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Acidity of Nickel Silicate and Its Bearing on the Catalytic Activity for Ethylene Dimerization and Butene Isomerization

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Catalytic activities of nickel silicates (montmorillonite and antigorite) for ethylene dimerization and butene isomerization run parallel when the catalysts are activated by evacuation at elevated temperatures, giving two maximums in activities. The variations in catalytic activities are closely correlated to the acidity of catalysts. The acid site responsible for the catalytic activity is protonic on montmorillonite, while nonprotonic on antigorite, as evidenced by the effect of water content or of sodium ion contamination, and the infrared spectra of adsorbed pyridine. This was confirmed by incorporation of proton held by the montmorillonite into the initial product of ethylene dimerization, 1-butene.

INTRODUCTION

The nickel oxide–silica catalyst has been known to be effective for the dimerization of ethylene (*1–4*). The catalyst is also active for the isomerization of *n*-butene, the mechanism of which has been proved to be of a proton donor–acceptor type (*5*). In a preceding paper, it was reported that the active sites on NiO–SiO_2 catalysts for ethylene dimerization are classified into two types, montmorillonite and antigorite, the optimum activation temperature for them being around 100 and 600°C, respectively (*6*). It was also previously reported that the dimerization activity is related to acidic property of the catalyst (*3, 7*), by which the isomerization of butene proceeds. In this view, the role of acid site would be important in the mechanism of dimerization, although no single acid can be as effective as NiO–SiO_2 for the dimerization of ethylene. Since the two types of active sites for the dimerization can be prepared separately as demonstrated in the preceding paper, it would be revealing to study the mechanism of dimerization on the separated active sites. Thus the correlations between dimerization and isomerization activities and acidic property have been reexamined, the role of acid site being elucidated by a tracer study.

EXPERIMENTAL

Catalysts. The nickel oxide–silica catalysts used in this study were the same as those described in the preceding paper (*6*). The A series of catalysts were prepared by precipitation from a mixed $NiSO_4$–Na_2SiO_3 (1/4) solution with NaOH at different final value of pH and are denoted by symbol A followed by the pH value. The NiO contents (wt%) of A-series catalysts were as follows: A-6(3), A-7.4(18), A-8(25), A-9(27), and A-10(30). The B series of catalysts were prepared by precipitation from different compositions of $Ni(NO_3)_2$–Na_2SiO_3 solution at a fixed pH of 7.5 and are denoted by symbol B followed by NiO content (wt%), i.e., B-4, -10, -24, -34, -56, -66, -73, -80, -85, and -90.

Procedure. The catalytic activity for ethylene dimerization was determined at 20°C by the same procedure as previously described (*6*). The isomerization of 1-butene was carried out at 20°C in a closed circulating system. The products were analyzed by gas chromatography using a VZ-7 column at room temperature. Both ethylene

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and 1-butene were obtained from Takachiho Co. and purified by distillation.

Acidity of noncolored catalyst was determined by *n*-butylamine titration in benzene using dicinnamalacetone as the indicator, while chemisorption of ammonia was employed as a measure of acidity of colored catalysts. The amount of chemisorption was obtained as an irreversible part of adsorption of ammonia (*8*). Thus the first adsorption of ammonia at 20°C and 300 Torr was followed by evacuation at 230°C for 1 hr and readsorption at 20°C, the difference between two adsorptions at 20°C giving the amount of chemisorption.

RESULTS AND DISCUSSION

Correlation between Activities for Ethylene Dimerization and Butene Isomerization

It has been shown that the catalytic activity of $NiO-SiO_2$ for ethylene dimerization varies with temperature of pretreatment (evacuation), giving two optimum temperatures, around 100 and 600°C. The dimerization activity of A-10 changed with the evacuation temperature as shown in Fig. 1. In the preceding paper (*6*) the two activity peaks were ascribed to two different types of active sites, montmorillonite (100°C) and antigorite (600°C). Although the activity decrease by pretreatment at high temperatures above 600°C is reasonably explained by sintering or solid phase rearrangement of the catalyst as demonstrated by irreversible decrease of specific surface area (1b) as well as the activity, little information has been obtained about what causes the activity decrease in the first peak region. It would be advisable to examine the mechanism of activity decrease.

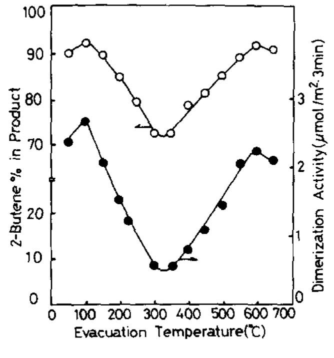

FIG. 1. Variations with evacuation temperature of catalytic activity and product composition in ethylene dimerization on catalyst A-10 at 20°C.

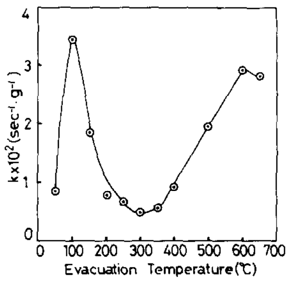

FIG. 2. Variation of 1-butene isomerization activity of catalyst A-10 with evacuation temperature.

It was found that the activity decrease is accompanied by a decrease in the extent of isomerization of *n*-butene produced by the dimerization. The compositions of *n*-butene obtained by dimerization runs on A-10 catalyst for 30 min are plotted against the evacuation temperatures in Fig. 1. It is obvious that the selectivity to 2-butene runs parallel with the dimerization activity. Since the initial product of ethylene dimerization seems to be 1-butene (*7*), the above result suggests that the isomerization activity runs parallel with the dimerization activity. Thus the isomerization of 1-butene was carried out at 20°C on the catalyst A-10 in a circulating system. The time course of isomerization was in agreement with the first order rate law. Thus the isomerization activity is represented by the first order rate constant. As shown in Fig. 2, it is confirmed that the isomerization activity also gives two maximums and one minimum at the same pretreatment temperatures as those for the dimerization activity.

The above results are in conformity with the view that 1-butene is the initial product of ethylene dimerization. This view was further confirmed by the following experiments. In order to avoid the secondary isomerization of initial product, a cold trap cooled to −160°C by isopentane bath was put in the circulating system and the catalyst bed height was minimized (about 10 mm). The partial pressure of ethylene was lowered to 4.5 Torr or lower. By taking these precautions, 1-butene was found to predominate (above 90%) in the products of dimerization runs at 20°C on B-10 catalyst evacuated at 100°C.

The catalysts B-4 and B-85 were taken as the typical example of, respectively, montmorillonite- and antigorite-type catalyst for the ethylene dimerization (*6*). The isomerization activities of B-4 and B-85 at 20°C and 22 Torr are shown in Fig. 3 as functions of evacuation temperature. The activity of B-4 passes a maximum at 100°C and decreases to a small plateau value, while that of B-85 increases all the way, with increase in the evacuation temperature, as is the case with the ethylene dimerization (*6*).

In a previous report on butene isomerization (*5*), it was shown that the activity of NiO–SiO_2 increases with increase in evacuation temperature from 100 to 500°C. The NiO–SiO_2 catalyst used in that study was prepared by precipitation of $Ni(OH)_2$ onto a preformed silica gel, while the catalyst employed in the present study was prepared by coprecipitation of $Ni(OH)_2$ and silicic acid to form nickel silicate. Since the precipitation of $Ni(OH)_2$ onto SiO_2 gives rise to accumulation of $Ni(OH)_2$ on silica surface, the nickel oxide content in the silicate thus formed tends to be much higher than the average. Thus it is very probable that the NiO–SiO_2 catalyst behaves like an antigorite type catalyst, although the NiO content was 30 to 50 wt% in the previously prepared catalyst and less than that for antigorite (65 wt%). It is clear that the improvement in the method of catalyst preparation revealed the existence of montmorillonite-type catalyst.

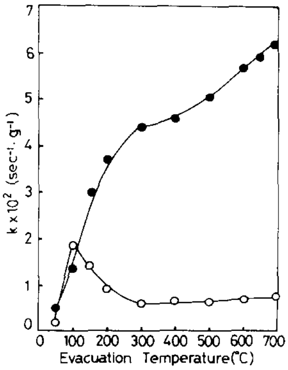

FIG. 3. Variations of isomerization activity on catalyst B-4 and B-85 with evacuation temperature. —○—, Catalyst B-4; —●—, catalyst B-85.

The foregoing results demonstrate that the ethylene dimerization activity is closely related to the butene isomerization activity which has been ascribed to the acidic nature of the catalyst (*5*, *7*). Thus the correlation between the catalytic activities and the acidity will be further examined in the following sections.

Correlation between Catalytic Activity and Acidity

The acidity of a NiO–SiO_2 catalyst was previously reported as a function of evacuation temperature (*7*). At that time the butylamine titration was made using dimethyl yellow as the indicator. The results showed that, although the acidity increases with increase in evacuation temperature in the regions 25–100°C and 300–500°C, it remains constant in the region 100–300°C in which the dimerization activity decreases with increase in evacuation temperature (*7*). At that time no explanation could be given for the observed discrepancy.

Since it was found in the present study that the isomerization activity also decreases by the evacuation at above 100°C, the acidity responsible for the isomerization also should decrease. It seemed likely that the acidity determined in the previous study did not reflect the real acid sites responsible for the dimerization because of the lower acid strength given by the indicator, dimethyl yellow (pK_a = 3.3). Thus dicinnamalacetone (pK_a = −3.0) was used in the present study.

The acidity of catalyst A-6 thus determined are given as a function of evacuation temperature in Fig. 4, where dimerization and isomerization activities are also given. It is clear that the catalytic activities decrease with decrease in acidity when the catalyst is evacuated at above 100°C, confirming the above hypothesis. In this experiment the catalyst A-6 was chosen because of its lightness in color associated with low NiO content. The dimerization activity of A-6 is accordingly of the montmorillonite type, i.e., less active when evacuated at higher temperatures as shown in Fig. 4.

The antigorite-type catalyst, on the other hand, gives maximum activity when evacuated at 600°C. Thus the acidity measurements were carried out with the B-series of catalysts evacuated at 600°C employing the ammonia chemisorption method. The specific acidities per surface area are shown as a function of NiO content in Fig. 5, where the activities for dimerization and isomerization are also given. Both of the activities as well as the acidity increase with increase in NiO content up to 70 or 80% NiO, again disclosing parallelism between them. Since those values are normalized by surface area, their variations with the NiO content demonstrate that the nature of active site changes from montmorillonite type to antigorite type with increase in the NiO content.

In this way it is demonstrated that the catalytic activities of NiO–SiO$_2$ substantially run parallel to the acidity. The nature of acidity will be examined in the following sections.

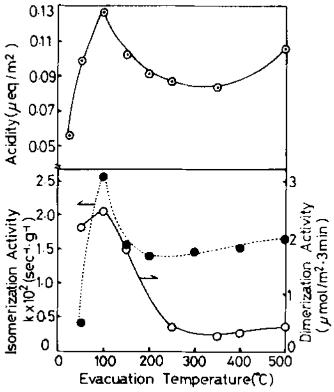

FIG. 4. Variations with evacuation temperature of acidity and catalytic activities for 1-butene isomerization and ethylene dimerization of catalyst A-6.

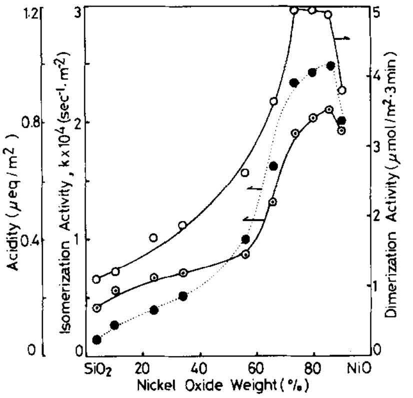

FIG. 5. Acidity and catalytic activities for 1-butene isomerization and ethylene dimerization as functions of NiO content of B series catalysts. —○—, Ethylene dimerization activity; —●—, 1-butene isomerization activity; —⊘—, acidity.

Reactivation of Deactivated Catalyst

It has been shown that the activation of NiO–clay by evacuation at elevated temperatures is caused by dehydration from the surface, because when the catalyst is exposed to water vapor after evacuation at a high temperature, the catalytic activity solely depends on the temperature of the second evacuation (*1*). For example, the catalyst evacuated at 500°C was cooled in water vapor to room temperature and reevacuated at 200°C. The activity thus obtained was identical with that obtained by direct evacuation at 200°C.

Applying this method, the mechanism of the activity decrease caused by the increase in evacuation temperature from 100 to 350°C was elucidated with ethylene dimerization activity of catalyst A-7.4. The results are illustrated in Fig. 6, where arrows indicate the order of evacuation as well as the atmosphere. It is clear that the catalyst deactivated by evacuation at 350 or 600°C can be reactivated by cooling in water vapor (20 Torr) followed by evacuation at 100°C, while the cooling in oxygen (8 Torr)

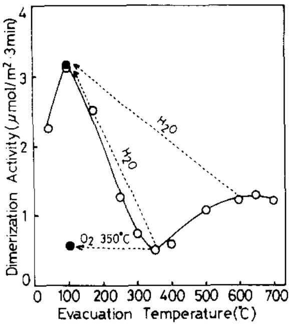

FIG. 6. Reactivation of deactivated catalyst (A-7.4) by water treatment.

does not result in reactivation. An analogous result was obtained for the isomerization activity of catalyst A-10. The catalyst was first evacuated at 300°C and cooled in water vapor. The second evacuation at 100°C reproduced the peak activity.

It is accordingly concluded that the deactivation is caused by dehydration from the surface. The peak activity appears to be associated with an optimum content of water, suggesting that the acid sites responsible for the catalytic activity are protonic in nature. In fact, it has been shown by a tracer work that the butene isomerization on $NiO-SiO_2$ evacuated at 100°C is catalyzed by the protonic acid (*5*). The present results suggest that the protonic acid sites are also responsible for the ethylene dimerization. On the other hand the catalytic activities developed by evacuation at above 300°C would be associated with nonprotonic acid sites because those are developed by dehydration. The nonprotonic nature of acid sites was previously shown with respect to the butene isomerization on $NiO-SiO_2$ evacuated at 500°C (*5*).

Identification of Acid Types by ir Absorption

It has been established that protonic and nonprotonic acid sites are distinguishable by infrared absorption spectra of adsorbed pyridine (*9*). This method was previously applied to a $NiO-SiO_2$ evacuated at 150, 200, and 400°C by Kageyama *et al.* But they failed to find any absorption band ascribable to a protonic acid (*10*). The $NiO-SiO_2$ catalysts employed in the present study were different from the catalyst used by Kageyama *et al.* in the method of preparation as well as the NiO content.

Figure 7 shows the ir spectra of pyridine adsorbed on catalyst A-7.4. Both the pyridinium ion band at 1543 cm^{-1} and the coordinated pyridine band at 1450 cm^{-1} are found with the catalyst evacuated at 100°C, while only the latter is found with the catalyst evacuated at 400°C. It is clear that the protonic acid site is lost by the increase in evacuation temperature.

Poisoning Effects of Sodium Ion Held by the Catalyst

The $NiO-SiO_2$ catalysts used in the present study were prepared by coprecipitation from mixed acidic solutions of nickel and silicate ions using sodium hydroxide as a precipitant so that the precipitates were contaminated with sodium ion even after repeated washing with pure water. It was found that the amount of sodium remaining after the washing depended largely on the final pH of precipitation. As shown in Table 1 the largest contamination is observed with the sample precipitated at pH 9. The remaining sodium ions were successfully removed by washing dried precipitate with an

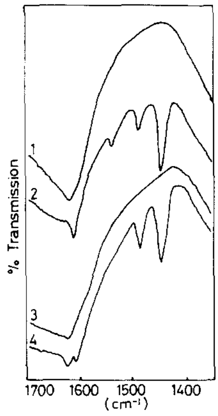

FIG. 7. Infrared spectra of pyridine adsorbed on catalyst A-7.4. (1) Background after evacuation at 100°C for 2 hr; (2) pyridine adsorbed on (1); (3) background after evacuation at 400°C for 2 hr; (4) pyridine adsorbed on (3), gas phase was evacuated at 200°C for 1 hr after adsorption in (2) and (4).

TABLE 1

Effect of Sodium Contamination on Ethylene Dimerization Activity

Evacuation temperature		100°C			600°C		
Precipitation (pH)	Na content (μmol/g)[a]	Activity[b]		Poisoning efficiency	Activity[b]		Poisoning efficiency[c]
		Na free	Na conta.		Na free	Na conta.	
6.7	8	1.53	1.47	8	0.49	0.48	~0
8	247	1.83	0.14	6.9	1.07	0.40	2.7
9	375	1.54	0.01	4.1	1.11	0.20	2.4
10	225	1.27	0.64	2.8	1.07	0.75	1.4
11	142	1.76	0.74	7.2	1.56	1.04	3.7

[a] μmol Na/cat/g after calcination.

[b] mmol C_2H_4/g/3 min at 230 Torr and 20°C.

[c] [(Na free) − (Na contaminated)]/(Na content).

aqueous ammonium nitrate solution to give sodium free catalysts (Na less than 3 ppm) which were used in the foregoing experiments.

Since the sodium ion is expected to occupy the acid site, it should give rise to degradation of the catalytic activities. Table 1 gives the activities of sodium-contaminated catalysts evacuated at the two optimum temperatures, 100 and 600°C. The sodium-contaminated catalysts are less active than the sodium-free catalysts as expected. A poisoning efficiency of sodium ion can be defined as the extent of activity decrease divided by the amount of sodium involved. It is noteworthy that the poisoning efficiency is generally about twice as large when evacuated at 100°C as that for the same catalyst evacuated at 600°C. Thus the activity of catalyst A-8 or A-9 evacuated at 100°C is substantially lost by the sodium contamination, while in the case of evacuation at 600°C, 20 or 40% of the activity still remains with the sodium-contaminated catalysts. An analogous result was obtained for the butene isomerization on A-9, i.e., little activity was found with the sodium-contaminated catalyst evacuated at 100°C, while the same catalyst evacuated at 600°C gave one-third the activity of pure catalyst.

The effect of sodium contamination was also found in the composition of butene formed by the ethylene dimerization. Figure 8 gives percentage 2-butene in *n*-butene obtained by the dimerization runs for 30 min at 20°C on catalyst A-9 with and without sodium. It is disclosed that an extensive isomerization of 1-butene to 2-butene proceeds on the pure catalyst rather irrespective of evacuation temperature, while the isomerization is effectively suppressed on the sodium-contaminated catalyst evacuated at temperatures lower than 350°C.

These results are in conformity with the view that a protonic acid site is responsible for the activities developed by the low-temperature evacuation, while a non-

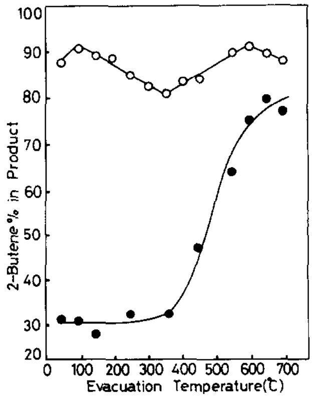

FIG. 8. Product composition in ethylene dimerization catalyzed by sodium-free and sodium-contaminated catalysts (A-9). —○—, Sodium-free catalyst; —●—, sodium-contaminated catalyst.

protonic acid site is responsible for those developed by the high-temperature evacuation. It is reasonable that the protonic acid sites are effectively blocked by sodium ions through the ion exchange, which is supported by the fact that the sodium ions remained after washing with water are readily removed by washing with ammonium nitrate solution. The nonprotonic acid sites are expected to be less sensitive to the poisoning by sodium ions, because the potential acid sites are shielded by hydroxyls and water molecules exhibiting no ion exchange property.

Role of Protonic Acid in Ethylene Dimerization

The foregoing results demonstrate that a protonic acid site plays a certain role in the ethylene dimerization on the montmorillonite-type catalyst activated at 100°C. If the proton is chemically involved in the reaction path, the ethylene dimerization on a deuterated catalyst should result in the formation of deuterobutene. In fact these sort of experiments were previously performed, and the formation of deuterobutene was confirmed. However it was found that 2-butene was much more deuterated than 1-butene, in conformity with the idea that the deuterium was incorporated into butene during isomerization from 1-butene to 2-butene (*7*). Thus no information about the role of protonic acid site could be obtained for the dimerization at that time.

In view of the clearer correlations between the dimerization activity and the protonic acidity as disclosed in the foregoing, it is worthwhile to repeat the tracer study on the montmorillonite-type catalyst, characterized by the protonic acidity. Particular precautions were taken in the present study to obtain the very initial product of the ethylene dimerization as mentioned earlier. Since the number of active sites could be very small, the extent of dimerization was controlled to give the initial product. As the catalyst, B-10 was chosen because it gave a high dimerization activity when evacuated at 100°C. The catalyst B-10 was first evacuated at 500°C to remove H_2O and treated with D_2O at room temperature for 12 hr followed by evacuation at 100°C. The runs were carried out at 20°C in a circulating system equipped with a cold trap (−160°C).

The results are summarized in Table 2. An appreciable part of the initial product, 1-butene, is found to be deuterated, demonstrating that the deuterium atoms held by the catalyst are transferred to the dimerization product. There are three possibilities of deuterium incorporation into 1-butene: (1) Incorporation in the reaction path of dimerization. (2) Exchange reaction of

TABLE 2

Ethylene Dimerization with Deuterated Catalyst B-10 at 20°C

Run	Wt. of catalyst (g)	Reaction time (min)	Reactant μmol (Torr)	Product					
				1-butene percentage in *n*-butene	1-butene obtained (μmol)	deutero-1-butene (%)		deutero-2-butene (%)	
						d_1	d_2	d_1	d_2
1	1	5	30 (4.5)	92	0.56	9.6	5.4	48	15
2	1.2	40	10 (1.5)	~100	0.03	38.8	—	—	—
3	1.2	10	15 (2.3)	~100	0.06	14.7	—	—	—

1-butene subsequent to the dimerization. (3) Exchange reaction of ethylene prior to the dimerization. The second possibility is ruled out because of the high selectivity of dimerization to 1-butene which demonstrates little chance of the secondary reaction. If the 1-butene molecule could have a chance to interact with the proton held by the catalyst, it would be very likely converted to 2-butene. Indeed the 2-butene obtained in Run 1 involved as high as 48% d_1 and 15% d_2, demonstrating that 1-butene was isomerized to 2-butene via a protonated intermediate, in agreement with the previous study (5). The 2-butene-d_2 may be ascribed to the secondary isomerization of 1-butene-d_1 formed by the dimerization. Similarly, the 1-butene-d_2 found in Run 1 would be due to reverse isomerization of 2-butene-d_1, as supported by the absence of 1-butene-d_2 in the absence of 2-butene although the content of 1-butene-d_1 was larger as found in Runs 2 and 3.

The third possibility would also be improbable because no C_2H_3D was detected in unreacted ethylene in the three runs shown in Table 2, although the same catalyst was confirmed to be active for the isotopic mixing of a C_2H_4–C_2D_4 mixture. Thus the 1-butene-d_1 must be formed in the reaction path of dimerization. It is likely that a cationic ethyl intermediate is involved in the reaction path on the montmorillonite-type catalyst.

If the active site has a proton as the necessary ingredient, the number of active sites for the dimerization would be obtained from the number of deuterobutene molecules formed. However the material balance indicated that 1.5 ± 0.5 μmol/g of butene was retained by the catalyst under the reaction condition. It is likely that the 1-butene-d_1 concentration in the adsorbed phase is much higher than that in the desorbed butene, because the adsorbed butene should represent the initial product. In fact 1-butene-d_1 content shown in Table 1 increases with decrease in the amount of butene formed. Thus if 100% d_1 is assumed for the adsorbed butene as a rough estimate, the number of active sites would be 1.5 ± 0.5 μmol/g or 2.0 ± 10^{11} sites/cm^2, which is a rather small value partly because of the high surface area, 470 m^2/g, caused by the presence of excess silica. The dimerization activity of catalyst B-10 evacuated at 100°C is 400 μmol/g/min. Thus the turnover number of dimerization is estimated to be 4 C_2H_4/sec site at 20°C and 230 Torr of ethylene.

Since a close correlation is found between the dimerization activity and the acidity, it is of interest to make a comparison between the site densities. Thus the acidity of the catalyst B-10 evacuated at 100°C was determined by butylamine titration using dicinnamalacetone as indicator to be 73 μequiv/g. This is about 50 times as large as the site density for the dimerization evaluated above, while it is of the same order of magnitude as the site density for the sodium ion exchange given in Table 1. It is likely that the number of protonic sites is much more than given by the site density for the dimerization.

Indeed, the isomerization of 1-butene subsequent to the dimerization brought about a further extensive incorporation of deuterium into the product 2-butene as disclosed by Run 1. In order to estimate the number of protonic sites active for the butene isomerization, 1-butene was isomerized on the deuterated catalyst B-10 at 20°C for 5 min. Both the reactant and the products were transferred from the catalyst to a liquid nitrogen trap by raising the catalyst temperature gradually up to 80°C. The recovery of butenes was almost 100%, demonstrating little oligomerization of butene. The results are represented in Table 3. The isomerization products are deuterated much more extensively than 1-butene in agreement with the previous paper (5). From this result the number of active protonic acid sites is estimated to be 13.6 μmol/g, about one order of magnitude larger than the number for the dimerization. Thus it appears that the active site for the

TABLE 3

1-Butene Isomerization with Deuterated Catalyst B-10 at 20°C

Catalyst wt. (g)	Reaction time (min)	1-Butene used (μmol)	Butene composition			Amount of butene (μmol)	D distribution					F_D
			1-,	*trans*-,	*cis*-,		d_0	d_1	d_2	d_3	d_4	
0.5	5	34	49			16.6	96.6	3.4	0	0	0	0.03
				29		9.9	79.3	18.4	2.3	0	0	0.21
					22	7.5	63.5	32.3	4.2	tr.	tr.	0.37

dimerization is different from that for the isomerization, with the latter being more abundant, although they are both cationic in nature.

Relevance to Homogeneous Catalysis

The above results may be briefly summarized in the following: A protonic acid is involved in the montmorillonite-type active site for the ethylene dimerization, while the antigorite-type site seems to involve a nonprotonic acid. Analogous catalyst systems are found with σ-aryl nickel compounds activated by trifluoroboron etherate (*11*), with which the turnover number of the dimerization is estimated to be 0.03/sec at 0°C (*11d*), assuming that all the nickel compound molecules are active. Since the nickel compound seems to be activated on removal of phosphine ligand by the acid component, not all of the nickel compound molecules may be active. Hence the turnover number can be higher than the above value with respect to the real active species, being closer to that found in the present study.

It is noteworthy, moreover, that the dimerization activity of the σ-aryl nickel–trifluoroboron etherate catalyst is enhanced by adding a small amount of water ($H_2O/Ni \simeq 0.4$) (*11g*), suggesting that a protonic acid participates in the dimerization as is the case with the nickel montmorillonite catalyst. Thus a striking resemblance exists between the nickel complex catalyst and the nickel oxide–silica catalyst in their properties. It is of interest that an oligomerization catalyst is obtained by reacting $CH_3Ni(C_3H_5)PR_3$ with the OH group on silica to give an immobilized complex (*12*) which involves a Ni–O–Si bond as does the nickel silicate. These facts seem to suggest that the mechanism of dimerization is essentially the same in both catalyst systems.

The mechanism of homogeneous catalytic dimerization of ethylene with nickel compounds has been understood in terms of a nickel–hydride intermediate (*11h*), although the source of hydride has not been identified (*11b*). The present result of the incorporation of catalyst deuterium into the product, 1-butene, suggests a cationic ethyl intermediate for the ethylene dimerization on the nickel–montmorillonite.

CONCLUSION

It is demonstrated in the present study that the catalytic activity of nickel silicates in the ethylene dimerization as well as in the butene isomerization is closely correlated with the surface acidity of the catalyst, while montmorillonite and antigorite are different from each other in nature of acidity, protonic and nonprotonic, respectively, as evidenced by the following results:

(1) Water is a poison for the nickel antigorite, while an appropriate amount of water is required for the nickel montmorillonite to give the catalytic activity.

(2) The protonic acid site is detected on the nickel montmorillonite, while undetected on the nickel antigorite, by ir absorption of adsorbed pyridine.

(3) Effect of sodium contamination on the catalytic activities is more pronounced with the nickel montmorillonite.

(4) Participation of the protonic acid site in the ethylene dimerization is demonstrated by the formation of 1-butene-d_1 on deuterated montmorillonite catalyst.

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