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Generation of Acid Sites by SiO_2 Deposition on Groups IVB Metal Oxides

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An ultra thin silica layer was prepared by chemical vapor deposition of $Si(OCH_3)_4$ onto titania and zirconia. The relationship between surface structure and acidity was studied by measurement of coverage, IR spectroscopy of probe molecules, and test reactions. Silica was deposited to form a 1 : 1 complex with the oxide cation (–M–O–Si–), until more than 90% of monolayer coverage was obtained. The silica overlayer showed weak Brønsted acidity only sufficient to catalyze the isomerization of 1-butene and the dehydration of *tert*-butyl alcohol. The acidity could not be correlated with the difference in coordination number or valence of cations but seemed to correlate with the interaction between silica and metal oxide.

INTRODUCTION

Solid acidity is often obtained by combining metal oxides, as in silica–alumina (*1*). In order to test the results of quantum-chemical calculations that employ cluster models of the acid sites (*2–4*), we have proposed a chemical vapor deposition (cvd) method using silicon alkoxide to generate a narrow distribution of acid sites. With this method, a homogeneously coated silica layer can be obtained on metal oxides and all the silicon cations can be exposed on the surface bonded with cations of the metal oxides through oxygen bridges (*5*). Our previous investigation on alumina (*6*) showed that the silica monolayer possessed weak acidity sufficient to catalyze the isomerization of 1-butene and the dehydration of *tert*-butyl alcohol. The origin of the acid site was ascribed to silanol groups on the surface. Similar investigations concerning the acidity of MgO and Al_2O_3 have been reported by Imizu *et al.* (*7*) and Sato *et al.* (*8*), respectively.

Due to the defect spinel structure of γ-alumina, it is a rather complex metal oxide with many surface cation sites (*9*). When combined with silica, the result is a typical Brønsted acid catalyst. Results are quite different on titania and zirconia, however; the mixtures with silica show Brønsted or Lewis acidities which vary with composition (*1, 10, 11*). Attention has currently focused on a mixture of SiO_2 and ZrO_2 (*12*), and titanosilicate (*13, 14*) as novel catalysts. The purpose of this investigation is therefore to apply the cvd method to titania and zirconia and to explore the generation of acidity.

EXPERIMENTAL

Materials and Chemical Vapor Deposition

Titania was supplied by Nippon Aerosil Co. Ltd., P-25. The surface area was 44 m^2 g^{-1} and the crystal phase was determined to be anatase containing a small amount of rutile. Zirconia was prepared from a $ZrCl_2O$ solution basified with NH_4OH to deposit the hydroxide, which was then dried and calcined in air at 773 K. XRD showed that the solid was baddeleyite. Its surface area was 66.4 m^2 g^{-1}.

Deposition of silica was performed as described previously (*15*). After evacuation at 673 K for 2 h, $Si(OCH_3)_4$ vapor was admitted to the metal oxide at 593 K. The Pressure in the vessel was ca. 10^{-3} Torr (1 Torr = 133.3 Pa), and the vapor pressure of the alkoxide was kept at 2.5 Torr by chilling the reservoir

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in an ice bath. Finally, water was reacted at 593 K to remove the methoxide residue. The number of deposited Si atoms was determined by monitoring the weight gain of the sample with the aid of a quartz microbalance, SiO_2 being assumed to be formed.

Characterization

The benzaldehyde–ammonia titration (BAT) (*16, 17*) was used to discriminate between surfaces of silica and titania or zirconia. Pulses of benzaldehyde were injected repeatedly (usually three times) to saturate the oxide surface with adsorbed benzoate anion, and then ammonia was reacted with the species to form benzonitrile. The number of coordinatively unsaturated sites of the IVB metal oxides was determined measured from the amount of benzonitrile.

The acidic strength profile was determined by test reactions run in pulse mode. Isomerization of 1-butene was carried out at 473 or 503 K on the catalyst pretreated at 673 K; products were analyzed with a capillary column silicone OV 101 at room temperature. Dehydration of ethyl- and *tert*-butyl alcohols was performed at 373 to 573 K on the catalyst pretreated at 673 K. The separation column for the alcohol dehydration was Porapak Q at 373 K. A liquid nitrogen trap was installed prior to the reactor in order to remove moisture and impurity oxygen in the carrier gas.

Infrared spectra were recorded on a Jasco FTIR-3 spectrophotometer in the range of 1000 to 4000 cm^{-1}. The thin wafer was compressed under a pressure of 12.3 MPa and was placed in a holder suspended from a platinum wire; the sample was evacuated and then exposed to the IR beam. Spectra of adsorbed pyridine and ammonia were taken after adsorption at 423 and 373 K, respectively, on the sample surface evacuated at 673 K.

RESULTS

Deposition of Silicon Alkoxide

Exposure to the alkoxide at 593 K increased the sample weight, until by-products such as methylalcohol retarded the diffusion of alkoxide. Replacement of the residual gas with the alkoxide vapor started the deposition again. Thus, stepwise increases of weight were observed on both titania and zirconia. In this investigation, the number of deposition–evacuation cycles was varied to obtain silica-deposited samples with different degrees of deposition. The highest concentrations of silica on titania and zirconia were 8.81 wt% (surface concentration, 17.5 Si nm^{-2}) and 8.77 wt% (13.2 Si nm^{-2}), respectively.

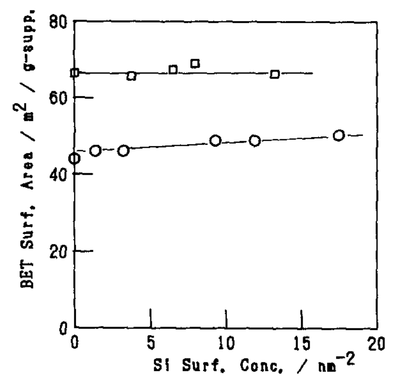

FIG. 1. BET surface area normalized by mass of support against the deposition concentration of silicon on TiO_2 (○) and ZrO_2 (□).

Characterization

Figure 1 shows the BET surface areas of the prepared samples. (We estimated the change of surface area of the supports from the surface area divided by the mass of the support, not by mass of the deposited sample.) Both kinds of samples maintained almost constant surface areas with increasing deposition, indicating little blocking of the micropores of the supports by the deposited silica.

The extent of the support covered by the silica was measured by the BAT method. Percentage coverage by silica, defined as 100 × (silica-covered surface area/total BET surface area), was plotted against the deposition concentration in Fig. 2. The coverage increased monotonically with Si con-

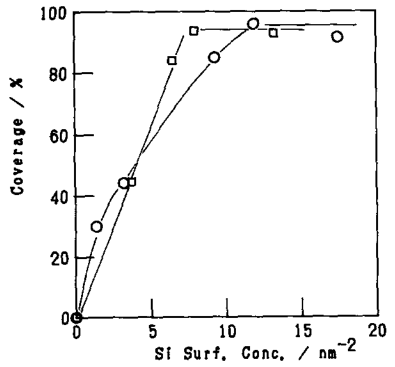

FIG. 2. Increase of coverage with increase of the deposition concentration of silicon on TiO_2 (○) and ZrO_2 (□).

centration on both TiO_2 and ZrO_2, eventually reaching 90%. Further deposition was possible, but did not lead to 100% coverage. The lowest concentration of silicon required to cover the supports almost completely, by extrapolating the initial linear portion of the uptake curves, was found to be 12 and 8 Si nm^{-2} on TiO_2 and ZrO_2, respectively. A sample with this concentration of silicon is termed a monolayer sample in the following description.

Stretching vibrations of hydroxides measured by IR spectroscopy showed a clear change with deposition, as shown in Fig. 3. Hydroxides observed initially at 3738 and 3630 cm^{-1} on TiO_2 and ZrO_2, respectively, disappeared and a 3745 cm^{-1} band ascribable to isolated silanol appeared on the monolayer sample. In addition, broad adsorptions of silanols or hydroxides of the supports overlapped at about 3600 cm^{-1}. Intensities of isolated silanols decreased upon further deposition of silica in amounts exceeding monolayer covering. This observation suggests that silanols replaced hydroxides until the formation of a silica monolayer.

Acidity was characterized by IR spectroscopy using base probes, ammonia and pyridine. Figures 4 and 5 show IR bands for absorptions of these molecules at 1700 to 1300 cm^{-1}. IR bands of hydroxides, at 4000 to 3000 cm^{-1}, are present only in the case of ammonia adsorption.

Adsorption of ammonia on the supports produced a physically adsorbed NH_3 indicated by the band at 1620 cm^{-1}. The NH_3 band plus an ammonium ion band at 1450 cm^{-1} were seen on monolayer samples. However, the NH_4^+ band had a weak intensity and was easily removed by evacuation of the samples at 473 K (spectrum B in Figs. 4a and 4b). The intensity of isolated silanol band on monolayer samples decreased upon adsorption of ammonia, simultaneous with the appearance of the absorption band at 3725 cm^{-1}. We infer that some of the isolated silanol interacted with ammonia and their IR bands shifted to lower frequencies. However, the original silanol bands were not recovered by evacuation at 473 K, contrary to the behavior of the NH_4^+ band.

Adsorption of pyridine gave rise to physically adsorbed and hydrogen-bonded pyridine bands at 1615 and 1455 cm^{-1}, both on supports and monolayer catalysts. The intensities of bands on the monolayer catalysts were weak, and, in addition, a small absorption at 1545 cm^{-1} for pyridinium cation appeared upon evacuation at 423 K (spectrum A in Figs. 5a and 5b). IR spectra of adsorbed bases indicated the formation of weak Brønsted acid sites on the monolayer catalysts.

Test Reaction

Test reactions that required different strengths of acidity were chosen in order to know the acidity profiles of the silica-deposited samples. Dehydration of ethylalcohol, isomerization of butene, and dehydration of *tert*-butylalcohol were tested, because these required strong acidity in the order: dehydration of ethylalcohol > isomerization of butene > dehydration of *tert*-butylalcohol. As mentioned below, the acitivity profile was independent of TiO_2 and ZrO_2.

Catalyst activity for the dehydration of ethylalcohol decreased with increasing silicon concentration, but was not inhibited

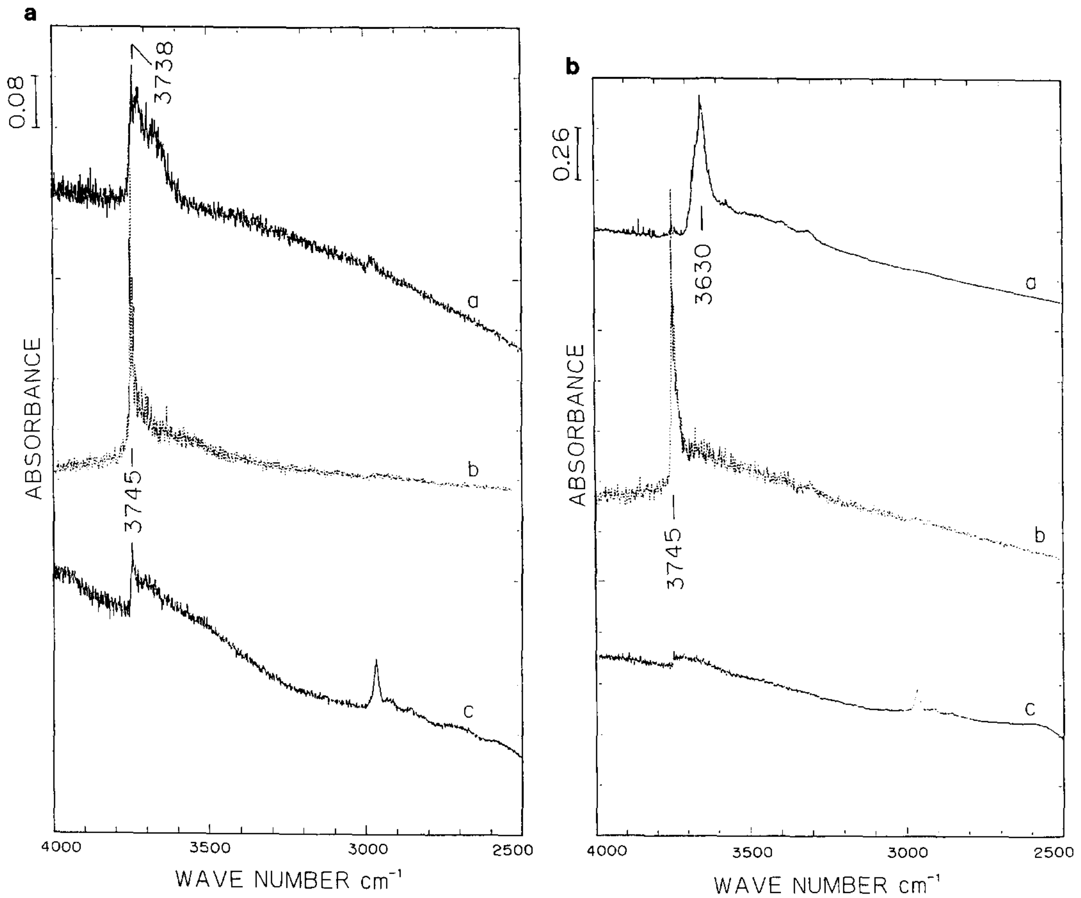

FIG. 3. IR spectra of support (a), monolayer sample (b) and secondary deposited sample (c) with the concentration of silicon, 17.5 and 13.2 Si nm^{-2} on TiO_2 and ZrO_2, respectively: TiO_2 (3a) and ZrO_2 (3b).

completely. Butadiene was formed as a byproduct on TiO_2, but the formation of butadiene was also suppressed by the deposition of silica. Isomerization of butene was, however, enhanced by the deposited silica, but suppressed by an excess amount of silica. Activity paralleled coverage, as can be seen by comparing Figs. 2 and 7. Isomerization activity attained a maximum at 12 and 8 Si nm^{-2} on TiO_2 and ZrO_2, respectively, where silicon covered the surface almost completely. On further loading, the activity decreased markedly. The *cis* to *trans* ratio of 2-butene was almost constant with support and loading: 1.6 to 1.4 on TiO_2, 1.4 to 1.3 on ZrO_2.

Very similar results were obtained in the dehydration of *tert*-butyl alcohol, as shown in Fig. 8. The monolayer catalyst showed the maximum activity, and it decreased with further deposition of silicon. The extent of loss of activity upon deposition of an excess amount of silica was, however, smaller than that of butene isomerization.

DISCUSSION

Titania anatase has a tetragonal crystal structure with dimensions and number of atoms: $a = b = 0.379$ nm; $c = 0.951$ nm; $Z = 4$ (*18*). Two metal atoms can be exposed in the (001) face, and the cation site density is less than 14 nm^{-2} and less than 11 nm^{-2}

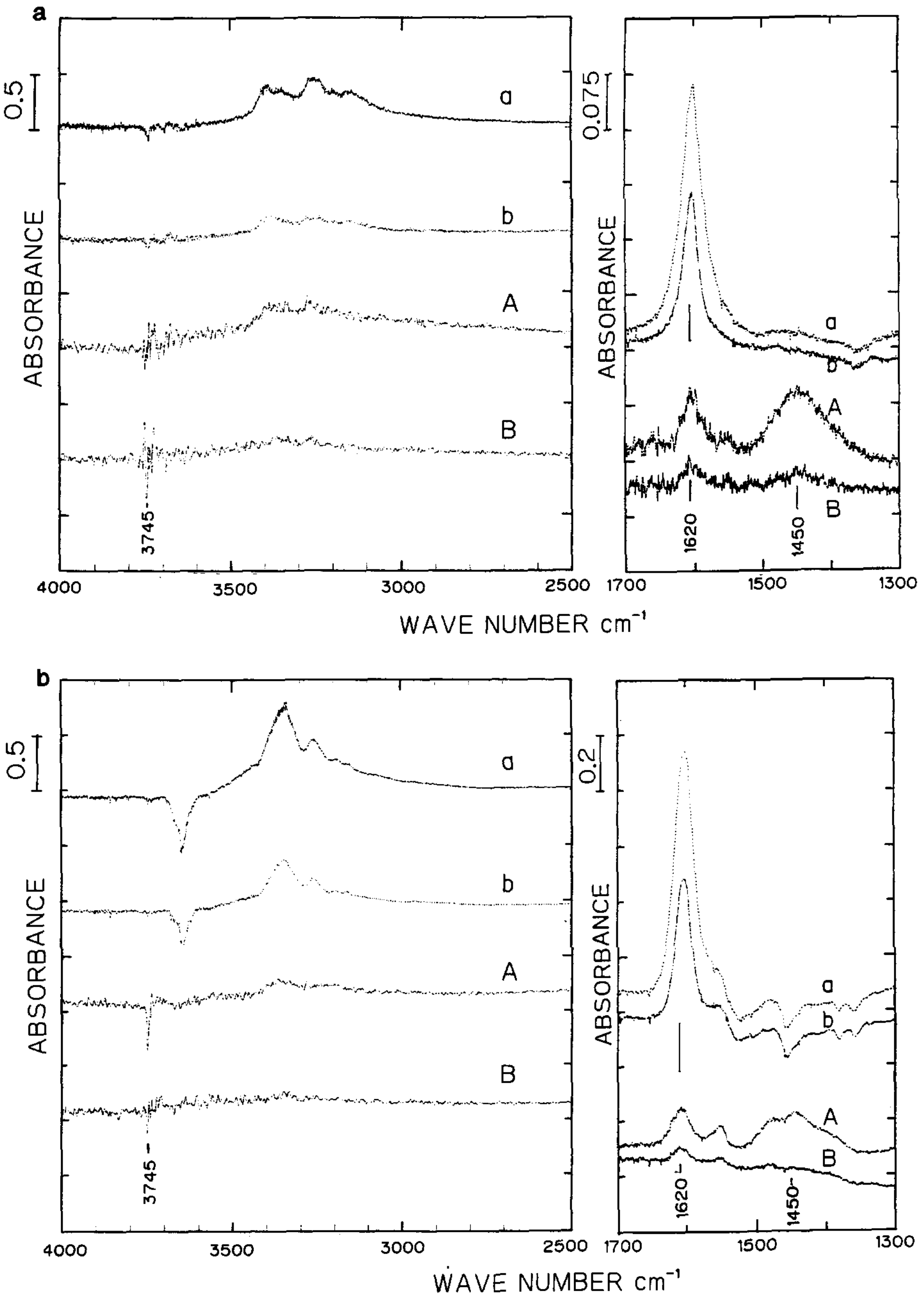

FIG. 4. IR spectra of ammonia adsorbed on support (a, b) and monolayer sample (A, B) after evacuation at 373 (a, A) and 473 (b, B) K: TiO_2 (4a) and ZrO_2 (4b).

on the (010) and (101) faces. Zirconia baddeleyite has a monoclinic crystal morphology with unit cell dimensions of 0.532, 0.521, and 0.515 nm enclosing 4 atoms (*19*). The cation site density, based on the same calculation, is less than 7.5 nm^{-2} in every face of the crystal. The maximum cation site densities thus estimated on titania and zirconia, 11–14 and 7.5 nm^{-2}, respectively, agree well with the lowest concentration of

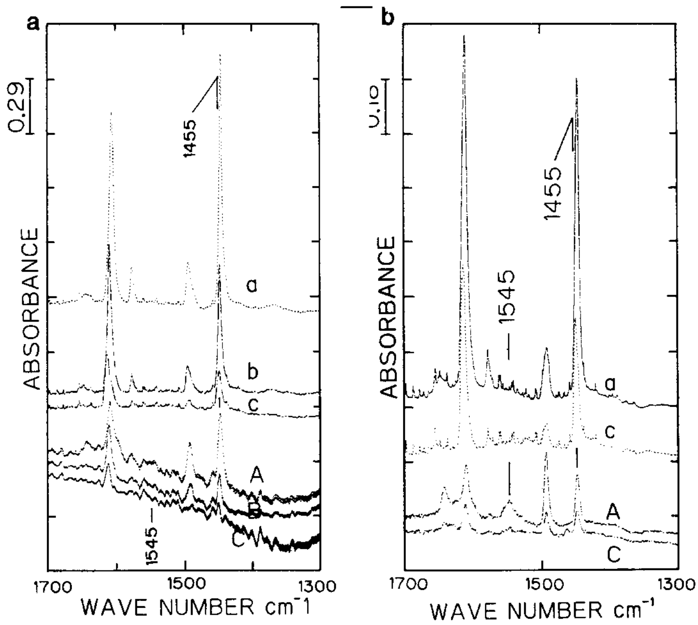

FIG. 5. IR spectra of pyridine adsorbed on support (a, b, c) and monolayer sample (A, B, C) after evacuation at 423 (a, A), 473 (b, B), and 573 (c, C) K: TiO_2 (5a) and ZrO_2 (5b).

silicon necessary to cover the surface of supports. We therefore suggest that silica overlayers with structures similar to the support surfaces are formed by the deposition of silicon up to these concentrations.

Linear increase of coverage with the concentration of silicon on zirconia shows that the silica layer with a common structure is formed from low to high extent of the coverage. In other words, the monolayer grows directly with the silicon concentration and finally covers the surface of zirconia almost completely. On titania, however, a subtle alteration in structure of silica is suspected, because the relationship between coverage and Si concentration is not linear. This may be caused either by the heterogeneous dis-

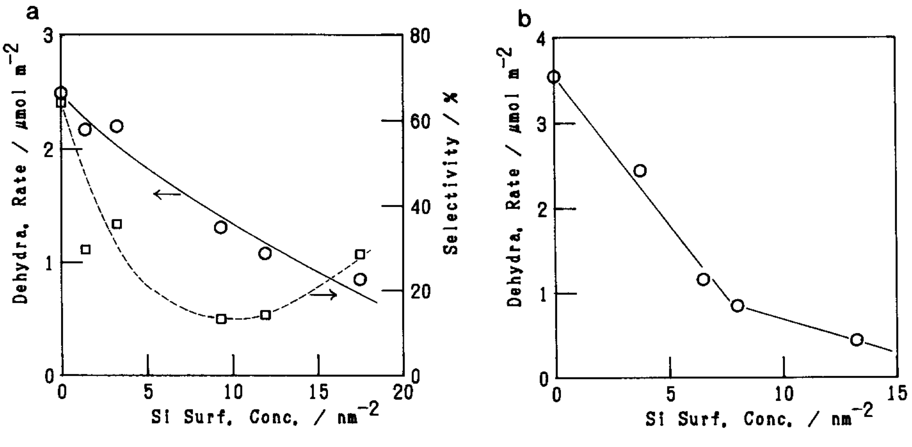

FIG. 6. Activity of ethanol dehydration against the deposition concentration of silicon on TiO_2 at 573 K (a) and on ZrO_2 at 543 K (b). The selectivity to the formation of butadiene was plotted on TiO_2.

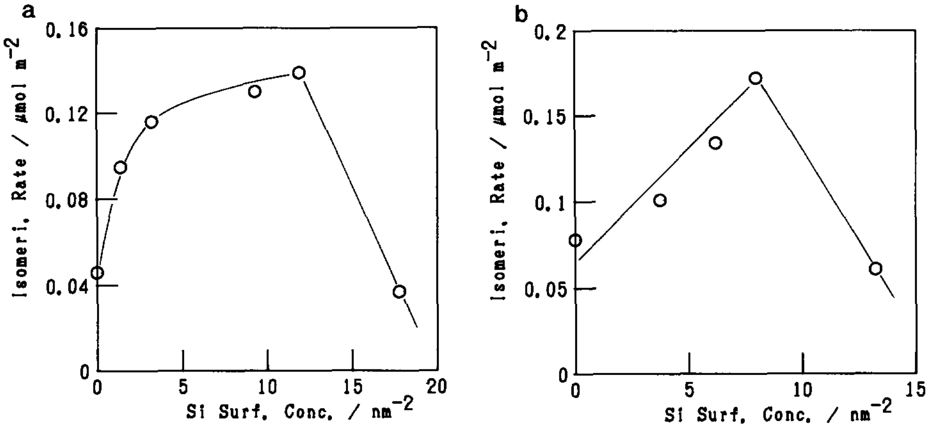

FIG. 7. Activity of butene isomerization against the deposition concentration of silicon on TiO_2 at 473 K (a) and on ZrO_2 at 503 K (b).

tribution of cations on titania, as calculated above, or by scrambling of titanium and silicon cations. White and co-workers (*20, 21*) reported that when silicon alkoxide was deposited in the ultrahigh vacuum apparatus such a scrambling occurred on titania but not on zirconia. Our study deals with the deposition in vacuum apparatus ($<10^{-3}$ Torr) below 673 K, and the deposition conditions are not so severe as to deteriorate the titania surface.

The formation of a silica monolayer was confirmed on Al_2O_3 in the previous study (*6*) and here on TiO_2 and ZrO_2. We infer a preferential deposition of silicon alkoxide on the support surface rather than on the growing silica. Otherwise, fairly large islands of silica would be formed with more of the surface of the supports remaining exposed.

Because $Si(OCH_3)_4$ possesses four methoxides, it can be polymerized through siloxane bonds (–Si–O–Si–); however, hydrolysis by water is necessary to do so. Without hydrolysis, deposition of silica on the silica overlayer should be suppressed. Al_2O_3,

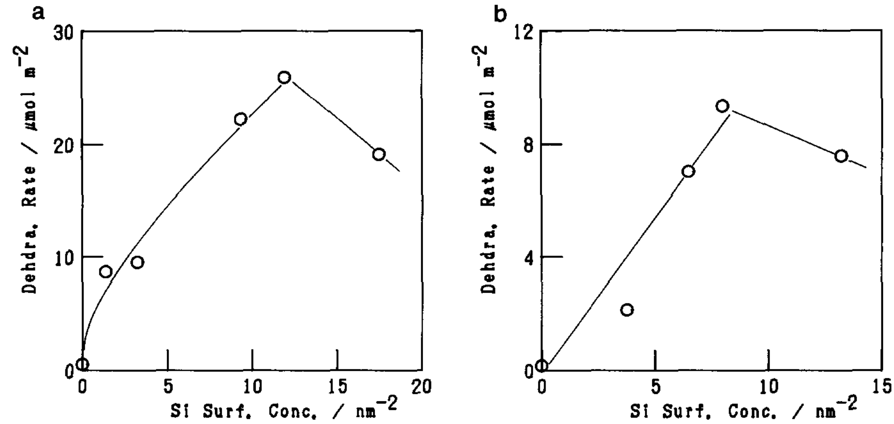

FIG. 8. Activity of *tert*-butyl alcohol dehydration against the deposition concentration of silicon on TiO_2 (a) and ZrO_2 (b) at 373 K.

TiO_2, and ZrO_2 possess basicity that is not observed on SiO_2. We therefore suspect that silica spreads easily on them. In our previous investigation concerning the spreading of V_2O_5 on various supports (*22*), a simple conclusion was obtained; the greater the difference in the electronegativity of cations of support and supported oxide, the easier the spreading of metal oxide on the support. Similarly, we expect that a silica overlayer should spread easily on such basic metal oxides as ZnO (*23*), SnO_2 (*24*), MgO (*7*), CeO_2, and La_2O_3, given the small electronegativity of cations. The formation of a thin overlayer can probably be related to the stability of bonds in the interface. Both the multifunctionality of silicon alkoxide and the difference in the acid–base properties between silica and the supports could stabilize the silica overlayer.

Generation of Brønsted acid sites on the monolayer catalyst is confirmed by IR measurements as well as test reactions. The IR measurements indicate that the sites are weakly acidic. Moreover, because only facile reactions, double-bond isomerization of olefin, and dehydration of *tert*-alcohol are catalyzed, the test reactions also suggest that the sample possesses only weak acid sites. The acidity of the silica overlayer is removed or weakened by secondary deposition both on titania and zirconia. This finding indicates the formation of acid sites only on the monolayer and submonolayer. There may be only hydroxides exposed on the surface of monolayer sample, and these are weak Brønsted acid sites, both on titania and zirconia.

At least two kinds of silicon hydroxides, isolated and nonisolated, were discerned on the monolayer catalyst from the infrared spectra. Although the intensity of the latter species seems to be weaker than that of the isolated silanol, the broadness of the latter band makes it difficult to evaluate quantitatively. Because the isolated silanol band at 3745 cm^{-1} was observed on the monolayer sample, and the intensity decreased on deposition of the secondary layer, we infer a relationship between the formation of isolated silanol and the generation of acid sites. The isolated silanol possessed only weak acidity. However, the IR band of some of the isolated silanols shifted to lower frequency upon adsorption of ammonia and was not restored by the evacuation at 473 K. Rather, the isolated silanol could be assigned to the sites for hydrogen-bonded ammonia. Thereby, a small portion of isolated silanol or other kinds of hydroxide with a weak IR intensity is a possible species for the acid sites.

Generation of acid sites by mixing of SiO_2 with TiO_2 or ZrO_2 was explained by Tanabe on the basis of differences in coordination number and/or valence (*1*). According to his proposal, the coordination number of M–O or the valence of a minor component cation changes on mixing to possess a common coordination number or valence and a change in cation induces Brønsted or Lewis acidity. The silica overlayer formed by cvd of silicon alkoxide, however, possesses weak Brønsted acidity irrespective of metal oxides, Al_2O_3, TiO_2, and ZrO_2 with coordination number of M–O (4, 6, or 8) and valence of cation (3+ or 4+). In other words, neither the coordination number nor the valence of the support oxides affects the generation of acidity. We suspect therefore the interaction between metal oxide and silicon oxide as a possible reason.

On the other hand, the silica overlayer plays a role of deactivation of catalytic activity of the surface also. The dehydration of ethylalcohol is one of the inhibited reactions. Ethanol dehydration may require dual sites consisting of basic and acidic sites (*25*) on TiO_2 and ZrO_2; these sites may be lost on the silica monolayer. Secondary deposition on the silica overlayer inactivated the silica monolayer, completely or incompletely; butene isomerization activity was lost, while *tert*-butyl alcohol dehydration activity still remained. The degree of inhibition caused by the secondary silica layer may be different according to the reaction.

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