# The Catalytic Activity of AgX-type Zeolite for the Isomerization of 1-Butene

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The catalytic activity of X-type zeolite exchanged by $Ag^+$ was studied for the isomerization of 1-butene. The activity gradually increased with the degree of exchange up to *ca.* 60%, whereafter it rose steeply. A good correlation was found between the activity and the number of acid sites of $H_0$ less than 3.3. Both preferences, that for the formation of *cis*-2-butene from 1-butene and that for the geometrical isomerization rather than the double-bond shift, indicated that the reaction proceeds *via* a carbonium-ion intermediate formed on an acidic site. In the region of exchange around 40%, however, the *cis*/*trans* ratio in the 2-butenes produced was less than unity and a change in the reaction mechanism was suggested. Treatment with $H_2$ enhanced the activity of exchanged zeolite by a factor of $10^2$—$10^3$ without any change in the character of the reaction. These results were attributed to the formation of proton-X-zeolite by the replacement of $Ag^+$ with a proton. This conclusion was confirmed by the analysis of deuterium exchange during the isomerization on $D_2$-treated AgX.

Zeolites have been chosen as the subjects of many studies because of their well-defined structures and distinguished properties in adsorption and catalysis. Catalytic activities enhanced by the replacement of $Na^+$ by rare earth or alkaline earth cations have often been correlated to the protonic acidity.[1,2]

Transition-metal zeolites have also been studied recently.[3] The lack of a simple relationship between activity and acidity on them, however, necessitates precise studies of the state of the exchanged cation and its role in the reaction mechanism for each zeolite.

As for the exchange effect of the silver ion, Ward found, using the IR technique, that AgX-type zeolite differs from other zeolites with monovalent cations in having acid sites of mainly the Brönsted type.[4] Yates observed X-ray diffraction due to the (111) and (200) planes of metallic silver after the reduction of AgX by $H_2$.[5] Recently Tsutsumi and Takahashi found that silver particles were formed during the course of cumene cracking on AgY and concluded that the zeolite becomes decationated-form in which metallic silver was dispersed.[6]

This paper will report the results of our study on the nature of active sites on AgX, using the isomerization of 1-butene as a test reaction. The degree of ion-exchange by $Ag^+$ was extended to the range of 11—100%. The effect of treatment with $H_2$ on the catalytic activity was examined; the deuterium distribution in butenes was also determined for the reaction on the catalyst treated with $D_2$.

## Experimental

*Materials.* AgX-type zeolites were prepared by immersing Linde Na 13X-zeolite, free of clay binder, in an aqueous solution of silver nitrate at room temperature for 12 hr. The amount of $Na^+$ exchanged by $Ag^+$ was determined by means of EDTA analysis.[7] Throughout this paper, the catalysts will be denoted by AgX, with the percentage of ion-exchange by $Ag^+$ in parentheses. The surface area of zeolite was evaluated from a Langmuir plot for nitrogen adsorption at 77 K. The X-ray diffraction pattern was recorded before and after the isomerization reaction; AgX-type zeolites were thus found to retain the original structures, irrespective of the degree of ion-exchange. The acidity of the catalysts was estimated from the adsorption of *n*-butylamine.[8] Methyl red ($pK_a=4.8$) and methyl yellow ($pK_a=3.3$) were used as indicators. Decationated X-zeolite, HX, was prepared by exchanging the $Na^+$ in the zeolite with $NH_4^+$ and by then heating to 350 °C under a vacuum.[9] The hydrogen (nominal purity, 99.9 mol%), deuterium (99.5 mol%), and 1-butene (containing less than 0.2 mol% of 2-butene) in a glass ampoule were obtained from the Takachiho Shoji Co. and were used without further purification.

*Procedure.* The reaction was studied using an apparatus which consisted of a reaction system of 440 ml combined with a circulation pump and a high-vacuum line. Samples were taken periodically from the reaction system and were analyzed by means of a reduced-pressure-type gas chromatograph[10] with a 16 m DMS–alumina column at room temperature. For kinetic measurements, 0.1 g of the catalyst was placed in the reaction vessel and the vessel was evacuated at 350 °C for 12 hr. After the subsequent degassing at the reaction temperature for 1 hr, 1-butene was admitted to the vessel to start the reaction. The pressure of 1-butene was maintained at 18 Torr in all the kinetic runs. In the treatment with $H_2$, $2.4\times10^{-4}$ mol of hydrogen was introduced into the system and was circulated over the AgX catalyst at 150 °C for 1 hr. The amount of hydrogen consumed corresponded to a *ca.* 45% reduction of the $Ag^+$ to $Ag^0$, regardless of the degree of ion-exchange in zeolites. AgX treated similarly with $D_2$ was also used for the reaction. The distribution of deuterium in butene was determined by using a mass spectrometer, Hitachi RMU-5B. The isomerization of *cis*-2-butene and *trans*-2-butene was also examined on $H_2$-treated AgX (93.2%) and AgX (32.9%).

## Results

The surface areas per unit of weight of dried catalysts are shown in Table 1. By taking into account the formular weight (NaX=13418, AgX(100%)=20719 and so on), the area per unit of weight of the zeolite framework was found to be almost independent of the degree of exchange and was estimated as $893\pm35$ $m^2/g_{fr}$. The surface area decreased when zeolite was exposed to 1-butene (2), but was recovered partly by a sub-

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TABLE 1. SURFACE AREAS OF ZEOLITES

| Catalyst (% $Na^+$ exchanged) | Surface area ($m^2/g_{dry}$) (1)[a] Evacuation at 350 °C | (2) Reaction at 150 °C | (3) Contact with hydrogen at 150 °C | (4) Reaction at 150 °C |
|---|---|---|---|---|
| NaX | 792 | 790 | — | — |
| AgX (11.3%) | 745 | 621 | 695 | 694 |
| AgX (32.9%) | 612 | 444 | 562 | 536 |
| AgX (42.6%) | 600 | 445 | 516 | 484 |
| AgX (72.3%) | 529 | 305 | 401 | 377 |
| AgX (93.2%) | 507 | 220 | 338 | 323 |
| AgX (100%) | 505 | 205 | 327 | 315 |

a) Number in parentheses shows the order of treatments.

sequent $H_2$-treatment (3). These changes may be attributed to the irreversible adsorption of 1-butene through the formation of the $Ag^+$–olefin complex,[11] thus blocking up the micropores of zeolite and its partial removal by hydrogen. This conclusion is supported by the finding that the decrease in the surface area becomes smaller when the zeolites are pretreated with hydrogen (4), since hydrogen reduces $Ag^+$ to $Ag^0$.[6]

Figure 1(a) illustrates the time course of 1-butene isomerization on AgX (93.2%) at 120 °C. The reaction did not have an induction period, and no product was detected other than 2-butenes. The reproducibility was satisfactory when the reaction temperature was kept below 150 °C. The rate of the disappearance of 1-butene was well expressed by the reversible first-order equation:

$$\log x_e/(x_e-x) = kt$$

were $k$ represents the rate constant ($min^{-1}\,g^{-1}$), and where $x$ and $x_e$ denote the fraction of 2-butenes at time $t$ and at equilibrium, respectively. The equilibrium compositions of three isomers were estimated from the literature.[12] The plots of this relation are shown in

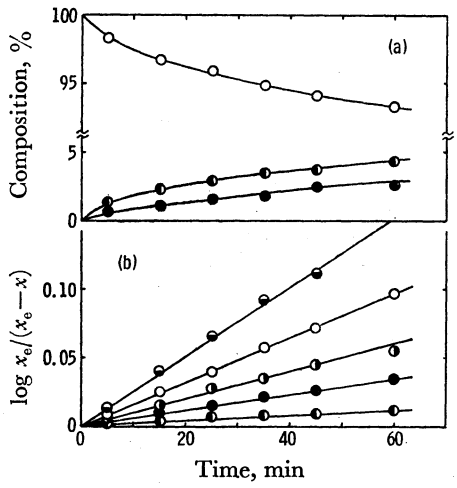



Fig. 1(a). Isomerization of 1-butene over AgX (93.2%) at 120 °C. ○, 1-butene; ●, *trans*-2-butene; ◐, *cis*-2-butene. 1(b). First-order plots for 1-butene isomerization. Reaction temperatures are 150, 140, 130, 120, and 100 °C in downward order.

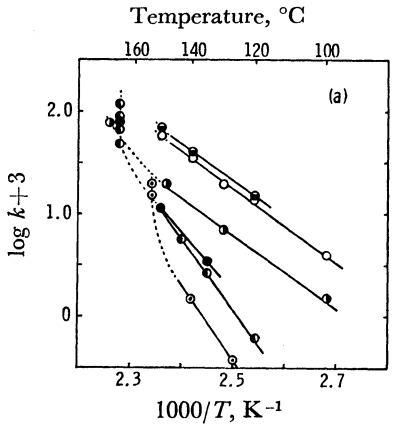



Fig. 2(a). Arrhenius plots for 1-butene isomerization over AgX. ⊙, AgX(11.3%); ◐, AgX(32.9%); ●, AgX(42.6%); ◑, AgX(72.3%); ○, AgX(93.2%); ◒, AgX(100%).

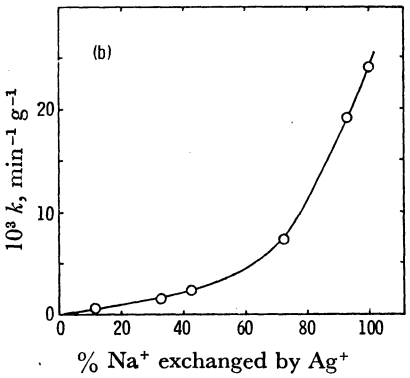



Fig. 2(b). Dependence of rate constants at 130 °C on the degree of ion-exchange.

Fig. 1(b) on AgX (93.2%) at temperatures ranging from 100 to 150 °C.

*Effect of Ion-exchange.* The dependence of the catalytic activity on the reaction temperature is given in Fig. 2(a). The broken lines indicate that the activity increases with repeated reactions above 150 °C. Figure 2(b) shows the first-order rate constants at 130 °C derived from these results. The activity increases gradually until the degree of exchange approaches 60% and rises steeply beyond that percentage. The energy of activation, as may be seen in Table 2, also changes abruptly at this degree of exchange. The initial ratio of the produced *cis*-2-butene to the *trans*-2-butene was larger than unity except in the case of AgX (42.6%) and increased with the temperature.

The results of acidity measurements are illustrated in Fig. 3. The total number of acid sites is linear with the degree of exchange, while strong acid sites of $H_0$ less than 3.3 increase drastically in number when the degree exceeds *ca.* 60%.

*Effect of $H_2$-treatment.* It was found that the silver particle was formed after the reaction at 200 °C, whereas this formation was not observed in the reaction below 100 °C. This fact suggests that olefins such as 1-butene can reduce AgX at high temperatures. Therefore, the effect of treatment with hydrogen as a reductant was examined.

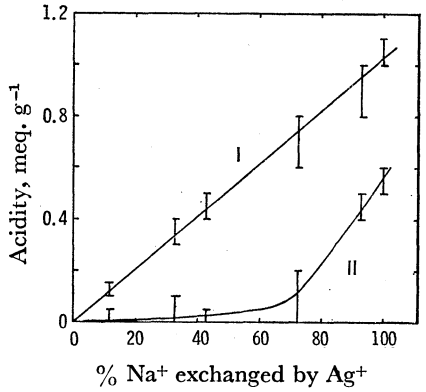



Fig. 3. Dependence of acidity on the degree of ion-exchange.
I, $H_0 \leqq +4.8$; II, $H_0 \leqq +3.3$ ($H_0$ is acidity function).

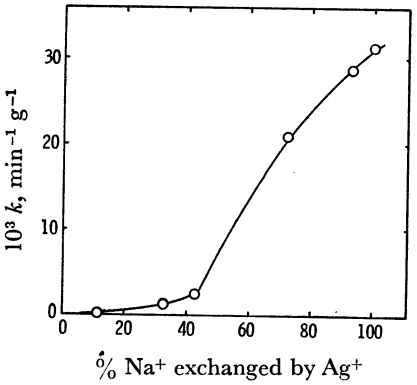
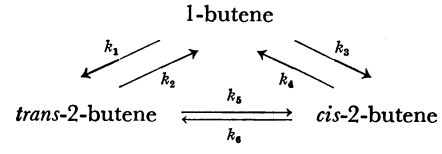



Fig. 4. Dependence of rate constants at 40 °C on the degree of ion-exchange over AgX pretreated with $H_2$.

Figure 4 shows the relationship between the rate constant and the degree of exchange for $H_2$-treated AgX. The abrupt increase in the activity begins at the degree of *ca.* 40%. The rate constants at 130 °C are greater than those for AgX without $H_2$-treatment by a factor of $10^2$—$10^3$. The contribution of the formed silver particle to the activity may be negligible; a separate study of the silver powder catalyst has shown that the reaction became appreciable only above 350 °C. The energies of activation and the *cis*/*trans* ratios in the products are listed, together with the degrees of exchange, in Table 2. The ratio is less than unity for AgX (32.9%) as well as for AgX (42.6%).

Experiments with three butene isomers as the starting material provided the relative rate constants shown in the scheme below:[13]




In the case of $H_2$-treated AgX (93.2%) at 72 °C, $k_1=12.8$, $k_3=17.3$, $k_4=3.5$, $k_5=2.1$, and $k_6=5.3$ were obtained by putting $k_2$ at unity, while $k_1=7.3$, $k_3=5.5$, $k_4=1.6$, $k_5=0.5$, and $k_6=1.1$ were obtained for $H_2$-treated AgX (32.9%) at 125 °C in a similar manner. On the reaction of 2-butenes, the treated AgX (93.2%) was evidently more active for the geometrical isomerization than for the double-bond shift. The preferential formation of *cis*-2-butene from 1-butene was also indicated. The treated AgX (32.9%) showed, on the contrary, a preference for the double-bond shift rather than for the geometrical isomerization and was active for the formation of *trans*-2-butene from 1-butene.

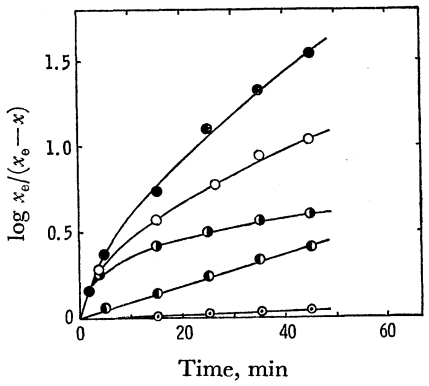



Fig. 5. First-order plots for 1-butene isomerization at 54 °C over AgX(100%) pretreated with $H_2$. Treatment temperature (⊙, 100 °C; ◐, 150 °C; ●, 250 °C; ○, 350 °C; ◑, 450 °C)

In Fig. 5, the effect of the treatment temperature on the activity is illustrated in terms of the first-order plot for the isomerization. The activity was raised slightly with $H_2$-treatment at 100 °C and became moderate and reproducible after treatment at 150 °C. When the treatment and the reaction were done alternately, the activity increased step by step and exceeded that of the decationated X-type zeolite, HX. When the temperature of treatment was higher than 250 °C, the initial rate became larger, but the degradation of activity occurred rapidly.

Parallel to this study of the activity, the X-ray diffraction of $H_2$-treated catalysts was examined. As the temperature of treatment was raised above 150 °C, a rapid growth of silver particles was recognized from the increase in the (111) and (200) diffraction intensities. The zeolite structure began to collapse above 250 °C and vanished completely after treatment at 450 °C.

*Isotope Effect and Deuterium Distribution.* In the case of treatment with $D_2$, the formation of HD as the result of exchange with surface hydrogen was negligible and the amount of deuterium atoms adsorbed on AgX (100%) was $9.30\times10^{20}$ atom/g. This value was coincident with that of hydrogen atoms adsorbed when treated with $H_2$ under the same conditions. The initial rate constant for the isomerization of 1-butene at 56 °C was estimated to be $1.12\times10^{-1}$ min$^{-1}$ g$^{-1}$, compared with $1.67\times10^{-1}$ min$^{-1}$ g$^{-1}$ over the $H_2$-treated catalyst; hence, the isotope effect was straightforward. The observed deuterium distribution is shown in Table 3. *trans*-2-butene, not quoted, had a distribution similar to that in *cis*-2-butene.

$H_2$- and $D_2$-treatment on AgX (32.9%) produced the rate constants of $1.10\times10^{-1}$ min$^{-1}$ g$^{-1}$ and $1.00\times10^{-1}$ min$^{-1}$ g$^{-1}$ respectively at 125 °C. The isotope effect appears to be small. The initial product by the isomerization of 1-butene on $D_2$-treated AgX (32.9%) consisted of 39% 2-butene-$d_0$ and 61% 2-butene-$d_1$.

## Discussion

The preliminary experiment showed that the starting material, NaX, was inactive for the isomerization of 1-butene below 200 °C. As is evident from Fig. 2(b), the partial replacement of $Na^+$ by $Ag^+$ increases the activity, particularly when the degree of exchange exceeds 60%. There are several kinds of sites available to nonframework cations in zeolite: SI is at the center of the hexagonal prism; SII and SIII are in the sodalite cage; SIV faces the supercage, and SV is at the entrance into the supercage.[14] Shoemaker *et al.* determined the positions of the cation in AgY-type zeolite by means of X-ray diffraction and showed that all of the SI sites were occupied with silver ions.[15] Although the X-type zeolite differs from the Y-type in its Si/Al ratio and, consequently, in the number of cations, a similar site preference of $Ag^+$ is feasible. The preferential occupation of the interior sites, SI and SII and/or SIII, by $Ag^+$ is responsible for the slight increase in activity up to an exchange of *ca.* 60%. The cations which occupy the surface sites are expected to bring about a profound effect on the activity.

TABLE 2. KINETIC RESULTS OF 1-BUTENE ISOMERIZATION ON AgX-TYPE ZEOLITES

(a) Without $H_2$-treatment

| Catalyst | Temperature range (°C) | *cis*/*trans* ratio | Energy of activation (kcal/mol) |
|---|---|---|---|
| AgX(11.3%) | 127—141 | 1.4—1.6 | 34.2 |
| AgX(32.9%) | 120—144 | 1.8—2.1 | 31.9 |
| AgX(42.6%) | 135—150 | 0.7—0.9 | 29.2 |
| AgX(72.3%) | 100—150 | 1.3—1.7 | 16.4 |
| AgX(93.2%) | 100—150 | 1.8—2.1 | 16.4 |
| AgX(100%) | 120—140 | 1.9—2.1 | 16.4 |

(b) With $H_2$-treatment

| Catalyst | Temperature range (°C) | *cis*/*trans* ratio | Energy of activation (kcal/mol) |
|---|---|---|---|
| AgX(11.3%) | 125—183 | 1.3—1.7 | 15.4 |
| AgX(32.9%) | 77—125 | 0.3—0.8 | 13.4 |
| AgX(42.6%) | 71—144 | 0.4—0.7 | 13.4 |
| AgX(72.3%) | 27—86 | 1.3 | 11.2 |
| AgX(93.2%) | 40—83 | 1.2—1.5 | 11.0 |
| AgX(100%) | 40—83 | 1.5 | 11.1 |

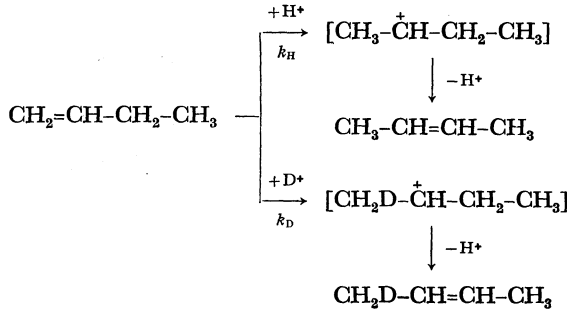
The variation in the number of acid sites with the degree of exchange also reflects this location of cations. Exchanged zeolites with $Ag^+$ in the interior sites have only weak acid sites of $H_0$ between 3.3 and 4.8. Strong acid sites of $H_0$ less than 3.3 are observed on zeolites in which $Ag^+$ occupies the surface site. The correlation between the number of strong acid sites and the activity is remarkable when we combine Fig. 3 with Fig. 2(b). This result suggests that the isomerization on AgX proceeds on acidic sites.

*cis*-2-Butene was produced preferentially on all the AgX-type zeolites except AgX (42.6%). In the case of 2-butene, the geometrical isomerization was more rapid than the double-bond shift. These features are characteristic of the isomerization by a carbonium-ion mechanism on acidic sites. On the other hand, studies of basic catalysts have shown that, if the reaction proceeds *via* an allyl carbanion, much larger *cis*/*trans* ratios and higher selectivities toward the double-bond shift may be expected because of the restricted rotation of the intermediate.[16] The repetition of reactions above 150 °C or $H_2$-treatment on AgX enhanced the activity, accompanied by the formation of silver particles. However, the effect of $H_2$-treatment on the activity increase is larger than that of repeated reactions by a factor of $10^1$—$10^2$. The $H_2$-treatment lowers the energy of activation (Table 2) and also shifts the threshold of the increase in the activity to a 40% exchange (Fig. 4); nevertheless, the features of the reaction are similar to those of the reaction on AgX without the treatment. The region of the degree of ion exchange, where the *cis*/*trans* ratio becomes anomalous and less than untiy, shifts to around 35% upon $H_2$-treatment. In this region, an alternative mechanism such as a hydrogen-switch seems to hold, where the double-bond shift is favored on the isomerization of 2-butene.[17]

TABLE 3. DEUTERIUM DISTRIBUTION IN PRODUCTS FOR 1-BUTENE ISOMERIZATION OVER $D_2$-TREATED AgX (100%) AT 56 °C

| Conversion (%) | 1-butene | | | | *cis*-2-butene | | | |
|---|---|---|---|---|---|---|---|---|
| | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_0$ | $d_1$ | $d_2$ | $d_3$ |
| 1 | 99.5 | 0.5 | — | — | 52.0 | 47.4 | 0.6 | — |
| 6 | 98.9 | 1.0 | 0.1 | — | 51.2 | 43.1 | 4.7 | 0.4 |
| 20 | 97.5 | 2.3 | 0.2 | — | 66.0 | 30.0 | 3.7 | 0.3 |
| 25 | 97.3 | 2.5 | 0.2 | — | 69.2 | 27.3 | 3.2 | 0.3 |
| 94 | 80.1 | 17.9 | 1.9 | 0.1 | 80.0 | 17.4 | 2.4 | 0.2 |

The deuterium distribution obtained by the use of $D_2$-treated AgX (100%) gives the following information (Table 3): the deuterium content in both 1-butene and *cis*-2-butene is 23% at 94% conversion, and the total number of deuterium atoms entering the butenes during the isomerization is estimated to be $7.80 \times 10^{20}$ atom/g. Therefore, the finding that the number of deuterium atoms adsorbed upon $D_2$-treatment is $9.30 \times 10^{20}$ atom/g predicts that the majority of deuterium atoms participate in the reaction. The result that the fraction of 2-butene-$d_0$ produced attained 50% even at 1% conversion requires some source of hydrogen. If the AgX (100%) treated with $D_2$ or $H_2$ is used for the isomerization of 1-butene and if a carbonium-ion mechanism is operative, the initial step in the formation of 2-butene may be supposed to be:



The ratio of rates on $H_2$- and $D_2$-treated catalysts can be given by:

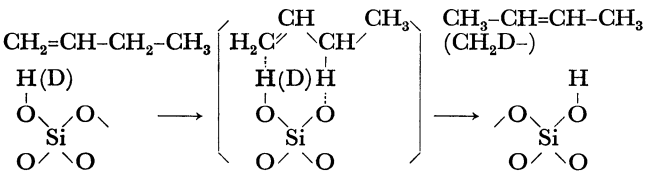
$$V_H/V_D = k_H(n_H^0+n_H)/(k_Hn_H^0+k_Dn_D) \quad (1)$$

where $n_H$ and $n_D$ correspond to the numbers of hydrogen and deuterium atoms produced by the treatments, where $n_H^0$ is the number of hydrogen atoms existing in AgX before the treatment, and where $k_H$ and $k_D$ are rate constants. In a similar manner, the ratio of 2-butene-$d_1$/2-butene-$d_0$ produced in the reaction on $D_2$-treated AgX can be expressed by:

$$d_1/d_0 = k_Dn_D/k_Hn_H^0 \quad (2)$$

when the reaction is extrapolated to zero conversion. By substituting the observed values for $V_H/V_D$, $d_1/d_0$, $n_H$, and $n_D$ in Eqs. (1) and (2), one can evaluate $k_H/k_D$ to be 2.03 and $n_H^0$ to be $5.0\times10^{20}$ atom/g. The latter value is comparable with the estimated total number of acid sites, $6.02\times10^{20}$ site/g. This result strongly indicates that the acid sites in AgX are mainly of the Brönsted type and conforms to the finding of the IR study that AgX zeolite lacks Lewis acid sites.[4]

A similar analysis of the reaction on AgX (32.9%) gave a $k_H/k_D$ ratio of 1.16 and an $n_H^0$ value of $2.3\times10^{20}$ atom/g. The observed small isotope effect suggests that an alternative path is merged in the carbonium-ion mechanism. In the consideration of the tetrahedral geometry of SiOH on the surface, a hydrogen-switch mechanism[17] may be applicable to the reaction on AgX, with the degree of exchange around 35% expressed as follows:




Since the surface hydrogen is protonic, the O–H bond may be thought to be weaker than the C–H bond. The rupture of the C–H bond is rate-determining, and there appears to be no direct isotope effect associated with the surface hydrogen. Accordingly, it is probable that the reaction proceeds by means of a simultaneous mechanism involving a hydrogen-switch and a carbonium-ion respectively, because 2-butene undergoes a *cis-trans* isomerization on this catalyst. This change in mechanism occurs in the limited range of ion exchange where $Ag^+$ would probably be located in the sodalite cage. This correlation between mechanism and structure requires further investigation.

The treatment with $H_2$ reduces silver ions into atoms, and an equivalent number of protons is produced. Since the number of acidic sites after treatment is, at most, three times as large as that before treatment, the remarkable increase in activity by a factor of $10^2$—$10^3$ cannot be explained unless we introduce the increase in acid strength. Unfortunately, the acidity measurement is not possible because of the darkening of the treated AgX, but it seems reasonable to say that the distribution of acidic sites on the treated AgX became similar to that on the HX, spreading over a region of lower $H_0$ values. The $H_2$-treated AgX in the present study retains its crystal structure even though many of the $Ag^+$ ions are replaced with protons. As long as the $H_2$-treatment of AgX was performed at the relevant temperature, no water molecule was evolved and the $Ag^+$ ions remained as nonframework cations to maintain the zeolite structure. Protons with a strong acid strength are possibly stabilized in the structure.

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