November, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3329—3333 (1972) 3329

The Isomerization of *n*-Butenes over Acidic Ion-exchange Resin

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(Received March 13, 1972)

The isomerization of *n*-butenes and the polymerization of propylene were studied in a gas-phase reaction on a sulfonic acid-type resin catalyst. These reactions were considered to proceed *via* the carbonium ion formation on the functional groups, and a strong correlation was found between the activities in these two reactions. The acidity and the acid strength of the resin catalyst were measured by means of amine titration in a nonpolar solvent using Hammett indicators. The value of the acidity obtained at $pK_a = 6.8$ seemed to correspond to the number of the ion-exchangeable hydrogen on the functional groups. The effects of poisoning by ion exchange with Na^+, Mg^{2+} or by adsorption of NH_3 were also studied. The decrease in the activity for the isomerization was not proportional to the amount of cations exchanged. The catalytic activities of the protonic hydrogen seemed not to be equal as was suggested by the result of resin catalysts in polar solvents. The possible heterogeneity of the active sites on the resin catalyst was discussed. The six relative rate constants were calculated on the basis of the mutual interconversion among the three isomers of *n*-butene. The apparent energy of activation for the double-bond migration of 1-butene was found to be 17 kcal/mol on the H-form resin, but it was changed by ion exchange with Na^+. The selectivities were characteristic of solid acid catalysts of the protonic type.

Many types of acidic oxide catalysts have been studied in hydrocarbon reactions. However, these catalysts have been found to show a very complicated behavior, reflecting their coexisting various acidic properties of the active sites. The catalyses have been accounted for by the surface-acid sites, which are usually classified into two typical acid types: protonic (Brönsted) acid and non-protonic (Lewis) acid site.[1-3] In some cases, they were extended to oxidative sites to form a cation radical complex on the surface.[4-6] Furthermore, these acid sites have a widespread distribution in terms of acid strength and activity.[7] Thus, a typical solid acid with a single type of acid and homogeneous activity has been expected to be studied.

Attempts have been made to use acidic ion-exchange resins of a conventional gel-type structure in solution[8-10] or in the vapor phase of polar reactants.[11,12] These catalyses have been considered to be similar to those by homogeneous acid catalysts, such as hydrochloric acid or sulfuric acid.[13] An acidic resin of the macroreticular-type was used in the gas-phase reaction.[14] Manassen and his co-worker prepared a sulfonated and a phosphonated polyphenyl resin catalyst which were stable up to 350°C, and observed no special surface effects over them.[15] In the dehydration of alcohol on an acidic resin catalyst, the homogeneous catalytic activities of the functional groups have been reported,[16] while the heterogeneity of the active sites has also been suggested by the different results regarding the poisoning effect by Na^+ and Li^+.[17]

In the present investigation, the catalytic behavior of a sulfonated styrene–divinylbenzene copolymer was studied in terms of olefin reactions, which can give more information about resin catalysts in a gas-phase reaction. The heterogeneity of the resin catalyst will be discussed also.

Experimental

Materials. The sulfonated styrene–divinylbenzene copolymer with a macroreticular structure was prepared from commercial ion-exchange resin Amberlyst-15. The resin was washed with methanol and then with decationized water to remove any extraneous materials. It was converted to the Na-form by treating it with a 1N NaOH solution according to the conventional column method, and was again reversed to H-form (AMH standard) with a 1N HCl solution. After washing with decationized water, it was treated with methanol and dried under reduced pressure. The Na-poisoned catalysts (AMHNa series) were prepared by soaking AMH in a NaOH solution containing the desired quantity of Na^+ ions for 2 weeks at room temperature. They were then washed and dried in a manner similar to that for AMH. The purity of the reactant gases was above 99.8%. They were repeatedly distilled at −196°C prior to use.

Procedures. The ion-exchange capacity of AMH was determined by titration with a NaOH solution. The surface area was measured by the BET method of N_2 adsorption. The isomerization and the polymerization reaction were carried out in a closed circulating system. The catalysts were evacuated first at room temperature and then at 110°C

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for 2 hr. The products were analyzed by means of a gas chromatography, using a propylene carbonate–alumina column at 0°C. The isomerization reaction of 1-butene was also studied in a flow-type reactor, using N_2 as the carrier gas. The catalysts were pretreated in a N_2 stream at 110°C for 2 hr.

Results

Ion-exchange Capacity and BET Surface Area. The titration curve obtained with the powdered AMH is shown in Fig. 1. This result shows behavior characteristic of a strong electrolyte and quite resembles that of the sulfonated polyphenyl resin.[15] The total amount of NaOH added up to the neutral point of pH 7.0 was 3.79 meq/g of dry resin, while 4.03 meq/g was needed up to pH 11.0, above which no more pH change was detected upon the further addition of NaOH. The latter value was in good agreement with the ion-exchange capacity for the evacuated AMH (4.02 meq/g), but was slightly smaller than that of the standard AMH (4.32 meq/g).

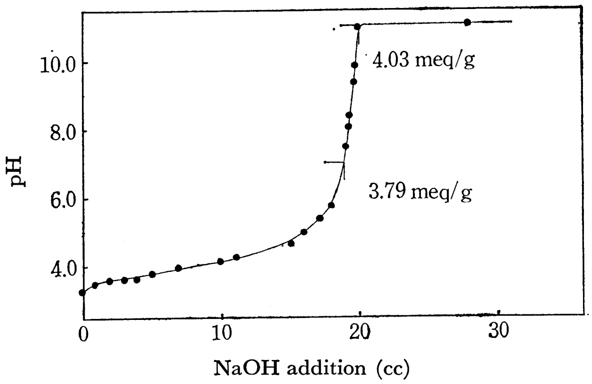

Fig. 1. Titration curve for AMH with 0.1N NaOH solution.

The BET surface areas obtained with the resin catalysts evacuated at 110°C for 2 hr were: 86 m^2/g (AMH), 57 m^2/g (AMHNa05), 74 m^2/g (AMHNa10), 67 m^2/g (AMHNa20), 54 m^2/g (AMHNa40), and 65 m^2/g (AMNa). These results appear not to show any systematic tendency in the effect of cation-exchange on the surface area. The decrease in the surface area of AMH was very small, even after evacuation at temperatures below 140°C. This suggests that the change in the substrate by the ion exchange or the pretreatment of evacuation at 110°C were negligible.

DTA and TGA Observations. The sulfonated styrene–divinylbenzene copolymer catalyst is expected to contain some water in the macro-pores or the channels in the resin matrix. A part of them may be in a hydrated sate to the functional groups. It was found from the DTA and TGA observations that the water of this kind can easily be removed by heating under atmospheric pressure. The total weight losses up to 150°C, above which the DTA and TGA curves showed no more changes, were 34.2 wt-% (AMH) and 22.0 wt-% (AMNa). These results correspond to losses of 4.7 $H_2O/\text{-}SO_3H$ and 2.9 $H_2O/\text{-}SO_3Na$ respectively, in good agreement with the hydration numbers of the polystyrene sulfonic acid-type resin reported in the literature: 3.9 (to H^+)+0.9 (to $\text{-}SO_3^-$) and 1.5 (to Na^+)+0.9 (to $\text{-}SO_3^-$).[18] When AMH and AMNa were evacuated at 110°C for 2 hr, the water content decreased remarkably, and the further weight loss by heating up to 140°C was less than 3—5%, and above that temperature desulfonation took place.

Polymerization of Propylene. The polymerization of ethylene was not promoted by AMH, but propylene and *n*-butene were catalyzed under the present experimental conditions below 100°C. The time course of the total pressure decrease could not be explained by Tamele's equation,[19] which is very often applied to the polymerization reaction of propylene over solid acid catalysts. A Langmuir-type rate expression (1) was found to be appicable, as is shown in Fig. 2;

$$r = -\,\mathrm{d}P/\mathrm{d}t = kP/1 + KP \qquad (1)$$

P: total pressure, t: time, k: rate constant, K: constant of the equilibrium factor, r: rate of the reaction.

The apparent energy of activation for the polymerization on AMH was found to be 10 kcal/mol in the range of temperatures higher than 84°C and 3.5 kcal/mol in the lower range.

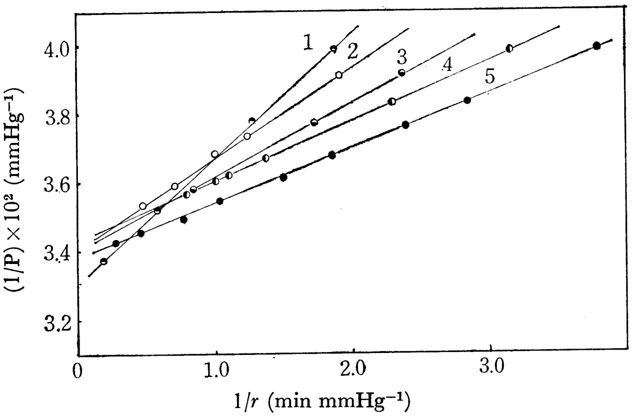

Fig. 2. Langmuir type plot for propylene polymerization over AMH.
1: 100°C 2: 92°C 3: 84°C 4: 72°C 5: 66°C

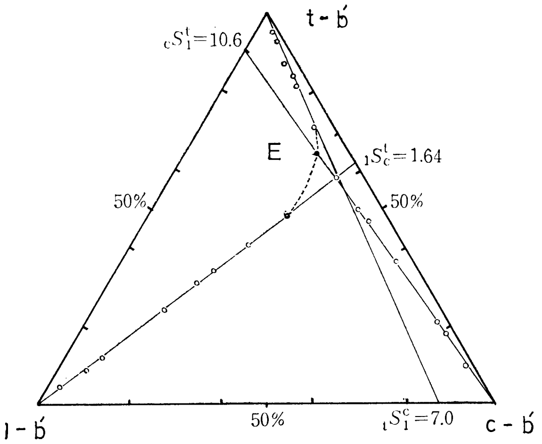

Fig. 3. Ternary system for the *n*-butene isomerization over AMH. Reaction temperature: 70°C. E: equilibrium composition. ${}_{1}S^{t}_{c}$: the initial selectivity obtained by extrapolation on the reaction curve from 1-butene.

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Isomerization of n-*Butenes*. Under the reaction conditions used for the isomerization of *n*-butenes, the polymerization reaction detected was negligible. Starting from any isomers of *n*-butene, only products from the double-bond migration and the *cis-trans* isomerization were observed. Thus, the reaction system can be approximately expressed by a three-component kinetic system of the Pines type.[20] The change in the relative compositions of the gas-phase products is illustrated by the ternary system as shown in Fig. 3. Starting from each isomer of *n*-butenes, the same equilibrium composition, the point E, was approached after prolonged reaction times, and the curve are nearly linear up to much higher conversions. These facts suggest that the selectivity of the catalyst did not change during the reaction, at least not during the early stage of the conversion. Selectivities expressed by the initial product ratios; ${}_{c}S_{1}^{t}$, ${}_{1}S_{c}^{t}$, ${}_{t}S_{1}^{c}$, were obtained from the tangents of the curves at zero conversion. There were several characteristic features of the behavior, especially in the stereo-selectivities; the double-bond migration of 1-butene showed a strong kinetic preference for the formation of *trans*-2-butene, though the relative ratio of the products, *trans*-2-butene/*cis*-2-butene, was less than that of the thermodynamic equiliblium. In the isomerization of *cis*-2-butene, the relative amounts of the products, *trans*-2-/1-butene, were nearly that of the equilibrium from the very low conversion, while the products from *trans*-2-butene favored the formation of *cis*-2-butene than that of 1-butene.

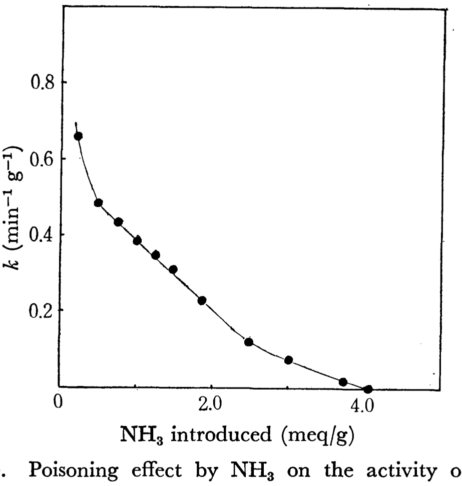

Fig. 4. Poisoning effect by NH_3 on the activity of AMH in flow system. AMH 100 mg. Carrier gas N_2 17.8 cc/min. 1-butene 1.08 cc/min. Temperature 70°C. NH_3 was introduced simultaneously into the carrier gas.

Assuming a mutual interconversion among the three *n*-butenes according to the first-order rate law, the six relative values of the rate constants were calculated from the initial selectivities and the equiliblium constants. They are listed in Table 2, together with the reported values for solid acid catalysts.

Ammonia Titration during the Reaction in the Flow System. The change in the activity by the poisoning of the adsorbed NH_3 was also observed, as is shown in Fig. 4. It can be noticed that, in the poisoning curve, the decrease in the activity was not so abrupt, but was rather proportional to the amount of NH_3 added. The total amount of the NH_3 required to poison the activity completely was 4.03 meq/g. This coincided with the effective ion-exchange capacity measured by Na^+ (4.02 meq/g). The double-bond migration of 1-butene was investigated on a series of partially ion-exchanged resin catalyst, AMHNa or AMHMg. The kinetic parameters are listed in Table 1. This behavior is quite different from that of the simultaneous poisoning by NH_3 adsorption. The selectivity, ${}_{1}S_{c}^{t}$, expressed by the initial ratio of the products, *trans*-2-/*cis*-2-, had a slight tendency to decrease upon cation exchange by Na^+ or Mg^{2+}.

TABLE 1. KINETIC PARAMETERS FOR 1-BUTENE ISOMERIZATION OVER AMHNa SERIES CATALYSTS

Catalyst	$k_1 \times 10^3$ (min^{-1} g^{-1})	${}_{1}S_{c}^{t}$	E (kcal/mol)	log A
AMH	45.6	1.35	17.0	9.8
AMHNa05	26.7	1.19	17.0	9.6
AMHNa10	14.3	1.17	16.0	8.5
AMHNa20	5.5	1.11	14.5	6.9
AMHNa40	1.5	—	—	—
AMNa	0.0	—	—	—

k_1: the first order rate constant for 1-butene double-bond migration at 60°C.
${}_{1}S_{c}^{t}$: selectivity expressed by the initial ratio of the products of the reaction, *trans*-2-butene/*cis*-2-butene.
E: apparent energy of activation.
A: pre-exponential factor.
AMHNa05: partially ion-exchanged catalyst. Added figures mean atom-% of H substituted by Na.

TABLE 2. RELATIVE VALUE OF RATE CONSTANT FOR MUTUAL INTERCONVERSION OF THE THREE *n*-BUTENES OVER THE TYPICAL SOLID-ACID

Catayst	Temp. °C	k_{1c}	k_{c1}	k_{ct}	k_{tc}	k_{1t}	k_{t1}
AMH	70	1.0	0.23	2.48	1.16	1.64	0.17
Silica-alumina[a)]	50	1.0	0.21	0.29	0.09	0.91	0.05
Alumina[a)]	50	1.0	0.21	0.91	0.25	0.45	0.03

k_{ij}: the first order rate constant for the reaction, i to j.
a) the deta are taken from Ref. 31.

Discussion

The catalytic activities of the sulfonated resin catalysts can presumably be attributed to the acidic properties of the hydrogens of the sulfonic acid groups. This was easily established by the fact that neither the substrate resin with no functional groups nor the Na-form resin showed any catalytic activities. This was consistent with the observations over the surface of *para*-toluenesulfonic acid and other various substituted benzenesulfonic acid.[21] It has been reported that deuterium adoption was observed in the course of isomerization of *n*-butenes over deuterated sulfonic

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acid resin catalysts[22] and deuterated *para*-toluenesulfonic acid crystals.[23] Thus, from this point of view, the catalysis over the acidic ion-exchange resin can be considered to be that of a typical type of solid acid catalyst with a protonic character.

The titration curve in Fig. 1 shows that the hydrogens of -SO_3H or AMH were dissociated to some extent to give pH 3.4—3.5 in decationized water. At the neutral point, pH 7.0, some of the exchangeable hydrogens survived. Manassen found that the number of exchangeable acidic groups calculated by the titration method was smaller than that obtained from the chemical analysis.[15] However, these two values do not necessarily correspond to the effective sulfonic acid groups in the working state of the gas-phase catalysis. The coincidence of the number of adsorbed NH_3 with that of the exchangeable hydrogens suggests that almost all the ion-exchangeable hydrogens are effectively active in the isomerization of *n*-butenes, even in the gas phase. The amount of NH_3, 4.03 meq/g, which was required for poisoning the activity correspond to the population of $H^+/3.1\ A^2$. This means that the sulfonic groups become close enough for them to interact with each other or with adsorbed species. If there were some hydrated water, the probability of the interaction would increase.

The acid strength of *para*-toluenesulfonic acid and benzenesulfonic acid in an aqueous solution is said to be $pK_a=0.6$.[24] However, the acid strength of the sulfonic acid resin has not been obtained directly. Using Hammett indicators, the acid strength of AMH was observed as strong as $pK_a=-3.0$—-5.6 at the minimum. The acidities measured by means of *n*-butylamine titration in cyclohexane proved to be 3.9 meq/g ($pK_a=6.8$), 2.6 meq/g ($pK_a=1.5$), and 1.0 meq/g ($pK_a=-3.0$). It should be noticed that the value of 3.9 meq/g, which include rather weak acid sites agrees with the total number of ion-exchangeable hydrogen, and that there is an apparent heterogeneity in acid strength among the functional groups on the resin catalyst. In contrast to the phosphonated polyphenyl-type resin,[15] the titration curve for AMH showed no step-by-step ion exchange in a NaOH solution. When the conventional resin catalyst was used in a polar solvent, the heterogeneity of the activity of the functional groups has been considered to have negligibly small effect on the nature of the acid catalysts.[17] In polar solvents, the hydrogens of the sulfonic acid groups on the resin would dissociate into protons and they would be loosely bonded to the counter ion, -SO_3^-, much as in a highly concentrated polyelectrolyte solution.[25,26] In the evacuated state, the protonic hydrogens are probably bonded more tightly to the counter groups and thus their activities are more affected by the properties of the substrate. An inhomogeneous structure of the substrate resin is known to be produced in the processes of the polymerization, the crosslinking, and the sulfonation.[25]

On the other hand, the possibility of an induced heterogeneity can not be neglected. Considering the population of the functional groups, which corresponds to one sulfonic group for each phenyl groups, the following interactions can be anticipated: 1) between adjacent sulfonic groups,[25] 2) between adsorbed species and neighboring sulfornic acid groups,[27,28] and 3) between adsorbed species and substrate resin. If these interactions can not be neglected, the catalysis and the poisoning effect will be complicated in a detailed mechanism. The differences between the behavior of the gradual poisoning caused by NH_3 adsorption in the flow system and that caused by Na^+ ion exchange are difficult to explain. However, in the former case, NH_3 molecules may be randomly adsorbed onto the active sites and the front of the poisoned area in the catalyst bed may advance linearly with the addition of NH_3, while in the latter case, the ion exchange proceeds in the static system, where the equilibrium is accomplished progressively from the stronger sites to the weaker sites, so that the activity decreases remarkably on the addition of only a small amount of NaOH. In this case, both the intrinsic and the induced heterogeneities may be responsible for the curvature in the poisoning curve.

The effectiveness of the poisoning per ion by Na^+ and Mg^{2+} are nearly equal irrespective of the different compositions. This fact indicates that the divalent cation, Mg^{2+}, may block only one counter ion, like the monovalent cation Na^+, and that the surface complexes, such as –SO_3MgCl and/or –$SO_3Mg(OH)$, may probably exist on the resin.

A compensation effect seemed to exist between the

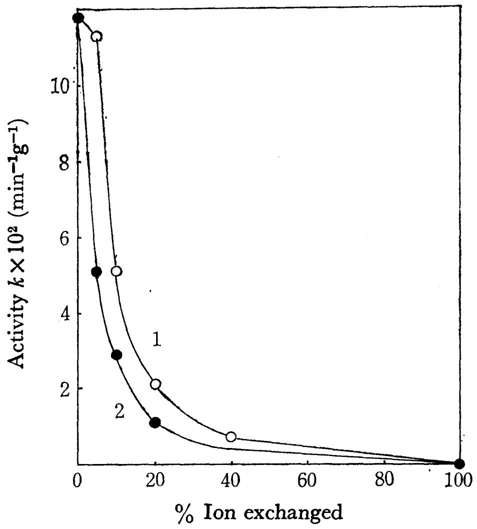

Fig. 5. Effect of partial ion exchange with Na^+ or Mg^{2+} on the activity for 1-butene isomerization. Temperature 70°C. Catalyst 100 mg. Initial pressure 300 mmHg. 1: AMHNa series 2: AMHMg series.

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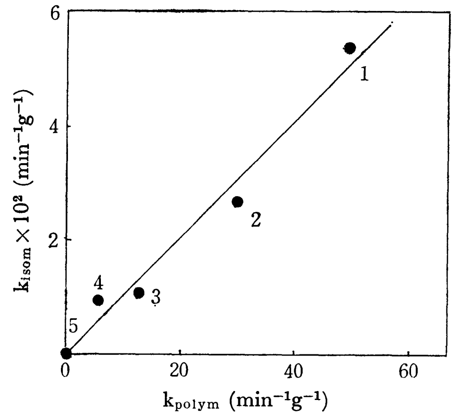

Fig. 6. Correlation of activities between the polymerization of propylene and the isomerization of 1-butene over AMHNa. Temperature 60°C. 1: AMH 2: AMHNa05 3: AMHNa10 4: AMHNa20 5: AMNa.

pre-exponential factors and the apparent energies of activation for the double-bond migration of 1-butene over AMHNa-series catalysts. A similar relation was reported in the decomposition of alcohol over the Dowex-50-Na and -Li series.[17] These facts suggest that the ion exchange provokes the effects on both the enthalpy and the entropy terms of the activated system. The observed change in the selectivities is due to the same causes. The apparent energy of activation for 1-butene isomerization on AMH, 17 kcal/mol, is a little different from the reported value for the 1-butene adsorption forming the carbonium ion on the resin surface, 13.8 kcal/mol.[29]

The relative values of the first-order rate constants based on the phenomenological ternary system are notably different from the results on the other solid acid catalysts, such as alumina, silica-alumina, and zeolites. The rate constants for *cis-trans* isomerization, k_{ct} and k_{tc}, are relatively large, and the selectivity from 1-butene, k_{1t}/k_{1c}, is more than unity. These findings are different from those for alumina or silica-alumina, as is shown in Table 2. It was found in the previous study that there was an inclination for Lewis-type acid sites to have smaller selectivities for the *trans*-2-butene formation than protonic acid sites on the several solid acid catalysts.[30] The relative values listed are consistent with this view.

The selectivity change during the strong fouling or as a result of poisoning was very samll. The isomerization of *n*-butenes over AMH can probably be explained by the mechanism *via* a common intermediate of the *sec*-butyl carbonium ion, as has already been proposed for similar acid catalysts.[20,31,32] The parallelism found between the catalytic activity for the polymerization of propylene and the double-bond migration can be said to support this idea.

The author wishes to express his thanks to Professor Emeritus Dr. Tadao Shiba for his valuable advice throughout the study.

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