Dehydration of Secondary Alcohols Catalyzed by Solid Acids

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In order to examine the correlation between the acidic properties of catalysts and their activity or selectivity and to elucidate the reaction mechanism, dehydration reactions of 4-methyl-2-pentanol and 2-butanol over Al_2O_3, SiO_2, SiO_2–Al_2O_3, ZnS, $NiSO_4$, $Al_2(SO_4)_3$ or Al_2O_3 poisoned with basic compounds were carried out at 80—250 °C by means of the conventional flow method or a thermal desorption method. The following results were obtained. 1) Both Brönsted and Lewis acids are active, the latter being so to a greater extent. 2) Even relatively weak acid catalysts of acid strength $H_0=4.8$—6.8 are active, the catalytic activity being correlated with the number of effective acid sites. 3) The selectivity of 4-methyl-1-pentene/4-methyl-2-pentene and 4-methyl-*cis*-2-pentene/4-methyl-*trans*-2-pentene is lower for Brönsted acids than for Lewis acids and higher for weaker Lewis acid strengths. 4) The composition of butene isomers varies greatly with changes in desorption temperature and the amount of adsorbed 2-butanol in the case of Al_2O_3, but not much for SiO_2–Al_2O_3. 5) The ratios of *cis*-2-butene/*trans*-2-butene and 1-butene/2-butene over Al_2O_3 are remarkably increased by poisoning with pyridine. A reaction mechanism including a new reaction path has been proposed.

The dehydration of secondary alcohols is found to be useful for investigating the properties of catalysts since the selectivity of the catalysts is indicated by the formation of 1-olefins, *cis*-2-olefins and *trans*-2-olefins and the ratios of 1-olefins/2-olefins and *cis*-2-olefins/*trans*-2-olefins.

The dehydration of alcohols is known to be catalyzed by solid acids[1] and it has been pointed out that the basic properties of some solid acids play an important role in dehydration reactions.[2–4] Some problems concerning the effective acid strength of catalysts[5,6] and the nature of reaction intermediates[7] have also been studied. However, the catalysts used for the dehydration of secondary alcohols are limited to several kinds, including alumina. No systematic work has been done on the correlation between acidic properties (the amount, strength and type —Brönsted or Lewis— of the acid sites) of catalyst surfaces and catalytic activity or selectivity.

In the present work, we examined the correlation by employing aluminum sulfate,[8] nickel sulfate,[8] zinc sulfide,[9] silica[10] and silica-alumina[10] in addition to alumina as catalysts whose acidic nature is fairly well understood. From the secondary alcohols, 4-methyl-2-pentanol was selected because of the importance of its main product, 4-methyl-1-pentene, as a synthetic material in surface active agents and perfumes. 2-Butanol was used as another secondary alcohol since it is the simplest secondary alcohol and is suitable for thermal desorption experiments which provide data on dehydration with a known amount of adsorbed alcohol without being accompanied by the isomerization of product olefins.

The dehydration mechanism of secondary alcohols and the catalytic action of solid acids are discussed in the light of the observed results.

Experimental

Catalysts and Reagents. Three kinds of alumina were used. Al_2O_3-I (Kishida Chemicals and Co. Ltd.) was calcined in air at 500 °C for 3 hr (specific surface area: 382 m^2/g). Al_2O_3-II was prepared by the hydrolysis of aluminum isopropoxide and calcination in air at 800 °C for 3 hr. Al_2O_3-III, an alkali-poisoned catalyst, was prepared by immersing Al_2O_3-I in NaOH solution for 24 hr, drying at 120 °C for 24 hr and calcining in air at 500 °C for 3 hr. For thermal desorption experiments, Al_2O_3-I was evacuated at 450 °C for 3 hr. For poisoning experiments, pyridine was adsorbed on the catalyst in a vacuum system. Silica (Kishida Chemicals and Co., Ltd.) was calcined in air at 720 °C for 2.5 hr. Silica-alumina (Shokubai Kasei Co., 25% Al_2O_3, specific surface area: 514 m^2/g) used for thermal desorption experiments was calcined in a vacuum at 450 °C for 3 hr. Nickel and aluminum sulfate catalysts were prepared by heating guaranteed reagents of the heptahydrate (Kanto Chemical Co.) and the octadeca-hydrate(Wako Pure Chemical Industries) respectively in air at various temperatures for 3 hr. The 16—24 mesh powders were stored in sealed ampoules. Zinc sulfide (guaranteed reagent of Kanto Chemical Co.) was calcined in air at 400 °C for 2.5 hr.

4-Methyl-2-pentanol (Tokyo Kasei Kogyo Co.) was purified by fractional distillation. 2-Butanol (guaranteed reagent of Wako Pure Chemical Industries) was distilled over sodium metal and dehydrated and degassed by repeated freeze-thaw cycles after distillation over Molecular Sieve 3A *in vacuo*.

Measurement of Catalyst Acidity. The acid amounts at various strengths for the catalysts were measured by titrating with *n*-butylamine[10,11] using various indicators; benzalacetophenone ($pK_a=-5.6$), dicinnamalacetone (-3.0), benzeneazodiphenylamine($+1.5$), *p*-dimethylaminoazobenzene ($+3.3$), methyl red ($+4.8$) and neutral red ($+6.8$).

Reactions and Thermal Desorption. The dehydration of 4-methyl-2-pentanol was carried out by the conventional flow method using nitrogen as carrier gas at temperatures 150—200 °C. The alcohol vapor, whose pressure (25 mmHg) was kept constant in an alcohol saturator, was passed together with nitrogen through a reaction tube containing 1—2 g of catalyst. In order to prevent the condensation of alcohol and its products, the necessary parts of the apparatus were heated by resistance wires. The reaction products were collected in a liquid nitrogen trap and analyzed by gas chromatography. A one meter column of 30% TCP on Kacelite was used for the analysis of olefins and unreacted alcohol, and a 10 m column of Silicone DC-550/Bentone 34/Celite 545 for that of olefins alone. Catalytic activity was obtained from the linear plot of conversion percentage against contact time (W/F, W: catalyst weight, F: flow rate of alcohol).

The thermal desorption experiments of 2-butanol were carried out with a vacuum apparatus in the following way. After alcohol was introduced over 100—200 mg of evacuated catalyst at room temperature, the gas phase and weakly adsorbed alcohol were removed by condensation in a liquid

Table 1. Acid amounts and strengths of various catalysts

Catalysts	Acid amount (mmol g^{-1}) at various pK_a's					
	−5.6	−3.0	+1.5	+3.3	+4.8	+6.8
Al_2O_3-I	+	+	0.665	0.765	0.753	0.850
Al_2O_3-II				0	0.052	2.40
SiO_2	0	0.041	0.052	0.091	0.101	0.204
ZnS		0	0.054	0.10	0.173	0.322
$Al_2(SO_4)_3$-250[a]	0	0.040	0.332	0.348	0.353	0.456
-300[a]	0	0.126	0.357	0.399	0.454	0.694
-350[a]	0	0.124	0.313	0.388	0.421[b]	0.565
-400[a]	0	0.106	0.287	0.342	0.324[b]	0.467
-500[a]	0	0.026	0.135	0.127	0.133[b]	0.261

a) Calcination temperature (°C). b) pK_a = +4.0.

nitrogen trap, and the amount of irreversibly adsorbed alcohol at room temperature was measured as follows. The temperature of the system was elevated and the system kept at this temperature for 1.5 hr. All the species desorbed by the temperature elevation were collected in a liquid nitrogen trap and dried over Molecular Sieve 3A. The amount of each constituent was determined from the total pressure and gas chromatography analysis (1 m column of TCP for the analysis of alcohol-olefins and 5 m of VZ-7 for olefins).

The dehydration of 2-butanol over poisoned catalysts was carried out at 180 °C with a closed circulation apparatus. The initial pressure of alcohol was 12.5±0.3 mmHg. The catalysts were poisoned with pyridine or ammonia in a vacuum apparatus equipped with Tefron greaseless stopcocks. The amount of poisoning was estimated from the values obtained under the same condition as in the following adsorption-desorption experiments. Pyridine or ammonia was adsorbed at 100 °C for 1 hr on 30 mg of Al_2O_3-I which had been calcined *in vacuo* at 500 °C for 5 hr. After the catalyst was evacuated at 100 °C, the amount of adsorbed pyridine or ammonia was obtained by measuring the increase in catalyst weight with a microbalance (sensitivity: 3.4—3.5 mm/mg). The catalyst temperature was then elevated and the amount of pyridine or ammonia remaining on the catalyst was determined from its weight.

Results

Dehydration of 4-Methyl-2-pentanol. The reaction products were only olefins; 4-methyl-1-pentene, 4-methyl-*cis*-2-pentene and 4-methyl-*trans*-2-pentene.

Acidity and Activity of Catalysts: The acid amounts at various strengths of Al_2O_3-I, Al_2O_3-II, SiO_2, ZnS, $NiSO_4$ and $Al_2(SO_4)_3$ are shown in Table 1 and Fig. 1 and their catalytic activities for dehydration are shown in Table 2 and Fig. 1.

The acid strength of Al_2O_3-II was very weak, but its activity fairly high. This is considered to be due to the large number of acid sites having acid strength H_0=4.8—6.8. On the other hand, SiO_2, which has much stronger acid sites $H_0=-3$, showed relatively low activity. This is partly due to the small total acid amount (only 0.20 mmol/g at $H_0 \leqq +6.8$) and partly due to the fact that the acid sites on SiO_2 are of Brönsted type whose activity is less than that of Lewis type sites. The smaller activity of ZnS than that of Al_2O_3-II is also explained by the smaller total acid amount. In the case of metal sulfates calcined at various tem-

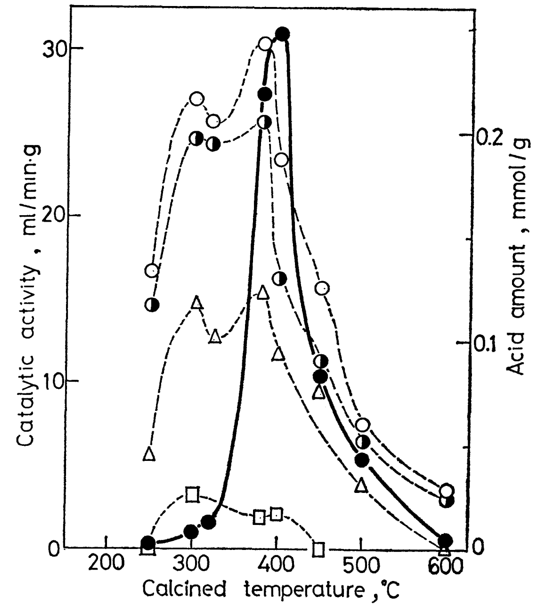

Fig. 1. Acidity and catalytic activity of $NiSO_4$ calcined at various temperatures. Solid line; catalytic activity for dehydration of 4-methyl-2-pentanol. Broken line; acid amount: (○) pK_a=6.8, (◑) pK_a=4.8, (△) pK_a=1.5, (□) pK_a=−3.0.

Table 2. Catalytic activities of various catalysts

Catalysts	Reaction temp. (°C)	Activity (ml g^{-1} min^{-1})
Al_2O_3-I	170	35
	186	80
Al_2O_3-II	170	55
	186	—
ZnS	170	1.0
	198	5.5
SiO_2	167	1.9
$Al_2(SO_4)_3$-250[a]	150	25
-300[a]	150	77
-350[a]	150	81
-400[a]	150	17
-500[a]	150	4.5

a) Calcination temperature (°C).

peratures, the activities were roughly correlated with total acid amount as seen in Fig. 1 and Tables 1 and 2. The activity of Al_2O_3-III decreased with increasing sodium hydroxide, but the catalyst poisoned with 1.75 mmol/g of NaOH which has no acid sites of $H_0 = +3.3$ did not completely lose activity.

These results indicate that the acidic properties of the catalysts are an important factor in activity, and even weak acid sites are active in the dehydration of 4-methyl-2-pentanol. This is in good agreement with the result observed by Misono *et al.*[5] that weak acid sites on silica-alumina poisoned with pyridine were active for the dehydration of tertiary butanol.

The number of acid sites on $NiSO_4$ calcined at 300 °C was large, but activity was very low (Fig. 1). However, the acid amount gives the sum of the amount of Brönsted and Lewis acid sites. According to the infrared study of pyridine adsorbed on nickel sulfate,[12] the maximum amount of Brönsted acid is observed on the sulfate calcined at 250—300 °C, and that of Lewis acid on the sulfate calcined at 400 °C. Since the Lewis acidity change caused by calcination is similar to the activity change, Lewis acid sites are believed to be more active than Brönsted acid sites of the same acid strength.

Since it is known by infrared study that a Lewis acid site can be converted into a Brönsted acid site in the presence of a water molecule,[13] the effect of water formed by the dehydration reaction on the type of acid site should be taken into consideration. However, a comparison of activity and acidity in Fig. 1 shows that the Lewis acid sites which might interact with water molecules differ entirely from the Brönsted acid sites originally present on the catalyst. The same kind of difference was also found for the vapor phase hydrolysis of methylene chloride catalyzed by various solid acid.[14] Matsuzaki *et al.*[15] showed that the acid strength of silica-alumina does not change with the adsorption of water when the temperature of adsorption is high. If a conversion of Lewis sites into Brönsted sites occurred, the acid strength should have changed. These facts indicate that Lewis sites are not converted into Brönsted sites at high temperatures, or that Lewis sites, even if they interact with water molecules, are distinguished from the original Brönsted sites.

Acidity and Selectivity of Catalysts: The ratios of 4-methyl-1-pentene/4-methyl-2-pentene (abbreviated as 1-P/2-P) and 4-methyl-*cis*-2-pentene/4-methyl-*trans*-2-pentene (*cis*-P/*trans*-P) for each catalyst are shown in Table 3. The 1-P/2-P ratio decreased in the order $Al_2O_3\text{-II} > Al_2O_3\text{-I} > ZnS > NiSO_4 > Al_2(SO_4)_3 > SiO_2$. In the case of Al_2O_3-III, the ratio increased with an increase in the amount of NaOH added as shown in Fig. 2. The lowest ratios were found for SiO_2, a well-known Brönsted acid,[16] while the higher ratios were found mainly for Lewis acids such as Al_2O_3-II, Al_2O_3-I, ZnS and $NiSO_4$ calcined at 400 °C. The selectivity of the latter catalysts changed with the Lewis acid strength and the basic properties. The Al_2O_3 catalysts which have basicity[10,17] together with Lewis acidity showed a high selectivity. Among aluminas, Al_2O_3-II which has the weakest acid strength showed the highest selectivity. An intermediate selectivity was found for metal sulfate and ZnS which have no basicity,[9] a higher selectivity being observed with the weaker Lewis acid strength. In Al_2O_3-III catalysts, the selectivity became higher as the strong acid sites were poisoned with sodium hydroxide (Fig. 2).

Table 3. Selectivity of various catalysts

Catalysts	Reaction temp. (°C)	1-P/2-P	*cis*-P/*trans*-P
Al_2O_3-I	150	0.58	3.2
	170	0.49	2.9
Al_2O_3-II	150	1.14	—
	170	0.58	5.5
$NiSO_4$-400[a]	150	0.28	1.2
$Al_2(SO_4)_3$−350[b]	150	0.23	1.0
SiO_2	190	0.23	0.35
ZnS	198	0.41	0.83
equilibrium[c]	170	0.12	0.72

a) Calcined at 400 °C. b) Calcined at 350 °C. c) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. E. Rossini, *J. Res. Nat. Bur. Stand.*, **36**, 559 (1946).

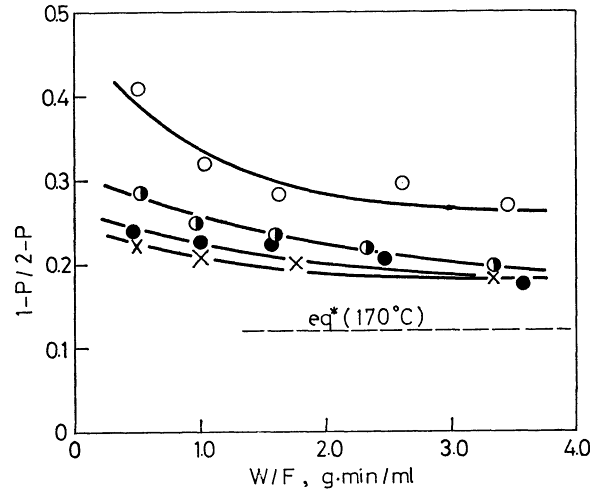

Fig. 2. Poisoning effect of NaOH on selectivity (1-P/2-P).
Reaction temperature: 150 °C, Amount of NaOH on Al_2O_3-III (mmol g^{-1}): (×) 0, (●) 0.12, ◑ 0.2, (○) 0.45.
* Thermodynamic equilibrium composition: J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **36**, 559 (1946).

The selectivity for *cis*-P/*trans*-P was similar to that for 1-P/2-P.

Dehydration of 2-Butanol. The reaction products were 1-butene, *cis*-2-butene and *trans*-2-butene.

The changes in the ratios of 1-butene (abbreviated 1-B/2-B) and *cis*-2-butene/*trans*-2-butene (*cis*-B/*trans*-B) with the rise in desorption temperature for Al_2O_3 are shown in Fig. 3. The ratio 1-B/2-B was almost the same as that in equilibrium independent of the amount of adsorbed alcohol above 150 °C, but was higher below 150 °C and increased with increasing amount of adsorbed alcohol (Fig. 3(a)). The ratio *cis*-B/*trans*-B was almost the same as the equilibrium ratio when the amount adsorbed was 0.354 mmol/g, but increased an increase of the amount adsorbed, a higher increase

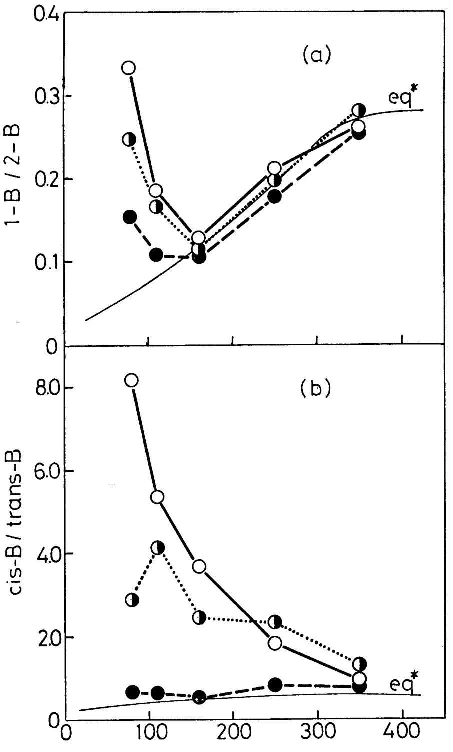

Fig. 3. Changes in 1-B/2-B and *cis*-B/*trans*-B with change in desorption temperature over Al_2O_3-I. Amount of adsorbed 2-butanol ($mmol\,g^{-1}$); (○) 1.106 (◑) 0.700, (●) 0.354.
* Thermodynamic equilibrium composition.

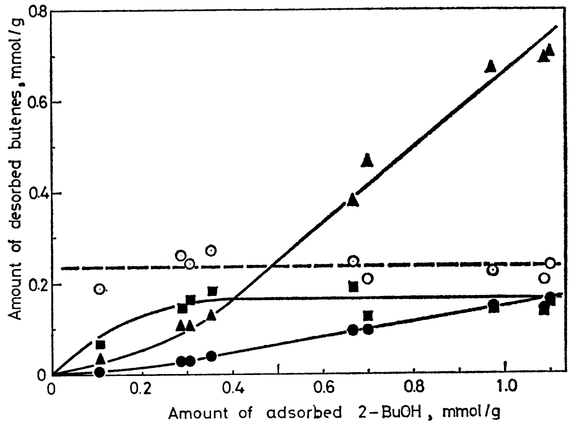

Fig. 4. Amounts of butenes desorbed up to 350 °C *vs.* amount of 2-butanol adsorbed on Al_2O_3-I: (●) 1-B, (▲) *cis*-B, (■) *trans*-B, (○) ratio of 1-B/*cis*-B.

being observed at the lower desorption temperature (Fig. 3 (b)). In Fig. 4, the amount of each butene isomer desorbed up to 350 °C is plotted against the amount of adsorbed alcohol in the case of Al_2O_3. The amount of *trans*-2-butene formed was almost constant independent of the amount of adsorbed alcohol, while that of 1-butene and *cis*-2-butene increased with the amount of adsorbed alcohol. In the case of SiO_2–Al_2O_3 catalyst, both ratios were very close to the equilibrium ratio independent of the amount of adsorbed alcohol, except that a higher *cis*-B/*trans*-B ratio was observed below 160 °C.

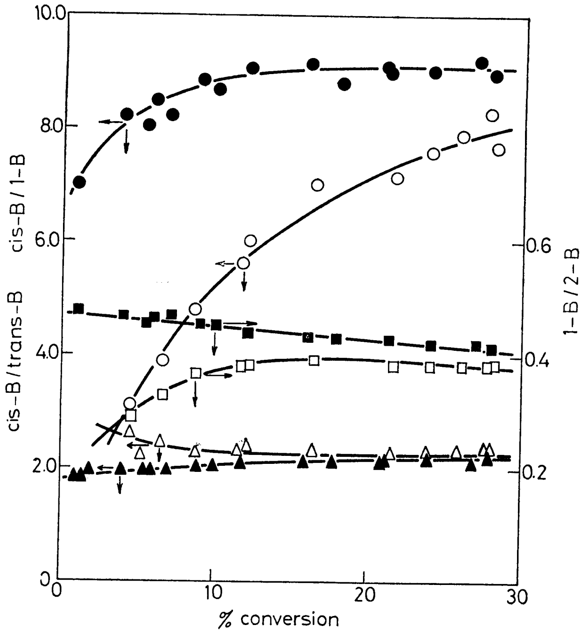

Fig. 5. Poisoning effect of pyridine on dehydration of 2-butanol.
Reaction temperature: 180 °C, Al_2O_3-I without poisoning, (○) *cis*-B/*trans*-B, (□) 1-B/2-B, (△) *cis*-B/1-B. Al_2O_3-I poisoned with 0.11 $mmol\,g^{-1}$ pyridine, (●) *cis*-B/*trans*-B, (■) 1-B/2-B, (▲) *cis*-B/1-B.

The fact that SiO_2–Al_2O_3 which has only high acid strength gives low selectivity, while Al_2O_3 which has different acid strengths gives different kinds of selectivity, depending on the amount of adsorbed alcohol, is discussed later.

The effect of pyridine poisoning on the dehydration of 2-butanol over an alumina catalyst is shown in Fig. 5, where the ratios of butene isomers formed are plotted against the % conversion of 2-butanol. The ratios of *cis*/*trans* and 1-B/2-B over the poisoned catalyst were high compared to the unpoisoned ones at low % conversion. The ratios for the two catalysts approached the same value as the % conversion increased, while the ratio of *cis*/1-B over both catalysts was almost the same and remained nearly constant. Since no isomerization takes place under the present reaction conditions,[18] the results indicate that the formation of *trans*-2-butene was strongly retarded by the poisoning of the catalyst with pyridine. The poisoning effect of ammonia on selectivity was similar to that of pyridine, but the degree of retardation for the formation of *trans*-2-butene was lower. In the case of pure alumina, the ratios were approximately equal to the equilibrium value at low % conversions, but increased with increasing % conversion (Fig. 5). These phenomena are believed to be due to *trans* isomer formation being retarded by poisoning with water molecules formed by the dehydration reaction.

Discussion

The reaction mechanism is discussed in the light of the observed catalyst selectivity. The following two are well-known mechanisms of olefin formation from alcohol; one includes oxonium ion and carbonium ion as reaction intermediates[19] (type El mechanism) represented by Scheme (A), and the other is an acid-base concerted mechanism[2] (type E2 mechanism), represented by Scheme (B), taking the dehydration of 2-butanol as an example.

$$C_4H_9OH \xrightarrow{H^+} C_4H_9OH_2^+ \xrightarrow{-H_2O} C_4H_9^+ \xrightarrow{-H^+} C_4H_8 \qquad (A)$$

$$C_4H_9OH \xrightarrow{-H^+,\ -OH^-} C_4H_8 \qquad (B)$$

Scheme (A) includes an alkoxonium ion $C_4H_9OH_2^+$ and carbonium ion $C_4H_9^+$ and the reaction is catalyzed only by Brönsted acid. In Scheme (B), the fissions of C–O and C–H bonds of alcohol occur simultaneously to eliminate a hydroxyl ion and a proton. The latter is effectively catalyzed by solid catalysts such as Al_2O_3 which has both Lewis acidity and basicity.

All the results can not be fully explained only by the above two mechanisms. In particular, it is difficult to explain the effect of Lewis acid strength on catalyst selectivity. We therefore propose a dehydration mechanism of secondary alcohols shown in Fig. 6, which presents a new route for the formation of carbonium ion from alcohol on a Lewis acid catalyst.

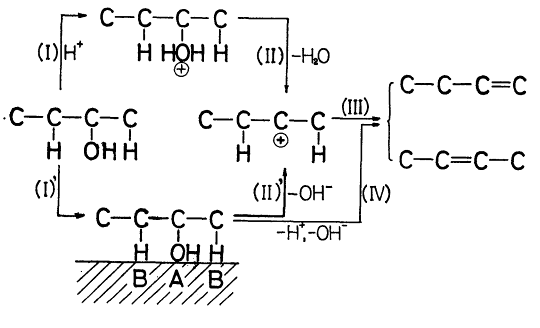

Fig. 6. Reaction paths of dehydration of secondary alcohols.
A: Lewis acid site, B: basic site.

The reaction path (I)-(II)-(III) is an alkoxonium-carbonium ion mechanism catalyzed by Brönsted acid. The dehydration of secondary alcohols over SiO_2 proceeds by this path. Since carbonium ion is formed in this case, the ratio 1-B/2-B tends to approach the equilibrium value. The ratio *cis*-B/*trans*-B also tends to approach the equilibrium value because of free rotation about the C–C bond. The observed selectivity of SiO_2 showed this tendency.

The reaction path (I)′-(IV) is a concerted mechanism, where H^+ and OH^- are eliminated simultaneously for either *cis*-elimination (Fig. 6) or *trans*-elimination. In this case, high ratios of 1-B/2-B and *cis*-B/*trans*-B are usually observed.[2]

A third reaction path (I)′-(II)′-(III) consists of adsorption of alcohol on Lewis acid sites A, the formation of carbonium ion by elimination of OH^- and the formation of an olefin by the elimination of a proton. This mechanism is possible when the Lewis acid strength is so high that the C–O bond is easily broken. Since a carbonium ion is formed as in the case of a Brönsted acid catalyst, both ratios 1-B/2-B and *cis*-B/*trans*-B approach the equilibrium values. Thus the stronger the Lewis acidity, the larger the possibility of reaction path (II)′ and the lower the selectivity for 1-olefin and *cis*-2-olefin. On the other hand, as the strength of the Lewis acid becomes weaker, the fission of the C–O bond becomes harder and comparable to that of C–H bond. Thus, the probability that the dehydration proceeds *via* path (IV) becomes large and the selectivity for 1-olefin and *cis*-2-olefin increases. In the case of Al_2O_3, the formation of an alkoxide from an alcohol molecule and an aluminum atom on the surface has been reported,[7,20] but does not affect the conclusion of the above discussion concerning selectivity and reaction mechanism.

Now let us discuss the observed selectivity of various catalysts. Since the acid strength of Al_2O_3-I is higher than that of Al_2O_3-II, the probability that the dehydration proceeds *via* path (II)′ becomes larger in Al_2O_3-I and hence the ratios of 1-olefin/2-olefin and *cis*-2-olefin/*trans*-2-olefin over Al_2O_3-I are higher than those of Al_2O_3-II (Table 3). However, since both Al_2O_3-I and Al_2O_3-II have basic properties as well as acidic properties, the probability of the concerted mechanism (IV) over alumina is large and the selectivity is higher than that of SiO_2 over which the dehydration takes place only *via* path (I)-(II)-(III). The selectivity of $Al_2(SO_4)_3$ is low compared with that of $NiSO_4$, because of the higher acid strength of $Al_2(SO_4)_3$. However, since both metal sulfates have no basic properties, the selectivity is low compared with Al_2O_3. Zinc sulfide which has no basicity,[9] but weak acidity (Table 1) shows an intermediate selectivity between Al_2O_3 and sulfates. The decrease in selectivity with increase of the amount of NaOH poisoning over Al_2O_3 is interpreted by assuming that path (IV) is favored over path (II)′, because the acid strength is weakened by the poisoning.

In thermal desorption experiments, the fact that the ratio of desorbed butenes is close to the equilibrium value over SiO_2–Al_2O_3, but deviates from the equilibrium value over Al_2O_3 at low temperatures or for large amounts of adsorbed alcohol, is also explained by the scheme shown in Fig. 6. Reaction paths (I)′-(II)′-(III) and (I)-(II)-(III) are favored over SiO_2–Al_2O_3, since the catalyst has high acid strength and contains Brönsted acid sites.[10] In the case of Al_2O_3, the path (I)′-(IV) becomes preferred due to the concerted action of acid sites of weaker Lewis acid strength and basic sites. However, the high selectivity is lowered at higher temperatures, since the C–O bond is more readily broken so that path (II)′ is favored. The high selectivity also decreases with decreasing amounts of adsorbed alcohol, since the fraction of adsorbed alcohol reacting with strong acid sites becomes large and path (II)′ is thus also favored. The participation of basic sites on Al_2O_3 in the dehydration of secondary alcohols was verified by experimental results in which the isotope effects of the β-hydrogen of 2-propanol[21] and 2-butanol[4] were 4.1 and 2.3 at 160 °C, respectively.

The high ratios 1-B/2-B and *cis*/*trans* observed with Al_2O_3 poisoned with pyridine are explained by the disappearance or the weakening of strong acid sites with pyridine.

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