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The Hydrothermal Activation of Silica–Alumina for Butene Isomerization. A Device to Prepare a Standard Sample

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Three kinds of silica–alumina catalysts were prepared by hydrothermal treatment (heating a sample in hot water) over the range of 25—250 °C for various periods. It was found that the hydrothermal treatment significantly increased its catalytic activity for butene isomerization. The dependencies of various surface properties (the production ratio of 2-butene isomers, the surface acidity, the surface area, the pore-size distribution, and the shape and size of the catalyst particle) on the hydrothermal conditions and the kind of starting catalyst sample were systematically investigated, too. It was concluded that the increase in the catalytic activity might be due to the progress of the Si/Al isomorphic substitution in the tetrahedral surface silica network. Hot water might serve as a solvent for the cations and facilitate their movements. Since the hydrothermal treatment can erase the effects of the blending method on the catalytic activity and other surface properties almost completely, this treatment can be used to prepare a standard sample.

Structural change in minerals is accelerated by the action of hot water.[1] Numerous minerals, including optically active quartz and various kind of zeolites, are synthesized using this action in the laboratory.[2,3] We have attempted similarly to use the action of hot water for the preparation and/or activation of various metal oxide catalysts.

Silica–alumina is a strong solid acid and is widely used as a catalyst for various reactions.[4] From the similarities to zeolite in composition, acidic nature, and other aspects, it has been accepted by many workers that the acid center of silica–alumina originates from the isomorphic substitution of a silicon atom by an aluminum atom in the tetrahedral silicate network.[4,5] To obtain an active catalyst, one must devise a method to promote the isomorphic substitution effectively. The action of hot water may be appropriately used for this purpose.

In the present paper, we will demonstrate that hydrothermal treatment (heating a sample in hot water) significantly increases the catalytic activity for butene isomerization. The reasons for this increase were studied by measuring systematically the variations in the surface acidity, the production ratio of 2-butne isomers, the surface area, *etc.* with the hydrothermal time and temperature. A systematic elucidation of the relationship between the structure of an acid site and its catalytic function for butene isomerization has been made elsewhere, using a catalyst prepared by means of the hydrothermal activation technique.[6]

Experimental

Materials. Three kinds of hydrothermally activated silica–alumina (SA) materials were prepared as follows. Silica hydrogel was prepared by the hydrolysis of one part of doubly distilled tetraethyl silicate by five parts of water at 100 °C under vigorous agitation.[7] Alumina hydrogel was prepared by the hydrolysis of vacuum-distilled aluminum isopropoxide by dropping water into it under vigorous agitation. To prepare the SA-25MHT sample, these two hydrogels were mixed thoroughly (alumina content: 25 wt%) and dried at 110 °C for 1 d. Then, the sample was calcined at 400 °C for 20 h and at 550 °C for 5 h in air, and finally exposed to wet air in a rotary kiln at 110 °C for 5 h. The silica–alumina dry gel (SA-25M) thus prepared was heated in hot water over the range of 25—250 °C in a Pyrex ampoule for various periods. To prepare the SA-*n*KHT sample, silica and alumina hydrogels were dried separately at 110 °C and then blended using an agate mortar and pestle for 30 min. (*n* denotes the alumina content, ranging from 0.1 to 50 wt%). The blended dry gel (SA-*n*K) was heated in hot water at 110 °C for various periods. To prepare the SA-*n*JHT sample, the silica and alumina hydrogels were mixed thoroughly (the alumina content, *n*, ranged from 0.1 to 50 wt%) and then heated in hot water in a Pyrex ampoule at 110 °C for 3 d. All these three kinds of samples were dried at 110 °C for 1 d before storage. Tokyo Kasei reagent-grade 1-butene was kept in a 3-L Pyrex bulb after having been passed through dry molecular sieves 3A. Nakarai reagent-grade butylamine was dried with sodium hydroxide and distilled before use. Nakarai reagent-grade color indicators (methyl red, dicinnamylideneacetone, and anthraquinone) were used without further purification.[8]

Procedure. A conventional vacuum apparatus equipped with a circulation reactor (240 ml) was used to measure the catalytic activity for the 1-butene isomerization. A catalyst (0.15 g) was degassed at 300 °C for 2 h and kept at 0 °C during the reaction. At appropriate intervals after the introduction of about 16×10^3 Pa of 1-butene, small portions of the reacting gas were withdrawn in sequence into gas samplers kept at 77 K. The composition of the reacting gas was analyzed by means of a gas chromatograph equipped with a 5-m dioctyl phthalate column kept at 0 °C. To measure the acidity, the catalyst (0.2 g) was degassed at 300 °C for 2 h. After having been cooled to room temperature, the catalyst was covered with 10 ml of dry benzene. The acidity was, then, determined by the conventional butylamine titration method.[9,10] The pore-size distribution of the catalyst was determined by applying the Cranston-Inkley method.[11] An electron microscopic photograph was taken by a Hitachi HU-11A with 11,000-times magnification. The X-ray powder pattern was measured by means of a Rigaku Geigerflex.

Results and Discussion

SA-25MHT Series. The variation in the catalytic activity for 1-butene isomerization was measured at 0 °C as functions of the hydrothermal time and the hydrothermal temperature. Since the isomeriza-

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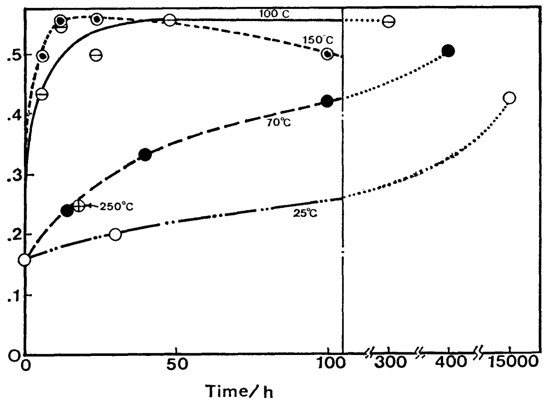

Fig. 1. Variation of apparent rate constant for 1-butene isomerization at 0 °C with hydrothermal time and temperature on SA-25 MHT.

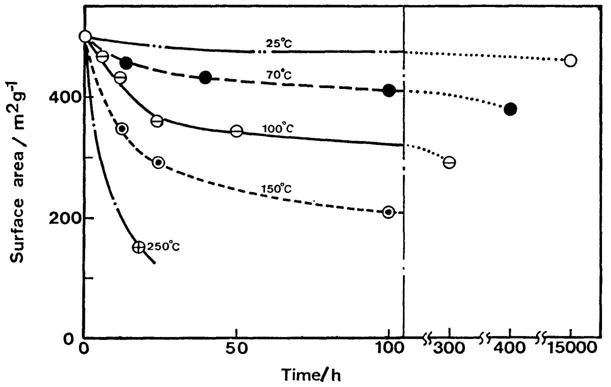

Fig. 2. Variation of surface area with hydrothermal time and temperature on SA-25 MHT.

tion of 1-butene to 2-butenes could be approximated to a simple first-order reaction at the initial stage, the apparent rate constant, k_1, was obtained from Eq. 1:

$$k_1 = (1/t) \ln (P_0/P_t). \qquad (1)$$

Here, P_0 and P_t are the partial pressures of 1-butene at times zero and t respectively. The results are shown in Fig. 1. The figure shows that the catalytic activity of SA-25MHT increased with the increase in the hydrothermal time at first, reached a maximum, and then gradually decreased. This variation became prominent with the increase in the hydrothermal temperature. For instance, it took 50 h at 100 °C to attain the maximum activity, while it took only 12 h at 150 °C.

To elucidate the reason for the increase in the catalytic activity, the changes in the "macroscopic" surface structure (surface area, pore-size distribution, and particle shape), the production ratio of *cis*-2-butene *vs.* *trans*-2-butene (c/t), and the surface acidity with the hydrothermal treatment were measured.

The BET surface area decreased with the increase in the hydrothermal time, as is shown in Fig. 2. Its rate of decrease became prominent with the increase in the hydrothermal temperature. For instance, the surface area decreased to one-third after 18 h at 250 °C, while it remained almost constant even after 15000 h (one year and eight months) at 25 °C. It has been observed by several workers that the surface area of silica–alumina decreases significantly when exposed to hot water-vapor, too.[12] However, to attain the same effect as hot liquid-water, vapor needs a much higher temperature (480—950 °C).[12] The measurement of the pore-size distribution showed that the most probable size changed from 4 to 7 nm in diameter over a period of 14 d at 100 °C. Electron microscopic measurement showed that the shape of the elementary particle of the catalyst powder was quite thin and slender before the hydrothermal treatment, but became fat and thick after 14 d at 100 °C. These results clearly showed that the "macroscopic" surface structure changed significantly with the hydrothermal treatment.

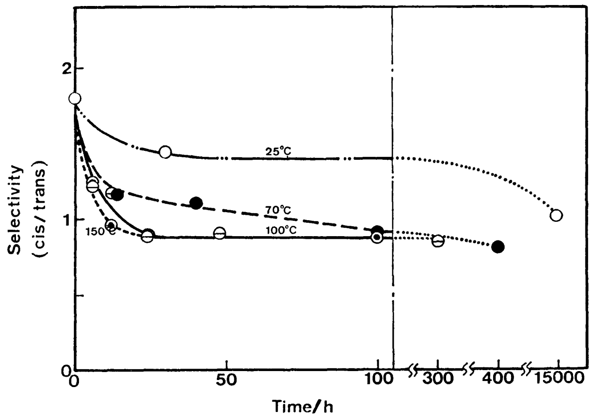

Fig. 3. Variation of selectivity to produce *cis*-2-butene against *trans*-2-butene at 0 °C with hydrothermal time and temperature on SA-25 MHT.

The dependency of the c/t ratio upon the hydrothermal treatment is shown in Fig. 3. The value decreased from 1.8 to 0.9 with an increase in the hydrothermal time. It has been observed by many workers that the c/t ratio depends strongly upon the structure of the active site. For instance, the ratio was larger than 3.5 on dry active alumina, while it was around 1 on a typical silica–alumina catalyst.[13] It can be concluded that the hydrothermal treatment changed the structure of the active site ("microscopic" surface structure) from the active-alumina type to the typical silica–alumina type.

The acid amounts, as determined by the butylamine titration method using methyl red (pK_a=4.8), dicinnamylideneacetone (pK_a=−3.0), and anthraquinone (pK_a=−8.2), were 0.95, 0.55 and 0.35 meq g^{-1} respectively before the hydrothermal treatment, but became 0.60, 0.35, and 0.35 meq g^{-1} respectively after the hydrothermal treatment at 100 °C for 14 d. This means that the less active SA-25M had more numerous active sites than the more active SA-25MHT. It was, therefore, concluded that the increase in the catalytic activity with the hydrothermal treatment did not arise from the change in quantity, but resulted from the change in quality, of the active sites in the case of the SA-25MHT series.

The dependencies upon the degassing temperature of the catalytic activity and the c/t ratio for the butene isomerization, the numbers of the surface hydroxyl

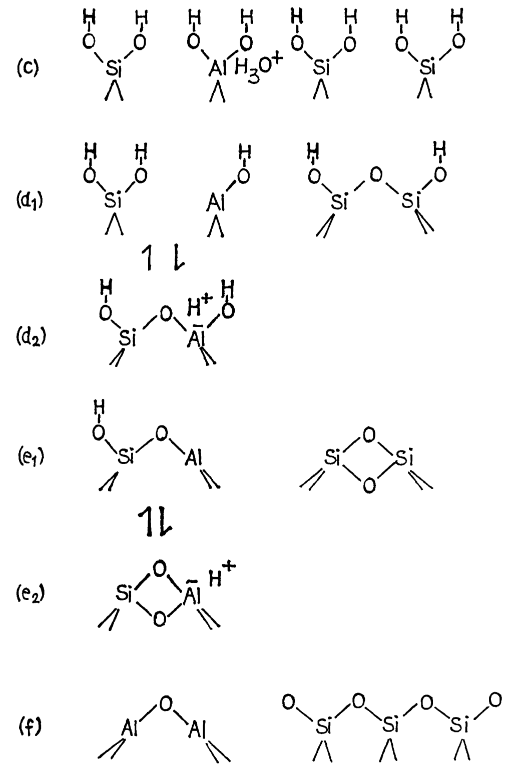

Fig. 4. A schematic representation of the structures of active site existed on SA-25 MHT before and after the hydrothermal treatment.

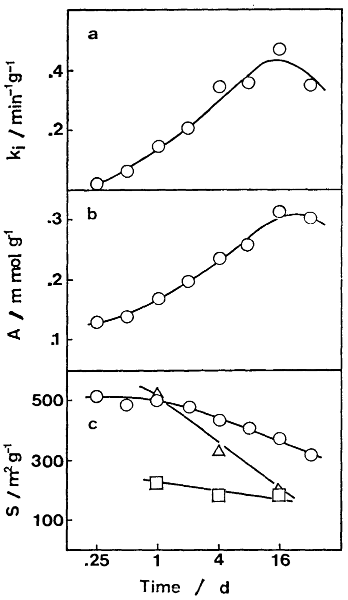

Fig. 5. Variations of (a): apparent rate constant for 1-butene isomerization (k_1) at 0 °C, (b): amount of acid site ($A(H_0 \leq -3.0)$), (c): surface area (S), with hydrothermal time at 110 °C.
○: SA-10KHT, △: silica gel, □: alumina gel.

group and acid sites, and the catalytic activity for the butene polymerization have been studied elsewhere.[6] It has been concluded that the structure of the acid site (*i.e.*, the active site for the butene isomerization) changed thus: (c)→(d)→(e)→(f) with an increase in the degassing temperature from 25 to 700 °C (Fig. 4).[6] The most active site is the (d) site, which has the most suitable structure for the occurrence of proton-donation-acceptation to promote the isomerization.[6] The (f) site lacks a proton, resulting in quite a low catalytic activity with a high c/t ratio for the isomerization.[6] However, the acid strength of both (d) and (f) sites are equivalent to, or higher than, 48 wt% of sulfuric acid.[6,8] The present results, when combined with those of a study made elsewhere (Ref. 6), can lead to the conclusion that the active site had a structure like (f) (the pseudo-active alumina type) before the hydrothermal treatment, but changed to the (d) site upon the action of hot water. That is, all results could be explained consistently by the assumption that the Si/Al isomorphic substitution was promoted by the hydrothermal treatment.

SA-10KHT Series. The effect of hot water in increasing the catalytic activity was more clearly demonstrated in the experiment using the SA-10KHT sample. Variations in the catalytic activity, the acid amount, and the surface area with the hydrothermal time at 100 °C are shown in Fig. 5. Figure 5a shows that the catalytic activity was negligibly low before the treatment, but increased gradually with the increase in time. It reached a maximum after 16 d and then started to decline. Although the rate of increase was very low (about one-eighth as low as that for the SA-25MHT series), the values of maximum activity did not differ much from each other. The c/t ratio was around 0.9, irrespective of the hydrothermal time.

Figure 5b shows that the acid amount, $A(H_0 \leq -3.0)$, as determined using dicinnamylideneacetone, also increased with the increase in the hydrothermal time.[14] The trend was quite similar to the trend of the catalytic activity.[15] Moreover, the maximum value was comparable with that of SA-25MHT, as in the case of the catalytic activity. As was noted in the experimental section, the SA-10K was prepared by a simple mechanical blending of dry silica and alumina gels only. It was unlikely that the active site originating from the Si/Al isomorphic substitution existed before the hydrothermal treatment. The appearances of the catalytic activity with a low c/t ratio and of the acid site ($H_0 \leq -3.0$) on SA-10KHT, therefore, may be proofs of the progress of the isomorphic substitution with the hydrothermal treatment.

The same conclusion was obtained from the trends of the variations in the surface area and the crystallinity of the silica, alumina, and SA-10K samples with the hydrothermal treatment. Figure 5c shows that the surface area of SA-10KHT decreased from 500 to 350 m^2 g^{-1} upon the hydrothermal treatment at 110 °C for 16 d. The surface area of silica decreased very rapidly from 530 to 200 m^2 g^{-1} while that of alumina remained almost constant (200 m^2 g^{-1}) during the same period. The combined surface areas of 90 wt% of silica and 10 wt% of alumina before and after the treatment were, therefore, 500 and 200 m^2 g^{-1} respectively. This decrease (300 m^2 g^{-1}) was almost twice as large as the decrease for SA-10KHT (150 m^2 g^{-1}). The X-ray powder pattern showed that silica and SA-10KHT kept their amorphous structures, while alumina was altered to boehmite during the hydrothermal treatment. These two facts may show that no pure silica and alumina surfaces were exposed on SA-10KHT.[16] During the hydrothermal treatment, either the Si and Al cations moved from the original particles to different particles and formed a new surface with an aluminosilicate network both on the parent silica and alumina particles.[16] This surface might be quite resistant to the action of hot water. Therefore, the surface area of SA-10KHT did not decrease so rapidly as that of silica,[17] and the boehmite phase was not formed in this sample.

Finally, we should discuss the mechanism of the effect of the hydrothermal process on the present silica–alumina samples. The kinetic behavior of the Si and Al cations in the solid and liquid phases was not paticularily explored in the present study. However, it may not be unrealistic to infer that Si and Al cations can be dissolved in hot water and move from surface to surface *via* the liquid phase (the liquid-phase mechanism). In other words, the role of hot water may be as a medium to take out the cations from the catalyst surface and transfer them to another surface. The idea that hot water is a solvent for metal cations is very common in studies of the hydrothermal syntheses of quartz and zeolite.[2,3] It is possible to imagine other mechanisms, for instance, that the metal cations move *via* surface and/or the bulk of a solid (the solid-phase mechanism). However, it is quite doubtful that those solid-phase mechanisms can account for the following facts more consistently than the liquid-phase mechanism can: (1) the Si/Al isomorphic substitution did occur, even in the SA-10KHT sample, in which Si and Al cations were originally separated in different particles, and (2) the "macroscopic" surface structure changed significantly and simultaneously with the isomorphic substitution. To attain the same effect with hot water-vapor (with which the solid-phase mechanisms actually work), a much higher temperature has been needed.[12] Therefore, the most reasonable conclusion may be that the isomorphic substitution mainly progressed through the liquid-phase mechanism, as far as the present study is concerned.

SA-nKHT and SA-nJHT Series. A series of SA-*n*KHT samples was prepared by hydrothermal treatment at 100 °C for 16 d, and their catalytic activity, surface acidity, and surface area were compared with those of the corresponding SA-*n*JHT samples. Figures 6a and b show that the dependencies of the catalytic activity and surface acidity upon the alumina content in the two series are quite similar to each other. Before the hydrothermal treatment, the catalytic activity and acid amount were about one-third as low as the maximum value in the SA-*n*JHT series, while they were quite low in the SA-*n*KHT series. The hydrothermal treatment could erase, easily and almost completely, the differences in the catalytic activity and surface acidity originating from the difference in the blending method. Thus, it may be concluded that the hydrothermal treatment can be a useful device for preparing a standard sample of the silica–alumina catalyst. The small but parallel difference between their surface areas shown in Fig. 6c may arise from the different hydrothermal times, 16 d for the SA-*n*KHT series and 3 d for the SA-*n*JHT series.

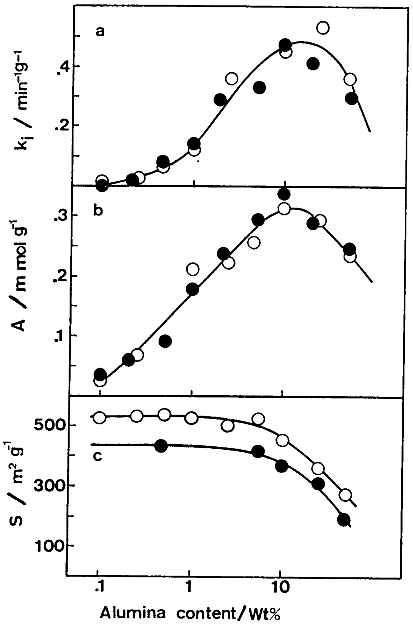

Fig. 6. Variations of, (a): apparent rate constant for 1-butene isomerization (k_1) at 0 °C, (b): amount of acid site ($A(H_0 \leq -3.0)$), (c): surface area (S), with alumina content.
●: SA-0KHT received hydrothermal activation at 110 °C for 16 d, ○: SA-*n*JHT received hydrothermal activation at 100 °C for 3 d.

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14) The acid amount, $A(H_0 \leq 4.8)$, determined with methyl red was independent of the hydrothermal time, while that, $A(H_0 \leq -8.2)$, determined with anthraquinone increased, similarly to the acid amount, $A(H_0 \leq -3.0)$, with the increase in the hydrothermal time.

15) Figure 5b shows that there apparently existed about 0.1 meq g^{-1} of acid sites ($H_0 \leq -3.0$) before the hydrothermal treatment. Perhaps, some kind of acid site other than (d) and (f), with a weak catalytic activity, was formed on the interface between silica–alumina particles during the mechanical blending.

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