

Hydrothermally Activated Silica-Alumina. II. Variations in Catalytic Activities for 1-Butene Isomerization and Polymerization, and in the Amount of Acid with Pretreatment Temperature

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The technique of hydrothermal activation was used to prepare well-mixed and fully hydroxylated silica-alumina catalysts, SA-*n*MHT (*n*=13, 25, or 50 denotes the alumina content (wt%)). Their catalytic activities and *cis/trans* selectivities for the 1-butene isomerization (k_i and c/t), the catalytic activities for the 1-butene polymerization (k_p), the amount of acid (A), and the number of the surface hydroxyl group (N_{OH}) were measured as a function of the degassing temperature (T_d) over the 25–700 °C range; the following results were obtained: (1) k_i changed prominently with T_d and reached its maximum around 300 °C. (2) c/t was about 0.9 below 500 °C, but exceeded 1.2 at 700 °C. (3) k_p increased till 300 °C and became constant above that temperature. (4) A was almost independent of T_d above 100 °C. (5) N_{OH} decreased from 11–15 (at 100 °C) to 0.5 group nm⁻² (at 700 °C). An analysis of these data led to the conclusion that the SA-*n*MHT sample underwent the surface structural changes three times during the thermal dehydroxylation between 25 and 700 °C. The sequence of the structural change was sketched, and the different dependencies upon T_d of k_i , k_p , and A were explained.

Silica-alumina is a strong solid acid and is widely used as a catalyst for various reactions. From the similarities to zeolite in composition, acidic nature, and other aspects, it has been established that the acid center (*i.e.*, the catalytic active site) of silica-alumina originates from the isomorphous replacement of a silicon atom by an aluminium atom in the tetrahedral silicate network.^{1–3} To obtain a catalyst with a high acidity and catalytic activity, one must devise a method to complete the isomorphous substitution.

In the previous studies, we developed the technique of hydrothermal activation to prepare a well-mixed and fully hydroxylated silica-alumina catalyst.⁴ The relationships between the catalytic activity for the 1-butene isomerization, the amount of acid, and the amount and distribution of the aluminium atom were then investigated on the catalyst.⁴

In the present study, the dependencies upon the degassing temperature of the catalytic activities for the 1-butene isomerization and polymerization, the amount of acid, and the number of the surface hydroxyl group were measured on a hydrothermally activated silica-alumina catalyst. The sequence of the surface structural changes with the dehydroxylation is depicted to explain those dependencies.

Experimental

Materials. Three kinds of silica-alumina SA-*n*M (*n*=13, 25, or 50 denotes the alumina content (wt%)) samples were synthesized from purified tetraethyl silicate and aluminium isopropoxide as has been described elsewhere.⁴ Three kinds of hydrothermally activated silica-alumina SA-*n*MHT samples were prepared by heating the corresponding SA-*n*Ms in hot water in Pyrex ampoules at 110 °C for 14 d.⁴ A commercial catalyst, SA-C (FCC high alumina (25 wt%) supplied by the Shokubai Kasei Co., Ltd.) was also used for comparison. The BET (N_2) surface areas of those samples

were almost independent of the degassing temperature, T_d , till 700 °C. They were 340, 280, and 310 m² g⁻¹ for the 13, 25, and 50 MHT samples; 550, 500, and 430 m² g⁻¹ for the 13, 25, and 50 M samples, and 280 m² g⁻¹ for the SA-C sample, respectively. Dicumylideneacetone was used without further purification. The Hammett (H_o) value of the acid center determined by this indicator is equal to or lower than -3.0; *i.e.* the acid strength of the acid center is equivalent to, or higher than, that of 48 wt% of sulfuric acid.⁵

Apparatus and Procedure. The apparatus and procedures used to measure the catalytic activity for the isomerization and the amount of acid were conventional ones which have been described elsewhere.^{4,6,7} To measure the catalytic activity for the polymerization, the catalyst (0.15 g) was placed in an adsorption cell (240 cm³) and degassed at 25–700 °C for 4 h. Butene gas (16×10^3 Pa=120 Torr) was then introduced into the cell maintained at 0 °C, and the drop in pressure of the reacting gas was followed to determine the amount of the butene adsorbed and polymerized. After a certain period, the reacting gas was withdrawn from the adsorption cell into a trap (kept at 77 K). The amount of butene gas which could not be recovered from the catalyst surface was defined as the amount of the butene polymer. The number of the surface hydroxyl group was determined by the successive-ignition loss method.⁸

Results

Isomerization. The apparent rate constant for the conversion of 1-butene to 2-butenes, $k_i/\text{min}^{-1}(\text{g-catalyst})^{-1}$, was determined at 0 °C by applying the usual equation for the first-order reaction.⁴ The k_i vs. T_d curve, plotted in Fig. 1, shows that the maximum activity $k_i(\text{max})$ was obtained around 300 °C in the cases of the 13MHT, 25MHT, and C samples, while it appeared around 320–350 °C in the cases of 50MHT and three kinds of M samples. The appearance of the maximum activity around 300–350 °C accords well with the results obtained by other laboratories.^{9–11} The value of $k_i(\text{max})$ of the MHT sample was about 3–4 times as large as that of the corresponding M samples. The position and magnitude of the $k_i(\text{max})$ of the SA-C were almost the same as those of the 25MHT, but its k_i vs. T_d curve obviously differed from that of the

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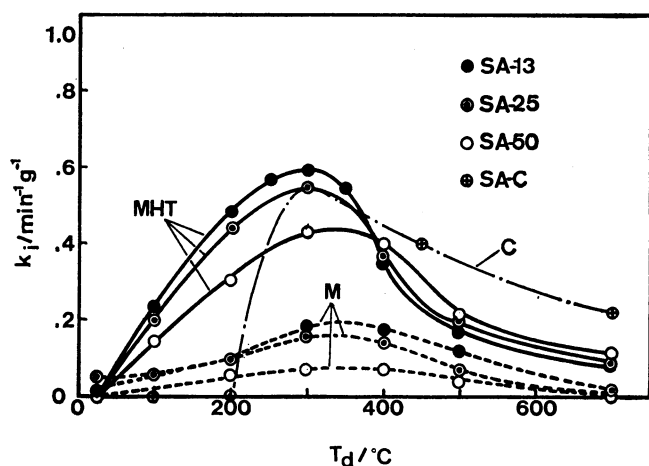


Fig. 1. Variation of apparent rate constant for 1-butene isomerization (k_i) at 0 $^{\circ}\text{C}$ with degassing temperature (T_d).

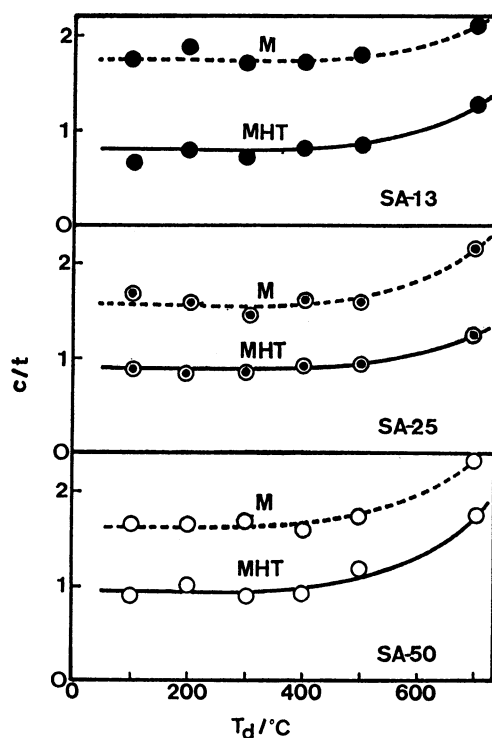


Fig. 2. Variation of c/t ratio for 1-butene isomerization at 0 $^{\circ}\text{C}$ with degassing temperature (T_d).

25MHT.

The value of the selectivity to form *cis*-2-butene against *trans*-2-butene, c/t , was measured at a 10% conversion point; it is plotted against T_d in Fig. 2. The values of the MHT samples fell in a range of 0.8–1.0, while those of the M samples ranged from 1.6 to 1.8 when degassed below 500 $^{\circ}\text{C}$. The c/t ratio started to increase when degassed at 500 $^{\circ}\text{C}$ and reached about 1.5 and 2.0 at 700 $^{\circ}\text{C}$ in the cases of the MHT and M samples respectively. The increase in the c/t with the increase in T_d above 500 $^{\circ}\text{C}$ was also observed by Gerberich and Hall.¹⁰⁾

The appearance of the $k_i(\text{max})$ around 300 $^{\circ}\text{C}$ and the increase in the c/t ratio from 500 $^{\circ}\text{C}$ suggest that the

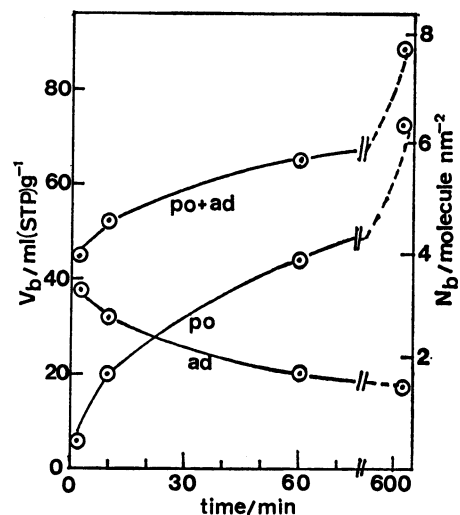


Fig. 3. Variation of amount of butene gas (V_b or N_b) adsorbed (ad) and/or polymerized (po) at 0 $^{\circ}\text{C}$ with contact time. Sample: SA-C degassed at 300 $^{\circ}\text{C}$.

structure of the catalytic active site of the silica–alumina changed around these temperatures. This will be discussed later.

The dependency upon T_d of the c/t ratio of the SA-C was almost the same as that of the SA-25MHT.

Polymerization. The amounts of butene gas adsorbed and polymerized were measured at 0 $^{\circ}\text{C}$ as a function of the contact period. An example (measured on the SA-C sample degassed at 300 $^{\circ}\text{C}$) is shown in Fig. 3. It can be seen in Fig. 3 that the adsorption was completed almost instantaneously, while the polymerization proceeded gradually, much slower than the isomeri-

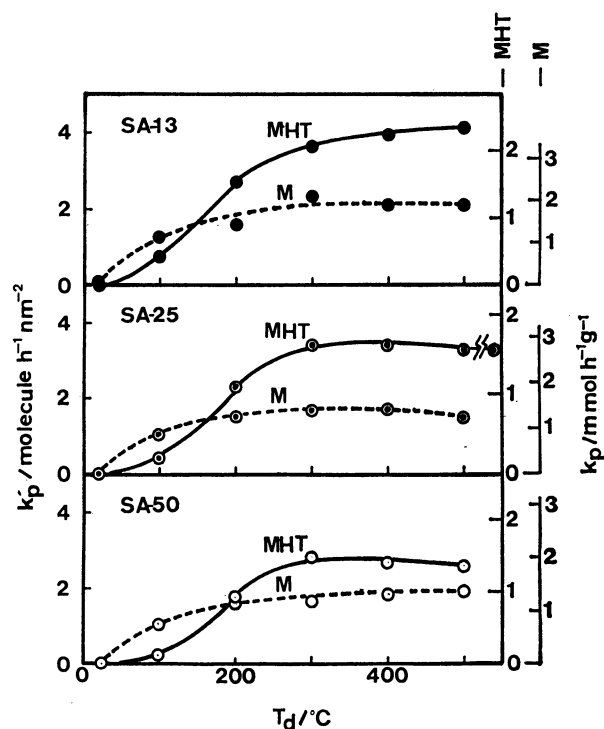


Fig. 4. Variation of amount of butene gas polymerized at 0 $^{\circ}\text{C}$ for 1 h (k_p or k_p') with degassing temperature (T_d).

zation. The amount of gas instantaneously adsorbed was almost 4 molecule nm^{-2} , irrespective of the sample and the degassing temperature. It was concluded that the rapid adsorption was probably a kind of physisorption and had no relation with the isomerization.

The amount of the butene polymer was quite small at first, but reached 4 and 7 molecule nm^{-2} at 1 and 10 h after the reaction started. The amount of butene polymerized in the first 1 h was designated as $k_p/\text{mmol h}^{-1} \text{g}^{-1}$ or $k_p/\text{molecule h}^{-1} \text{nm}^{-2}$; it is plotted against T_d in Fig. 4. The k_p value increased with the increase in T_d till 300 °C in the cases of the MHT samples and till 200 °C in the cases of M samples, and became almost constant above these temperatures. The k_p value of the MHT sample was smaller than that of the corresponding M samples at lower temperatures, but their values became almost comparable with each other at higher temperatures. These trends clearly differed from the trends observed in the k_i value.

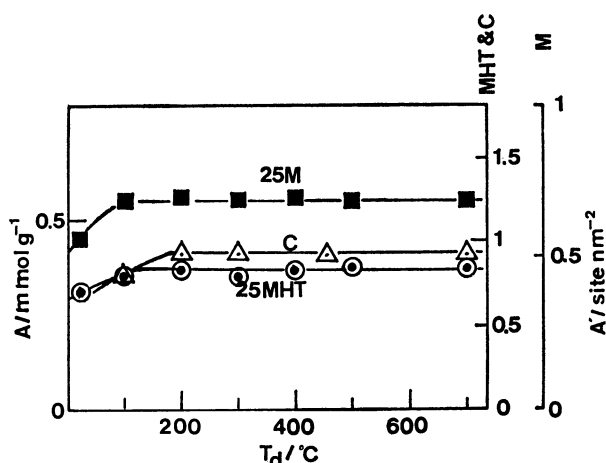


Fig. 5. Variation of acid amount (A or A') with degassing temperature (T_d).

Amount of Acid. The amount of acid, $A/\text{mmol}^{-1} \text{g}^{-1}$ (or the number of the acid center designated as $A'/\text{site nm}^{-2}$), was measured as a function of T_d , as is shown in Fig. 5. Figure 5 shows that the A value became almost independent of T_d when degassed above 100 °C. Even the value obtained at 25 °C did not differ much from the saturation value. The shape of A vs. T_d curve clearly differed not only from the shape of the k_i vs. T_d curve, but also from the shape of the k_p vs. T_d curve.

The preceding study revealed that the number of the acid center corresponded to the number of the Al atom exposed on the catalyst surface.⁴⁾ The value shown in Fig. 5 indicates that almost 0.7–1 molecule nm^{-2} of the Al atom is exposed on the surface of silica-alumina containing 25 wt% of alumina.

Surface Hydroxyl Group. The number of the surface hydroxyl group, N_{OH} , was measured as a function of T_d ; it is plotted in Fig. 6. Figure 6 shows that the N_{OH} values of the MHT and C samples were larger than 11 group nm^{-2} , while those of the M samples ranged from 4 to 6 group nm^{-2} , before the heat treatment. It is clear that the surfaces of the MHT and C samples were fully hydroxylated, while those of the M

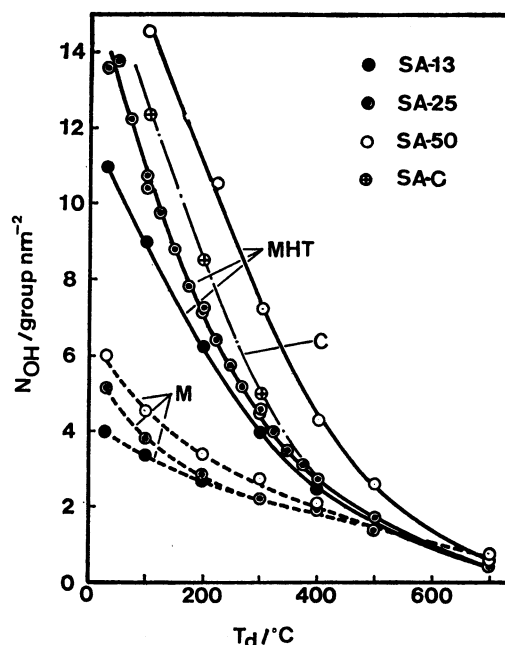


Fig. 6. Variation of number of hydroxyl group (N_{OH}) with degassing temperature (T_d).

samples were only partially hydroxylated. The N_{OH} value decreased with the increase in T_d and became 1/2–1/3, as small as the initial value, when degassed at 300 °C and nearly 1 group nm^{-2} at 600 °C. These values are very suggestive and will later be used to elucidate the sequence of the surface structural change.

Discussion

It was revealed by the present study that the k_i (including c/t ratio), k_p , and A values of the hydrothermally activated silica-alumina are different functions of T_d (and therefore, of N_{OH}), as is shown in Fig. 7. The k_i value varies with T_d very prominently, while the k_p value changes less prominently. The A is almost independent of T_d . These different dependencies upon T_d are very interesting; the causes must be elucidated in the present discussion. A complete set of data for k_i , c/t , k_p , A , and N_{OH} were obtained for the SA-25MHT

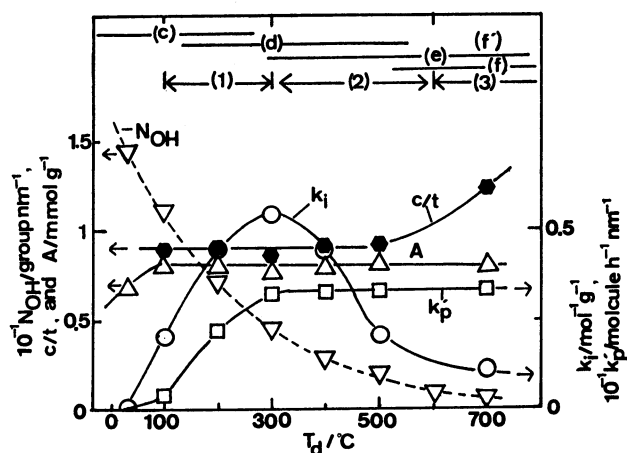


Fig. 7. Dependencies upon T_d of k_i , c/t , k_p , A , and N_{OH} of SA-25MHT sample.

sample. They are used for the explanation. Let us start with the simplest function, A .

The k_i vs. T_d curve, when combined with the c/t vs. T_d curve, suggests that the surface structure of the SA-25MHT changes three times during the dehydroxylation between 100 and 700 °C. These structural changes are characterized, respectively, by: (1) an increasing k_i value with a constant c/t ratio ≈ 1 between 100 and 300 °C, (2) a decreasing k_i value with a constant c/t ratio ≈ 1 between 300 and 600 °C, and (3) a decreasing k_i value with an increasing c/t ratio > 1 above 600 °C. The N_{OH} values of SA-25MHT degassed at 100, 300, 600, and 700 °C are 10.5, 4.5, 1, and 0.5 group nm⁻² respectively. Therefore, we designate the surface degassed at those temperatures as a highly hydroxylated surface (c), a partially dehydroxylated surface (d), a highly dehydroxylated surface (e), and an extremely dehydroxylated surface (f'), respectively (see Fig. 7).

The accumulated data show that the value of the monolayer capacity of the surface hydroxyl group of various metal oxides falls around 4–8 group nm⁻².¹² This implies that the (c) contains the hydronium cation, H₃O⁺, as the main acid source. On the other hand, since the A value of the SA-25MHT is 0.8 site nm⁻², about 40% of the acid center on the (f') must be of the Lewis-type (*i.e.*, an acid center having no proton, but a vacant orbital). The acid centers on the (d) and (e), therefore, are of the Brønsted-type (*i.e.*, an acid center having either a free proton or an acidic silanol (>SiOH Al<)).

The finding that the A value is almost independent of T_d above 100 °C, simply indicates that the acid strength of all the four structures including the (c) is equivalent to, or higher than, that of 48 wt% sulfuric acid. This conclusion is not surprising, because there must be no free proton, but a hydrated proton, in 48 wt% sulfuric acid.

We will explain the k_p vs. T_d curve next. Figure 7 shows that the temperature range of the increasing k_p accords to the temperature range of the surface structural change (c)→(d). This implies that only the (c) is inactive for the polymerization. This can be explained as follows. The butene polymerization may proceed through the cationic polymerization mechanism. Therefore, it is the acid strength which determines the magnitude of the k_p value. Since the acid source of the (c) is the hydronium cation, its acid strength must be much lower than those of (d), (e), and (f') (although they are all equivalent to, or higher than, that of 48 wt% sulfuric acid). This results in the increasing k_p value between 100 and 300 °C. On the other hand, the (d), (e), and (f') possess either a free proton, an acidic silanol, or a vacant orbital; their acid strengths are thus all strong enough to catalyze the polymerization equally. Therefore, the k_p value becomes almost constant above 300 °C. To elucidate how much the acid strength of the (c) differs from those of other structures, anthraquinone ($pK_a = -8.0$) and 4-nitro-toluene ($pK_a = -10.5$) were used.¹³ No clear conclusion was obtained, however.

Figure 7 also shows that the k_i values of the (c), (e), and (f') are all much smaller than that of the (d). The reason for the smaller k_i values of the (c) and (f')

compared to that of the (d) can easily be explained.

A number of mechanisms have hitherto been proposed for the 1-butene isomerization catalyzed by silica-alumina. Now it is widely accepted that the isomerization proceeds through the intermolecular hydrogen-exchange (IHE) mechanism (*s*-butyl cation intermediate mechanism) on a silica-alumina catalyst.^{9–11,14–16} However, a part of the isomerization proceeds through the intramolecular mechanism on the extremely dehydroxylated silica-alumina.¹⁰ According to the IHE mechanism, the transfer of a proton from the acid center to the α -carbon of 1-butene to form the *s*-butyl cation (*i.e.*, proton donation) occurs first. Then a different proton is transferred from the β -carbon of the *s*-butyl cation to the acid center to produce 2-butene (*i.e.*, proton acceptance). The reason why the c/t ratio becomes nearly unity with the IHE mechanism, but exceeds unity with the intramolecular mechanism, has already been elucidated.¹⁰ From the knowledge about the two mechanisms, we can explain the variations in the k_i and c/t ratio with T_d between 100 and 300 °C, and above 600 °C, as follows.

The acid source of the (c) is the hydronium cation, while that of the (d) is either the free proton or acidic silanol. The acid strength, *i.e.*, the ability of proton donation, of the (d) is much larger than that of the (c). Therefore, the intermolecular hydrogen-exchange reaction proceeds much faster on the (d) than on the (c), resulting in an increase in the k_i value with the constant $c/t \approx 1$ between 100 and 300 °C.

Since the (f') contains a Lewis-type acid center (about 40%), a part of the isomerization proceeds through the intramolecular mechanism. The decrease in the k_i value with the increase in the c/t ratio above 600 °C originates from the slow intramolecular hydrogen shift.

The reason for the decrease in the k_i value with the constant c/t ratio ≈ 1 between 300 and 600 °C is not easily explainable, because both (d) and (e) possess the same number of the Brønsted-type acid centers. To elucidate the reason, we will examine the structural difference between the (d) and (e) in more detail.

Silica glass displays a diffused X-ray diffraction pattern which provides bond parameters close to those obtained from cristobalite.¹⁷ Silica gel and silica-alumina also show a very diffused diffraction peak around $2\theta(\text{Cu } K\alpha) = 22^\circ$, where β -cristobalite shows the most intense peak.^{18,19} From these facts, it is widely accepted that the structures of amorphous silica and silica-alumina may be similar to that of β -cristobalite.⁹ A crystallographic examination shows that the (100), (110), and (111) planes of β -cristobalite contain about 4, 7, and 4.7 Si atoms per one nm² respectively.²⁰ It is a well-established theory that the plane containing the least number of atoms develops most (Bravais's law²¹). Therefore, it may be reasonable to approximate the surface of SA-25MHT to the (100) plane of β -cristobalite, which is shown in Fig. 8. As can be seen in Fig. 8, the Si (and Al) atom is disposed in an array of "OSiO...OSiO" linear lines, the spacing of which is about 0.5 nm. Since this spacing is wide enough to prevent interaction between the different lines, we can depict the two-dimensional surface one-dimensionally as in Fig. 9.

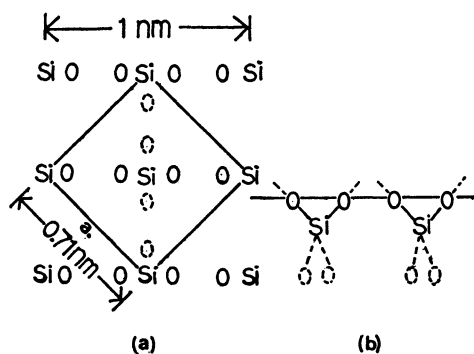


Fig. 8. A schematic representation of surface structure of silica-alumina assumed as the same as surface structure of (100) plane of β -cristobalite. (a): Perpendicular view, (b): horizontal view.

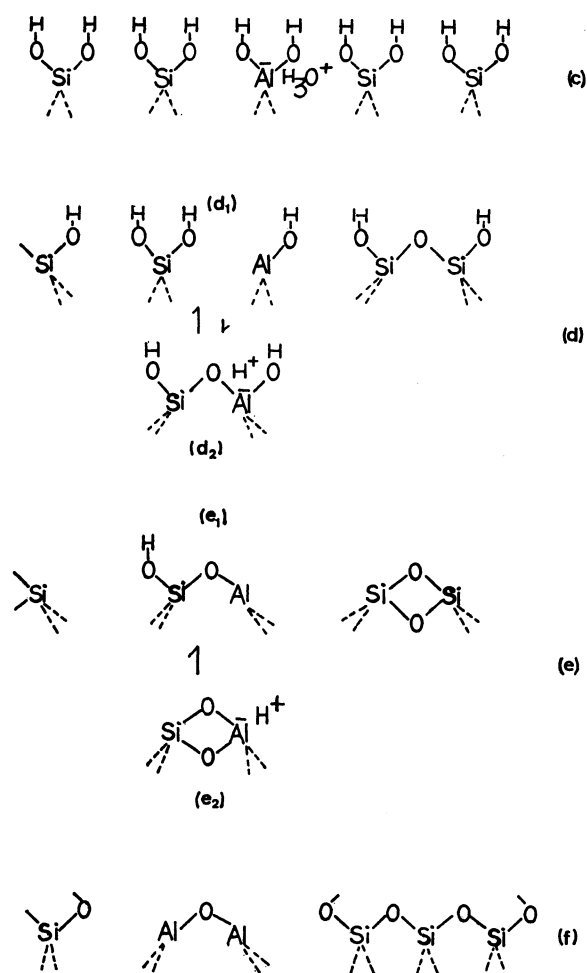


Fig. 9. One-dimensional schematic display of silica-alumina surface at different hydroxylation level. (c): Full hydroxylation (around 100 °C), (d): partial dehydroxylation (around 300 °C), (e): high dehydroxylation (around 600 °C), and (f): complete dehydroxylation (above 600 °C).

Since the acid amount of SA-25MHT is about 0.8 site nm^{-2} , we will set the Al/Si ratio as 1/4 in Fig. 9.

Figure 9 shows that the surfaces of full hydroxylation (c), partially dehydroxylation (d), and high dehydroxylation (e) contain 10.4, 4.8, and 0.8 OH group per one

nm^2 respectively. These values coincide with the values of the $N_{\text{OH}}/\text{group nm}^{-2}$ of 10.5, 4.5, and 1 obtained at 100, 300, and 600 °C. It can thus be concluded that the SA-25MHT takes surface structures like (c), (d), and (e) when degassed at 100, 300, and 600 °C respectively. To eliminate the last proton from the surface, two Al atoms must be paired. To bring about this situation, the surface network must be rearranged greatly. Only a temperature beyond 600 °C can give rise to this rearrangement, resulting in the (f). It must be noticed that the (c), (d), and (e) designations above correspond exactly to the earlier designations, while the (f) does not correspond to the (f'). The (f') consists of 40% of the (f) and 60% of the (e).

When we examine Fig. 9 carefully, we notice that the two M (M=Si or Al) atoms must approach each other to give rise to the structural change (c)→(d). This, in turn, limits the occurrence of the successive dehydroxylation to only the dehydroxylation between the paired M atoms, resulting in the structure of (e) being more strained than that of (d). In general, the surface strain increases with the increase in T_d .²²⁾ This increasing strain may be responsible for the lower k_i value of the structure (e) than that of (d). The following is one possible explanation.

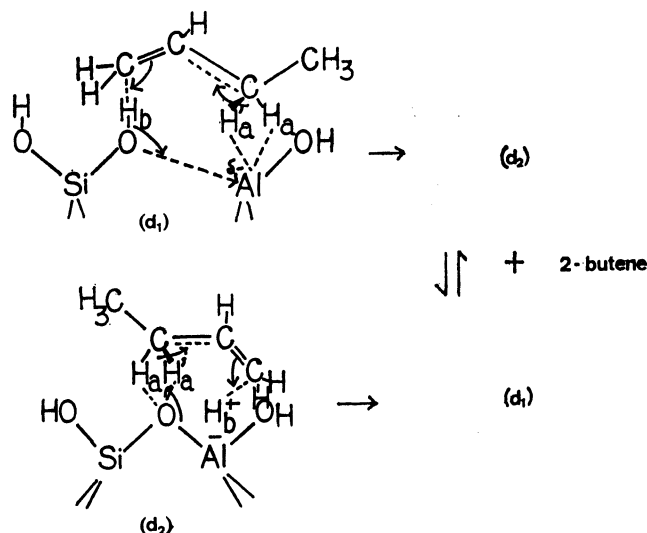


Fig. 10. A schematic representation of intermolecular hydrogen exchange between acid center and butene on the (d₁) and (d₂).

When we compare the structures of (e₁) and (e₂) (the two modifications of the (e)) with each other, we notice that the (e₂) is much more strained and, therefore, thermodynamically much more unstable than the (e₁). Therefore, the mutual transformation between (e₁) and (e₂) is extremely difficult, while the mutual transformation (d₁)⇌(d₂) is easy. As can be seen in Fig. 10, the intermolecular hydrogen exchange can proceed very smoothly (but not necessarily concertedly) on the (d) by using the (d₁)⇌(d₂) transformation. On the other hand, because of the extreme difficulty of the (e₁)⇌(e₂) transformation, the intermolecular hydrogen exchange does not occur smoothly on the (e). This results in k_i value of the (e) being smaller than that of the (d).

Here we can understand that the k_i value is determined by two factors. One is the acid strength (*i.e.*, the ability of proton donation), and the other is the special configuration (*i.e.*, the ability of proton acceptance) of the acid center. On the other hand, the k_p is determined by the acid strength alone.

Other Samples. The data for other samples are incomplete. However, the similar dependencies upon T_d of the k_i , c/t , and N_{OH} values show that the surface structures of the 13MHT and 50MHT are both close to that of the 25MHT. The slower appearance (about 20 °C) of the $k_i(\text{max})$ of the 50MHT may arise from its dehydroxylation, slower than that of the 25MHT (see Fig. 6).

Although the curves of c/t , A , and N_{OH} against T_d and the position of $k_i(\text{max})$ are similar to each other, there is a clear difference in the shape of the k_i vs. T_d curve between the 25MHT and the C sample (Fig. 1). The surface structures corresponding to the (e) may also be different.

Finally, we should mention the different surface characters between the M and MHT samples. The variations with the T_d of the k_i , k_p , and N_{OH} values of the M sample are not so prominent as those of the corresponding MHT sample. The starting N_{OH} value of the M is much lower than that of the MHT. Moreover, the c/t ratio of the M is much larger than that of the MHT. These facts indicate that the M sample originally contains large fractions of the (e) and (f). The presence of the less active (e) and (f) for the butene isomerization on the 25M sample results in its lower k_i value, with a higher c/t ratio, than those of the 25MHT, although the total acid amount of the 25M is larger than that of the 25MHT (Fig. 5).

Conclusion. The values of k_i , k_p , and A of the hydrothermally activated silica-alumina are different functions of T_d . An analysis of the N_{OH} vs. T_d curve shows that the surface structure of the catalyst changes in this fashion: (c)→(d)→(e)→(f) with the increase in T_d . By this, the different dependencies upon T_d of k_i and k_p are consistently explained.

The dependencies upon T_d of k_i , c/t , and k_p of the M sample differ from those of the corresponding MHT sample. This arises from the presence of the (e) and (f) in the original M sample. In other words, the role of the hydrothermal activation exists in the modification of the less active structures, (e) and (f), into the highly active structure (d).

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