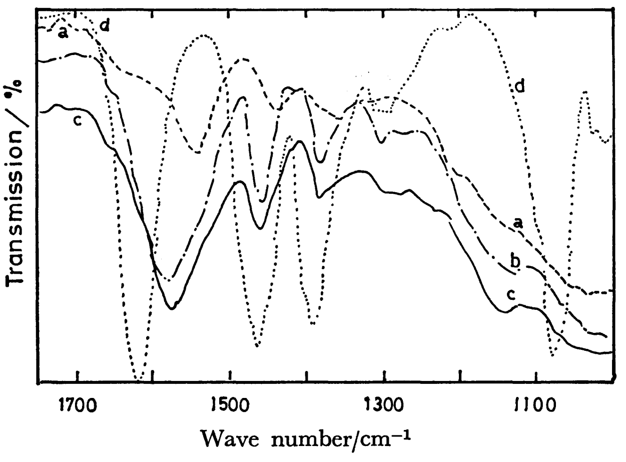
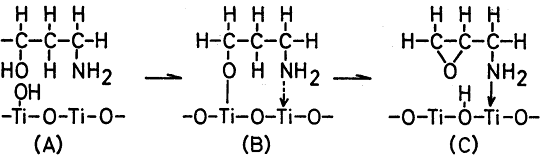


Fig. 5. IR spectra of 1-propylamine adsorbed on SA. (a) Initial surface, (b) exposed to 1-propylamine at room temperature, evacuated at room temperature, (c) heated with 1-propylamine vapor at 250 °C, evacuated at 120 °C, (d) 1-propylamine (gas).

probable, although not certain, that, besides the N atom, the OH group of the amino alcohol may also participate in the surface reaction to some extent. Thus, the following reaction scheme is conceivable:



Here, the $\beta$-hydrogen atom in the (B) structure may become acidic as a result of the withdrawal of electrons by the surface Ti ion through the O atom, thus forming the OH group shown in (C) structure. The molecule formed on the $TiO_2$ surface may be adsorbed through the bond resulting from the coordination of the free electrons of the N atoms to the Ti ion, as is shown in the structure.

The infrared spectra of 3-amino-1-propanol, 1-propanol, and propylamine, which were all adsorbed on SB, are shown in Figs. 6, 7, and 8 respectively. As the 3-amino-1-propanol was adsorbed on SB, absorption bands at 1605 and 1510 $cm^{-1}$ became observable. These are assigned to assymetric $NH_3^+$ (1560—1625 $cm^{-1}$) and symmetric $NH_3^+$ (1505—1550 $cm^{-1}$ respectively.[19] The bands also show that Brönsted acid sites on $TiO_2$ probably take part in the surface reaction with the amino alcohol. The participation of Brönsted acid sites was observed in the interaction of propylamine with the SB surface at 250 °C (Fig. 8, curve(C)). However, when SB was heated up to 250 °C together with the amino alcohol, the bands due to $NH_3^+$ almost disappeared (Fig. 6(c)), while the band at about 1590 $cm^{-1}$ related to the coordination bond between the Ti ion and the $NH_2$ groups became distinct with the heat-treatment. Such a change in the spectra indicates that the interaction of $NH_2$ groups with Lewis acid sites became predominant at higher temperature because of the decrease in the amount of OH groups, which may be Brönsted acid sites, as a result of dehydration. As is clear from the spectrum of the amino alcohol adsorbed on SA at 250 °C, there are no absorption bands which indicate the formation of C–O bonds. This suggests that the amino alcohol may interact with the SB surface mainly through the $NH_2$ groups.

Infrared spectroscopic studies of the reaction of 3-smino-1-propanol with $SiO_2$ surfaces have shown that free silanol reacted with alcoholic hydroxyl groups, while the $NH_2$ groups of the amino alcohol interacted only partially through hydrogen bonding.[20] The large difference in the mode of surface reaction between $TiO_2$ and $SiO_2$ may be due to the difference in the surface acidity. That is, the cation electronegativity

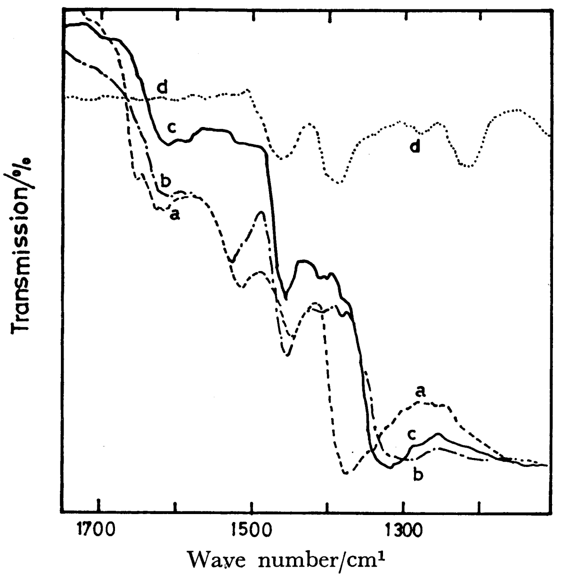


Fig. 7. IR spectra of 1-propanol adsorbed on SB. (a), (b), (c), and (d) are the same as in Fig. 4.

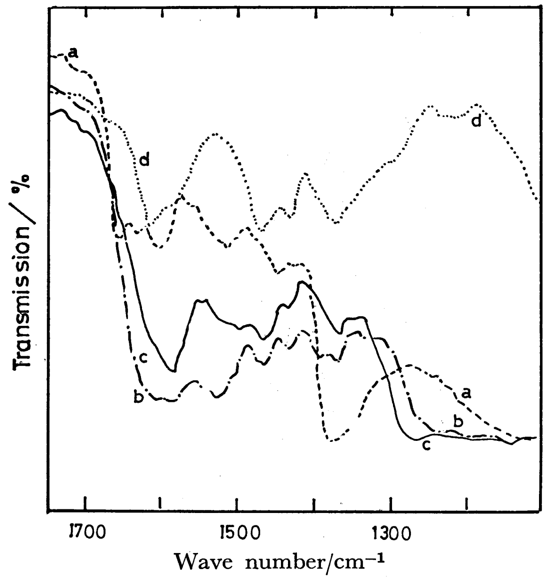


Fig. 6. IR spectra of 3-amino-1-propanol adsorbed on SB.
(a), (b), (c), and (d) are the same as in Fig. 3.

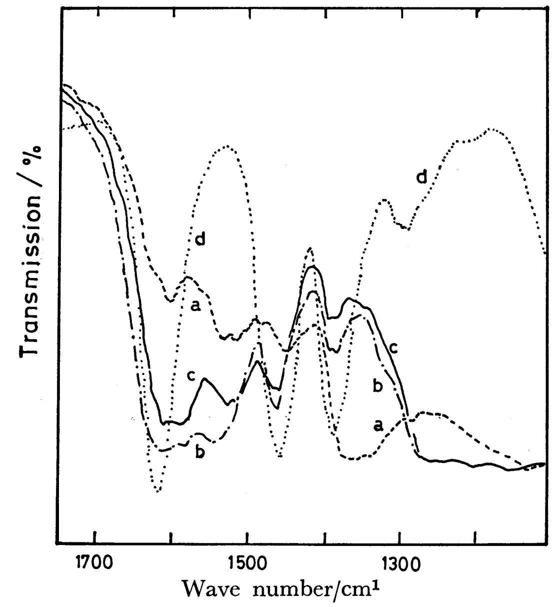


Fig. 8. IR spectra of 1-propylamine adsorbed on SB. (a), (b), (c), and (d) are the same as in Fig. 5.

TABLE 2. REACTIVITY OF $TiO_2$ TO VARIOUS REAGENTS AND DECOMPOSITION TEMPERATURES OF THE PRODUCTS

| Sample | Regent | Content in product wt% | | Degree of reaction Molecules per 100 Å² of surface calculated from content of | | Decomposition temperature °C | |
|---|---|---|---|---|---|---|---|
| | | C | N | C | N | Beginning | Active |
| SA | $CH_3(CH_2)_3OH$ | 2.67 | 0 | 4.9 | — | 140 | 240 |
| | $CH_3(CH_2)_3NH_2$ | 2.20 | 0.94 | 4.0 | 4.4 | 160 | 240 |
| | $HO(CH_2)_3NH_2$ | 2.67 | 0.99 | 5.0 | 4.7 | 150 | 230 |
| SB | $CH_3(CH_2)_3OH$ | 2.54 | 0 | 4.8 | — | 190 | 260 |
| | $CH_3(CH_2)_3NH_2$ | 2.45 | 1.12 | 4.6 | 5.4 | 210 | 255 |
| | $HO(CH_2)_3NH_2$ | 3.86 | 1.52 | 7.5 | 7.7 | 180 | 260 |

of $Ti^{4+}$ is much larger than that of $Si^{4+}$;[21] the OH groups bound to $Ti^{4+}$ are acidic in nature, unlike those bound to $Si^{4+}$, and so readily interact with $NH_2$ groups in the amino alcohol, resulting in the formation of $NH_3^+$ groups. In addition, $Ti^{4+}$ also functions as a Lewis acid site, and the Lewis acidity should also make the reactivity of the $TiO_2$ surfaces higher than that of $SiO_2$. On the other hand, $SiO_2$ which has essentially no surface acidity,[22] forms only an ester due to the reaction of the silanol with the alcoholic OH groups of the amino alcohol.[20]

*Comparison of the Reaction of 3-Amino-1-propanol with Those of 1-Propanol and Propylamine at Higher Temperatures in an Autoclave.* Table 2 shows the results of the reactions for SA and SB. The degree of reaction was calculated on the assumption that there were no C–C bond scissions during the reaction. Except for the reaction between 3-amino-1-propanol and SB, the degree of the reaction was roughly the same for all the reactions; thus, the OH and $NH_2$ groups of the reagents appeared to have the same reactivity toward $TiO_2$ under the reaction conditions tried here. In addition, as is shown at the right end of Table 2, the temperatures at which the desorption or decomposition takes place actively were nearly the same for 3-amino-1-propanol, 1-propanol, and propylamine as long as they are adsorbed on the $TiO_2$ sample (SA or SB). Thus, the resistivity against heating of the adsorbed phase is considered not to differ much from reagent to reagent.

The degree of reaction per unit of surface area is calculated to be 4—5 molecules/100 Å² of the $TiO_2$ surface (Table 2). The areas occupied by one molecule of the reagents (20—25 Å²) nearly equal those occupied by normal alkylamine (20.5 Å²) and normal alkanols (21.6 Å²) in a unimolecular layer on water.[23] This fact suggests the formation of oriented and close-packed alkyl groups on $TiO_2$ surfaces. The exceptionally small value of the area occupied by 3-amino-1-propanol on SB (13 Å²) may be due to the condensation (mainly, dimerization) of the amino alcohol on the surface. The intermolecular reaction of the amino alcohol due to the OH and $NH_2$ groups is probably promoted by the acid sites on SB.

*Effect of Surface OH Groups on the Reactivity of $TiO_2$ (SB).* Figure 9 shows a plot of the amount of the reaction of 3-amino-1-propanol *vs.* the amount of surface OH groups on SB treated at various temperatures. Except for SB heat-treated at 300 °C, at which SB exists not as $TiO_2$ but as titanium hydroxide or hydrate of $TiO_2$,[24] a linear relationship is observed between the two amounts. From the slope of the straight line, the ratio of the amount of the reaction to that of the surface OH groups is determined to

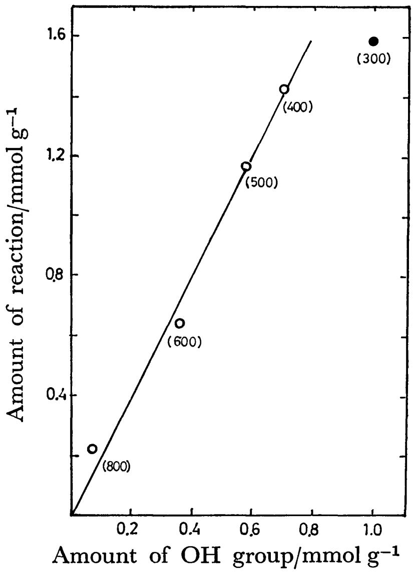


Fig. 9. Relationship between amount of reaction and that of surface OH groups on SB.
The numbers in parentheses show the heat-treatment temperature (centigrade) of the $TiO_2$ sample.

TABLE 3. REACTIONS OF VARIOUS AMINOALCOHOLS WITH $TiO_2$[a)]

| Sample | Aminoalcohol | Carbon content in products wt% | Density of organic groups Number per 100Å² of surface |
|---|---|---|---|
| SA | $HO(CH_2)_2NH_2$ | 1.82 | 5.0 |
| | $HO(CH_2)_2\diagdown NH$<br>$HO(CH_2)_2\diagup$ | 2.58 | 3.6 |
| | $HO(CH_2)_2\diagdown$<br>$HO(CH_2)_2-N$<br>$HO(CH_2)_2\diagup$ | 3.29 | 3.1 |
| SB | $HO(CH_2)_2NH_2$ | 3.98 | 12.0 |
| | $HO(CH_2)_2\diagdown NH$<br>$HO(CH_2)_2\diagup$ | 6.59 | 10.4 |
| | $HO(CH_2)_2\diagdown$<br>$HO(CH_2)_2-N$<br>$HO(CH_2)_2\diagup$ | 12.04 | 14.4 |

a) Preheated at 500 °C just before use.

be about 2. These facts show that $NH_2$ groups of the amino alcohol should react with surface OH groups on SB at a higher temperature under an autogeneous pressure, and that the amino alcohol may dimerize due to the $NH_2$ and/or OH groups of the molecules. The $H_2O$ molecules generated by the dimerization or condensation may convert the Lewis acid sites on SB to Brönsted acid sites or acidic OH groups as was previously been observed in the IR study of pyridine adsorption.

*Effect of Structure of Amino Alcohol on Reaction with $TiO_2$ Surfaces.* The results of the surface reactions of various amino alcohols with SA and SB are shown in Table 3. For the reactions with SA, the amount of reaction per unit of surface area of $TiO_2$ decreased as the structure of amino alcohol became more complicated. For the reactions with SB, the amount of reaction per 100 $Å^2$ are $\geqq 10$, markedly more than those for the reactions with SA. A maximum in the amount was obtained for the reaction of triethanolamine. The ratio of the amount of the reaction of the triethanolamine to that of the surface OH groups is above 4. Extensive condensations due to OH groups may be the main reason that the triethanolamine showed the highest value in the amount of the reaction in spite of its extremely bulky structure.

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