# Mechanism of Growth of Silica Monolayer and Generation of Acidity by Chemical Vapor Deposition of Tetramethoxysilane on Alumina

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The mechanism of chemical vapor deposition of tetramethoxysilane on  $\gamma$ -alumina was studied. A silica monolayer covered the suface almost completely upon the deposition at 593 K in a static system. Even at low temperatures (<473 K), tetramethoxysilane was deposited quickly, but the deposition was readily saturated at a low concentration of Si, and the silica layer thus covered only a part of the surface. The amount of methoxy groups on the surface was determined from gravimetry and product analysis by the pulse method; the ratio of CH<sub>3</sub>O-/Si was high at the low temperatures. The ratio decreased with increasing temperature, and, simultaneously, silanol appeared. On these findings, the following mechanism is proposed; gaseous tetramethoxysilane is deposited on alumina quickly until the silicon alkoxide and a fraction of methanol cover the surface; at high temperatures, contaminated water hydrolyzes the silicon alkoxide into silanol, which is reacted with another tetramethoxysilane; the successive deposition thus proceeds, and at last, the monolayer with a network of Si-O-Si covered the surface almost completely. The stoichiometry upon the proposed mechanism is consistent with the experiments. Catalytic activity for isomerization of butene was observed over the monolayer deposited at 493 and 593 K. The samples deposited at low temperatures (≤423 K) showed almost no activity. It is suggested that Al-O-Si-OH in the network of Si-O-Si possesses the Brønsted acidity, whereas the dispersed silica species has no acidity. At 673 K, the random deposition formed a heterogeneous structure of silica including thick layers and/or particles, which showed low activity.

### Introduction

On such mixed solid-acids as silica-alumina, the acidity is presumed to be generated at the interface between the two components. Several models of the acid sites have been proposed, and explanations about generation of the acidity have been made on the basis of various concepts,<sup>1,2</sup> including quantum-chemical calculations.<sup>3-5</sup> The origin of acidity is however difficult to be understood by such simple models, because the mixed oxides usually possess complicated structures. In order to overcome the difficulty, an ultrathin layer loaded on another oxide is promising. We have used chemical vapor deposition (CVD) of Si(OCH<sub>3</sub>)<sub>4</sub> (tetramethoxysilane) to form a thin SiO<sub>2</sub> layer on zeolite in order to control the pore-opening size.<sup>6,7</sup> We have then applied the CVD on several metal oxides. The silical monolayer was formed over  $\gamma$ -alumina,<sup>8</sup> titania, and zirconia<sup>9</sup> and found to possess the Brønsted acid sites. The acid strength of the monolayer on alumina was estimated to be weak compared with that of the acid sites on conventional silica-alumina, because the monolayer was active for only facile reactions such as the double-bond isomerization of olefin.<sup>10</sup> Species M-O-SiOH (M was the surface cation of the support oxide) was suggested to be the acid site. The lack of strong acidity suggested a fine distribution of acid strength due to the homogeneous structure. The silica monolayer was utilized for the Beckmann rearrangement of cyclohexanone oxime.<sup>11</sup> Similar methods of the preparation,<sup>12-15</sup> the characterization,<sup>16</sup> and the application<sup>17</sup> of silica layers were published.

In order to determine the microstructure of active sites, it is important to clarify the mechanism of preparation of the catalyst. The procedure of chemical vapor deposition is expected to be simple in comparison with that in the liquid-phase preparation of mixed oxides. In the present study, the mechanism of the formation of the monolayer will be investigated by varying the conditions of deposition. Various species of SiO<sub>2</sub> are suggested to be formed on  $\gamma$ -alumina, and the acidic property is studied in order to determine the microstructure of the acid site to show the origin of the generation of the acidity. **Experimental Section** 

**Chemical Vapor Deposition in Static System.** Alumina was supplied from the Catalysis Society of Japan, as a reference catalyst, JRC-ALO-4. The crystal phase was  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the surface area was 158 m<sup>2</sup> g<sup>-1</sup>.

The sample (0.1 g) was placed on a basket hanged by a quartz spring in a vacuum line, and the change of weight was monitored by a transducer. Evacuation was carried out at 673 K until no change of the weight was observed. The vapor of tetramethoxysilane was then admitted onto the sample; the cycles of introduction of vapor and evacuation were repeated in order to allow the alkoxide vapor to be contacted with the sample. The vapor pressure was kept at *ca*. 2.5 Torr (1 Torr = 133.3 Pa) by chilling the reservoir with an ice bath, and the degree of evacuation was *ca*.  $10^{-3}$  Torr. Finally, the sample was calcined with 200 Torr of oxygen at 673 K. Surface concentrations of Si and organic materials were estimated from gravimetry and BET surface area.

**Deposition in Pulse System.** Alumina (0.02 g) was set in a 4-mm-i.d. Pyrex-glass reactor. The carrier gas, 50 cm<sup>3</sup> min<sup>-1</sup> of helium, was passed through a liquid nitrogen trap in order to remove the moisture and impurity oxygen and fed into the sample. After pretreatment at 673 K for 1 h, 1 mm<sup>3</sup> ( $6.4 \times 10^{-6}$  mol) of tetramethoxysilane was injected repeatedly. Products were analyzed by a column of Benton-34 which was connected directly with the reactor. The amount of deposited Si was estimated from the difference in amounts of injected and eluded tetramethoxysilane. In order to show the influence of the degree of drying, the pretreatment temperature was varied in some experiments.

Infrared Spectroscopy. Alumina was molded into a thin disk and set in an *in-situ* cell which was connected to a vacuum line. The vapor of tetramethoxysilane was admitted onto the sample after the evacuation. The vapor pressure was ca. 2.5 Torr, and the degree of evacuation was ca.  $10^{-3}$  Torr. The spectrum was measured using a Jasco-FTIR/5300 spectrometer at the lower part of the cell with windows of CaF<sub>2</sub>, after the sample was treated in the upper part with a furnace.

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Figure 1. Weight increase by deposition of tetramethoxysilane at various temperatures over 0.1 g of alumina evacuated at 673 K in the static system.

Measurement of Coverage Using the Benzaldehyde-Ammonia Titration Method. Benzaldehyde is adsorbed on alumina (the saturated concentration, 1.8 nm<sup>-2</sup>), but only a little (<0.01 nm<sup>-2</sup>) on  $SiO_2$ . On the basis of this finding, the coverage of the alumina surface by SiO<sub>2</sub> was estimated by using the benzaldehydeammonia titration (BAT) method.<sup>18,19</sup> The sample was set in a Pyrex tube (i.d., 4 mm). The carrier gas was helium purified by using a liquid nitrogen trap. After calcination of 673 K for 1 h,  $1 \text{ mm}^3$  (9.8 × 10<sup>-6</sup> mol) of benzaldehyde was repeatedly injected into the sample. The eluded benzaldehyde and products were analyzed by a silicone grease column kept at 513 K, and the injections of benzaldehyde were repeated until the adsorption was saturated. Finally, 10 cm<sup>3</sup> ( $4.2 \times 10^{-4}$  mol) of gaseous ammonia was injected at 673 K, and the desorbed benzonitrile was quantified. The injections of ammonia were repeated until no products were observed. The coverage by  $SiO_2$  on alumina was calculated from the following equation: coverage = 1 - 1[density of adsorbed benzaldehyde on the sample/density on pure alumina  $(1.8 \text{ nm}^{-2})$ ].

Test Reaction of Acidic Property. The isomerization of butene was chosen to test the acidic property of various species of SiO<sub>2</sub>. The catalyst was treated in a Pyrex reactor (i.d., 4 mm) at 673 K for 1 h in flowing helium which was purified with a liquid nitrogen trap. Then, 1 cm<sup>3</sup> ( $4.2 \times 10^{-5}$  mol) of gaseous 1-butene was injected into the sample at 393 K. The flow rate of helium was 40 cm<sup>3</sup> min<sup>-1</sup>, and the total pressure was 4 atm. Conversion was adjusted less than 5% in order to measure the activity under the differential conditions. Products were analyzed by using a column of VZ-7 at room temperature.

#### Results

**Deposition in Static System.** Figure 1 shows the weight increase by deposition of tetramethoxysilane at various temperatures. The weight increased quickly up to *ca*. 7 wt % in all cases. At temperatures between 373 and 423 K, the deposition was readily saturated at 8 wt %, where the surface concentration of Si was calculated to be *ca*. 3 Si atoms nm<sup>-2</sup>. At 473 K, 12 wt % of SiO<sub>2</sub> was deposited, and more than 20 wt %, *i.e.* approximately 13 Si atoms nm<sup>-2</sup>, of the surface concentration was obtained at high temperatures above 493 K.

The deposition was suggested to form silicon alkoxide anchored on the surface, *i.e.* Al-O-Si(OCH<sub>3</sub>)<sub>n</sub>. Methanol, which was observed by the pulse method, is suggested to be adsorbed to form a surface alkoxide, Al-OCH<sub>3</sub>. In order to determine the composition of alkoxide, the amounts of SiO<sub>2</sub> and organic materials were estimated from the gravimetry on the basis of the following assumptions; the deposition formed the species Al-O-Si(OCH<sub>3</sub>)<sub>n</sub> and Al-OCH<sub>3</sub>; the calcination formed SiO<sub>2</sub>; and the physical adsorption of products and coke deposition were ignored. As shown in Table 1, the ratio of CH<sub>3</sub>O-/Si was almost constant against the time of deposition, but it decreased with increasing deposition temperature. Figure 2 shows the plot of

 TABLE 1: Estimated Composition of Deposited Materials

 Based on Gravimetry in the Static System

	deposn time/h	amount of materials/ (% g/g of Al <sub>2</sub> O <sub>3</sub> )			
deposn temp/K		SiO <sub>2</sub> ª	Organic Material <sup>b</sup>	concn of Si atoms/nm <sup>-2</sup>	CH <sub>3</sub> O–/Si ratio
423	4	3.8	3.2	2.3	2.2
	45	5.1	4.0	3.2	2.1
473	1	4.5	2.3	2.9	1.3
	45	8.1	3.8	5.2	1.2
493	4	7.4	2.6	4.5	0.9
	230	17.3	5.6	7.7	0.8

<sup>a</sup> Weight increase by deposition followed by calcination. <sup>b</sup> Weight decrease by calcination.



Figure 2. Composition of deposited materials after deposition at various temperatures. The pretreatment of alumina was carried out at 673 K, and the composition was estimated from gravimetry in the static system  $(\bullet)$  and from product analysis in the pulse system (O).



Figure 3. Concentration of Si deposited by pulses of tetramethoxysilane at various tempertures over alumina pretreated at 673 K. Pulse size was 1.21 (molecules of tetramethoxysilane)/nm<sup>2</sup> of alumina surface.

the CH<sub>3</sub>O-/Si ratio against the deposition temperature. The ratio of CH<sub>3</sub>O-/Si was *ca*. 2 at 423 K; obviously it decreased with increasing temperature and arrived to almost zero at 593 K.

**Deposition in Pulse System.** The concentration of deposited Si was calculated on the basis of the amount of deposited tetramethoxysilane and the surface area of alumina and plotted against the number of pulses in Figure 3. At the first pulse, 1.2  $nm^{-2}$  of tetramethoxysilane was deposited over the broad range of temperature, because almost all of the injected tetramethoxysilane (1.21 nm<sup>-2</sup>) was deposited. At 373 K, the concentration of Si was saturated at 1.7 Si atoms nm<sup>-2</sup>. However, the deposition was hardly saturated at tempeatures above 423 K. In the temperature range from 423 to 473 K, the deposition continued until large amounts of Si were deposited. At higher temperatures, the deposition was not saturated during the experimental runs. At 673 K, almost all the injected tetramethoxysilane was deposited.

Methanol and dimethyl ether were observed in the products. As shown in Table 2, the ratio of methoxy groups to deposited

TABLE 2: Products and Estimation of Composition of Deposited Materials in the Pulse System

	deposn	amount of material/(molecules of Al <sub>2</sub> O <sub>3</sub> /nm <sup>2</sup> )			distributions		
temp of		deposited Si(OCH <sub>3</sub> ) <sub>4</sub>	yielded		of CH <sub>3</sub> OH	of CH <sub>1</sub> OCH <sub>1</sub>	CH <sub>3</sub> O-/Si ratio
pretreatment/K			CH <sub>3</sub> OH	CH <sub>3</sub> OCH <sub>3</sub>	(a)	(b)	(4-a-b)
673	3734	1.8	0.53	0.03	0.30	0.032	3.7
	423ª	2.5	2.1	0.12	0.84	0.093	3.0
	4734	2.6	3.8	0.42	1.5	0.33	2.2
	523 <sup>6</sup>	4.2	5.0	2.0	1.2	0.93	1.9
	573 <sup>6</sup>	4.8	6.6	4.3	1.4	1.8	0.8
	623 <sup>ø</sup>	5.3	1.3	10	0.21	3.2	0.6
	673 <sup>ø</sup>	11.1	2.6	22	0.23	4.0	0
573	473ª	2.2	2.9	0.16	1.4	0.14	2.5
773	473ª	2.6	3.3	0.86	1.3	0.67	2.1

<sup>a</sup> Based on the total amounts of deposited and produced compounds until the deposition was saturated. <sup>b</sup> Based on the total amounts of deposited and produced compounds by the first 10 pulses. The deposition was not saturated.



Figure 4. Plot of composition on the surface against the number of pulses determined from the total amounts of deposited and produced molecules in the pulse system. The pretreatment of alumina was carried out at 673 K.

Si was calculated from the following equations:

 $a = (no. of formed CH_0OH molecules)/$ 

$$(4 \times no. of deposited Si)$$

 $b = (2 \times \text{no. of formed CH}_3\text{OCH}_3 \text{ molecules})/$ 

 $(4 \times no. of deposited Si)$ 

ratio of CH<sub>3</sub>O-/Si of deposited maerials = 4 - a - b

As shown in Figure 4, the CH<sub>3</sub>O-/Si ratio was almost constant against the number of pulses. Figure 2 shows that the ratio was about 4 at 373 K and decreased with increasing temperature. The decrease of the ratio by increasing the deposition temperature was observed also in the static system, but the value of CH<sub>3</sub>O-/Si in the pulse system was higher than that obtained in the static system.

Figure 5 shows the influence of the pretreatment temperature on the deposition amount. The amount of deposited tetramethoxysilane with the number of pulse was independent of the pretreatment temperature from 573 to 773 K.

IR Spectroscopy. As shown in Figure 6, absorptions of hydroxides (3585, 3677, 3730, and 3763 cm<sup>-1</sup>) were observed on alumina evacuated at 673 K. The deposition of tetramethoxysilane at 423 K changed the absorptions and increased the noise level, probably due to the large absorption by the deposited organic materials. Simultaneously, two absorptions of C-H stretching (2951 and 2847 cm<sup>-1</sup>) were observed. With increasing temperature, the intensity of C-H stretching decreased, and, simultaneously, isolated silanol (3745 cm<sup>-1</sup>) appeared.

Coverage of Surface by  $SiO_2$ . Figure 7 shows the coverage measured by the BAT method over the catalysts with various concentrations of Si, which were obtained by varying the time of deposition. The deposition at 593 K increased the coverage



Figure 5. Concentration of Si deposited over alumina pretreated at various temperatures. The deposition was carried out at 473 K in the pulse system.



Figure 6. IR spectra of alumina after the evacuation at 673 K (a) and after the deposition of tetramethoxysilane at 423 K (b), followed by the evacuation at 473 (c), 493 (d), 523 (e), 553 (f), 593 (g), and 673 K (h).

linearly against the concentration of Si, and it arrived at almost 100% with the concentration of 13 Si atoms nm<sup>-2</sup>. The deposition at tempertures lower than 593 K showed the coverage higher than that on the linear relationship obtained at 593 K. However, the silica layer deposited at temperatures below 473 K covered only a part of the surface (coverage <70%), because the deposited at 673 K showed the coverage lower than that estimated on the basis of the relationship obtained upon the deposition at 593 K.



Figure 7. Coverage by silica deposited at 423 ( $\bullet$ ), 473 ( $\blacksquare$ ), 493 ( $\bullet$ ), 523 ( $\blacktriangle$ ), 553 ( $\triangledown$ ), 593 ( $\odot$ ), and 673 K ( $\Box$ ) and calcined at 673 K in O<sub>2</sub> in the static system.



**Figure 8.** Activity for isomerization of 1-butene over alumina (O) and silica deposited at 373 ( $\oplus$ ), 423 ( $\blacksquare$ ), 473 ( $\phi$ ), 493 ( $\triangle$ ), 593 ( $\odot$ ) and 673 K ( $\Box$ ) on alumina. The isomerizations were carried out with the pulse method at 393 K in 40 cm<sup>3</sup> min<sup>-1</sup> of He (4 atm) under the differential conditions on the catalysts pretreated at 673 K.

Test Reaction. Figure 8 shows the change of activity for isomerization of 1-butene by increasing the Si concentration. The activity appeared with the deposition at 493 and 593 K. The activity over the samples deposited at 593 K showed the maximum at 13 Si atoms nm<sup>-2</sup>. The ratio of *cis*- to *trans*-2-butene was 1.3 at 13 Si atoms nm<sup>-2</sup>. Over the silica layers deposited at 473 K, only a small activity was observed. Almost no activity was observed by the deposition at 373–423 K. The deposition at 673 K made the activity lower than that estimated from the relationship between the activity and Si concentration obtained by the deposition at 593 K.

## Discussion

Mechansim of Saturation of Deposition. When the alkoxide was deposited at 593 K, the coverage by SiO<sub>2</sub> increased almost linearly against the concentration of Si. The coverage arrived at almost 100% with the deposition of 13 silicon atoms nm<sup>-2</sup>. Since the surface concentration of Al<sup>3+</sup> on  $\gamma$ -alumina is 9–14.5 nm<sup>-2</sup>,<sup>20</sup> the silica layer covers the surface almost completely at the concentration of Si close to that of Al<sup>3+</sup>. As described in our previous report,<sup>10</sup> this shows that the silica monolayer, which consisted of a 1:1 bond of Al–O–Si, covered the surface almost completely at 13 Si atoms nm<sup>-2</sup>.

Even at the low temperatures, tetramethoxysilane was deposited quickly in the early stage of deposition. However, the deposition at temperatures below 473 K was readily saturated at a low concentration of Si (<5 Si atoms nm<sup>-2</sup>), and the silica layer thus covered only a part of the surface (coverage <70%). Since the coverage was measured after the calcination, it is possible that the surface was saturated with the organic materials and exposed again by the calcination. The deposition of tetramethoxysilane may form the silicon alkoxide species Al–O–Si(O–CH<sub>3</sub>)<sub>m</sub>. In





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addition with this, methanol, which was observed in the products by the pulse method, is probably adsorbed on alumina to form the methoxide at such low temperatures. The ratio of  $CH_3O-/$ Si was high at low temperatures, and it decreased with increasing temperature. On the basis of these findings, it is suggested that the methoxides, *i.e.* the anchored silicon methoxide and the adsorbed methanol, covered the surface completely at the low temperatures, and the deposition was thus saturated.

Therefore, the mechanism in Scheme 1 is proposed; gaseous tetramethoxysilane was reacted quickly with the alumina surface to form the silicon alkoxide and methanol and/or dimethyl ether: the silicon alkoxides and a fraction of the methanol covered the surface completely (a); the silicon alkoxides and the adsorbed methanol were so stable that they inhibited the successive deposition at the low temperatures; increasing the temperature enhanced the elimination of methoxides and the successive deposition, which formed the siloxane (-Si-O-Si-) bond (b); at last, the silica monolayer with a network of Si-O-Si covered the surface almost completely (c).

The deposition by the pulse method was also saturated at the low temperatures. The ratio of  $CH_3O$ -/Si was determined from the products; it was high at the low temperatures, and it decreased with increasing temperature. Therefore, the same mechanism as in the static system is proposed.

Confirmation by Computer Graphics. According to Scheme 1, the surface was quickly saturated with the alkoxides of Si and methanol. In order to confirm this, computer graphics were used as follows: various silicon alkoxides were assumed, and the relationship of Si concentration against the ratio of CH<sub>3</sub>O-/Si was estimated on the surfaces saturated with the alkoxides. Figure 9 shows examples of the assumed species: a shows a surface trimethoxide isolated from the other Si with the ratio of CH<sub>3</sub>O-/Si = 3; b shows a dimer of silica with four methoxy groups with the ratio of  $CH_3O_-/Si = 2$ ; c shows the oligomer with the ratio of  $CH_3O$ -/Si = 1. On a simple plane, these species were packed as shown in Figure 10, and a relationship of the Si concentration against the  $CH_3O_-/Si$  ratio was obtained (Figure 11, +); the concentration of Si decreased with the increase of the ratio of  $CH_3O_-/Si$ . In a similar way, the alkoxides were assumed to be bonded to oxygen anions on the surfaces of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>21,22</sup> (Figure 12), and the concentration of Si was calculated (Figure 11,  $\times$ ). The relationship between the CH<sub>3</sub>O-/Si ratio and the Si



Figure 9. Assumed silicon alkoxides with various CH<sub>3</sub>O-/Si ratios. It is assumed that the van der Waals radii of CH<sub>3</sub> and O are 2.0 and 1.40 Å, respectively, and the covalent radii of C, O, and Si are 0.77, 0.66, and 1.17 Å, respectively, from ref 24.



Figure 10. Simple plane saturated with the silicon alkoxide at  $CH_3O-/Si = 3$  shown in Figure 9a.



Figure 11. Concentration of Si on surface saturated with alkoxides calculated from computer graphics. The alkoxides shown in Figure 9 (+ and  $\times$ ), Figure 13 ( $\Box$ ), and Figure 14 (O) were packed on a simple plane (+,  $\Box$ , and O) and the proposed alumina surface<sup>21,22</sup> ( $\times$ ). Experimental data measured by the static ( $\equiv$ ) and pulse ( $\parallel \parallel$ ) methods were overlapped.

concentration was similar to that obtained on the simple plane. Not only silicon alkoxide, but also methanol was assumed to cover the surface. Figure 13 shows an example of the simple plane saturated with the silicon alkoxides and methanol; the ratio of CH<sub>3</sub>O-/Si is 2. As shown in Figure 11 ( $\Box$ ), such assumptions gave a relationship similar to that obtained by assuming coverage only by the silicon alkoxides.

Experimental data obtained in the static system were overlapped on Figure 11 as a region shown by  $\equiv$ ; the Si concentration and the CH<sub>3</sub>O-/Si ratio were determined from the gravimetry in a region of more than 10 h of the deposition time. The broadness of the shaded relationship shows some uncertainties. From the pulse method, the Si concentration and the ratio of CH<sub>3</sub>O-/Si were calculated at the temperatures below 623 K and the number of pulses above 5 (Figure 11, ). The experimental data



Figure 12. Surface model of  $\gamma$ -alumina<sup>22</sup> saturated with the alkoxide shown in Figure 9a.





Figure 13. Simple plane saturated with the anchored silicon alkoxide and methanol.  $CH_3O-/Si = 2$ .

approximately agreed with the relationship obtained from the computer graphics. The proposed mechanism was thus confirmed.

At 2 of the CH<sub>3</sub>O-/Si ratio, the alkoxide species with a bridged structure shown in Figure 14 was assumed. As shown in Figure 11 (O), the relationship of the Si concentration and the CH<sub>3</sub>O-/Si ratio was estimated on the surface saturated with this alkoxide; it disagreed with the experimental data. Therefore, it is suggested that the silicon alkoxide did not have such a bridged form.

Mechanism of Formation of Si–O–Si. The C–H stretching of methoxy groups was observed by IR measurement. The intensity of the methoxy groups was decreased by the evacuation at high temperatures after the deposition, and, simultaneously, isolated silanol was observed. This indicates that the silicon alkoxide was reacted with water to form the silanol at the high temperatures, as shown in Scheme 2a. The silanol is supposed to be active for the reaction with gaseous tetramethoxysilane into Si–O–Si. Therefore, tetramethoxysilane is suggested to be deposited on



Figure 14. Assumed alkoxide with a bridged structure at 2 of the ratio of CH<sub>3</sub>O-/Si.

SCHEME 2: Formation of Si-O-Si from Alkoxide



the site of alumina located at the edge of silica layer to grow it as shown in Scheme 2b.

Because the pretreatment temperature did not affect the amount of deposited Si in the pulse system, the hydrolysis of silicon alkoxide is presumed to be independent of the water content of alumina. A quite low concentration of water vapor contaminated into the system is thus supposed to hydrolyze the alkoxides. It is concluded that the silicon alkoxide anchored on alumina was so reactive that it was decomposed by the low concentration of contaminated water at the high temperatures. The difference between the values of  $CH_3O$ -/Si in the static and pulse systems can be explained by the difference in the concentration of the water vapor.

Direct reaction of the anchored silicon alkoxide and gaseous tetramethoxysilane to form Si-O-Si and dimethyl ether at high temperature is supposed. However, no evidence of this reaction was shown.

Origin of Brønsted Acidity of Al-O-SiOH. According to the proposed mechanism, it is suggested that dispersed silicon alkoxides are formed by the deposition at low temperature, while a concentrated species is formed at high temperature. The dispersed alkoxides are suggested to form the dispersed silica species by calcination. For example, trihydroxide (Scheme 1, d1) and bridged (Scheme 1, d2 and d3) species can possibly be formed from the alkoxide with the ratio of CH<sub>3</sub>O-/Si of 3. On the other hand, the deposition at high temperature is suggested to develop the silica monolayer with the network of Si-O-Si, as shown in Scheme 1c. The coverage by silica deposited at the temperatures below 523 K was higher than that on the linear relationship against the Si concentration obtained over the monolayer formed at 593 K. This supports that the species prepared at low temperatures were dispersed, because the dispersed species is suggested to cover the surface more effectively than the concentrated species.

In contrast with this, the coverage was lower over the sample prepared at 673 K. This indicates that a structure including thick layers and/or particles of silica was formed by the random deposition because of a too high temperature.

The activity for isomerization of 1-butene was generated by the deposition at 493 and 593 K and showed the maximum at 13 Si atoms nm<sup>-2</sup>, where the monolayer covered the surface almost completely. The ratio of cis- to trans-2-butene in the products was close to 1 over the sample with 13 atoms nm<sup>-2</sup> of silicon deposited at 593 K. These findings indicate that the silica monolayer with the network of Si-O-Si had the Brønsted acidity. On the other hand, the deposition at the low temperatures (373-423 K) generated almost no activity. Therefore, it is suggested that the Brønsted acidity was generated on Al-O-SiOH in the layer with the network of Si-O-Si, whereas the isolated species of silica had no acidity.

The deposition at 673 K made the activity lower than that obtained at 593 K. It is presumed that the random deposition decreased the activity. This agrees with the notion that the thick layer of silica is suggested to be inactive, because the activity on the silica layer deposited at 593 K was decreased by SiO<sub>2</sub> more than 13 Si atoms nm<sup>-2</sup>. Silica gel was also inactive;<sup>23</sup> thus it is concluded that the deposited silica including the thick layers and/ or the particles was inactive.

The present study shows that the Brønsted acidity on Al-O-SiOH requires the network of Si-O-Si. It is suggested that the network of Si-O-Si developed on another oxide is strained due to the difference in the structures of two oxides. The acidity of Al-O-SiOH is therefore speculated to be generated due to the strained structure. On the other hand, some electronic interactions are also suggested between the two oxides. We suppose that the origin of acidity is both of the structural and electronic natures.

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