

The Isomerization of 1-Butene Over Cation-Exchanged Acidic Resin

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The isomerization of 1-butene over variously cation-exchanged acidic resin catalysts was studied in an attempt to elucidate the catalytic properties of the salt-type resin catalysts. The polyvalent cation-exchanged resins, hydrogen-metal form and sodium-metal form, were prepared by soaking a macroporous sulfonated resin in the solutions of the metal nitrate.

The ion-exchange curves for some polyvalent cations showed characteristic behavior which indicate that excess cations are contained on the resin.

The remarkable activities for the reaction were found over sodium-metal form resins which can be considered to have no $-\text{SO}_3\text{H}$ groups and the order of the activities and the stereoselectivities seemed to be strongly correlated with the electron negativities of the metal cations on the resin, i.e., the Lewis acidities of them.

It was therefore suggested that the metal cation on the resin can play a significant role in the catalysis by forming a sort of olefin-metal ion complex on the resin catalyst.

INTRODUCTION

Organic polymers of acidic ion exchange resin have recently been studied as a model of solid acid catalysts (1-6). The catalytic natures of these resins are presumably ascribed to the protonic character of their hydrogen on the functional groups, such as the sulfonic acid (3, 4, 6, 7, 10) or the phosphoric acid groups (4). Thus, over these resin catalysts, ion exchange of the protons with various alkali metal or alkaline earth metal cations proved to reduce the catalytic activities for the decomposition of the alcohols (7, 8), or formic acid (9), the isomerization of the butenes (10), and the polymerization of propylene (10). However, during the course of our studies on the poisoning effects of polyvalent cations, it was found that the cation-exchanged resin catalysts show the characteristic behavior according to the cation on the resin (11). It will pro-

vide valuable information to compare the catalytic behavior of the resin catalyst with those of many other solid acid catalysts, e.g., hydrogen-, or cation-exchanged zeolites (12-14) and cation-exchanged silica (15).

In the present investigation, the behavior in the activities and the selectivities for the isomerization of 1-butene are discussed in terms of the acidic properties due to the metal cation exchanged.

EXPERIMENTAL METHODS

Catalyst Preparation

Beads of a macroreticular sulfonic acid resin, derived from styrene-divinylbenzene copolymer, were commercially available, Amberlyst 15. Samples taken from a single lot of the resin were used as the starting material for the various salt-type resin catalysts. All treatments for the catalyst

preparation and for the analysis were similarly described in the previous work (10). They were treated with methanol and with a HCl solution and then washed repeatedly with deionized water followed by washing with methanol. The H-form resin catalyst thus obtained, was dried under a reduced pressure, and finally heated at 110°C over night and stored in a desiccator. A portion of H-form resin was converted to Na-form by ion exchange with Na⁺ in a NaOH solution. The partially cation-exchanged resin catalysts, hydrogen-metal form and sodium-metal form were obtained, respectively, by soaking the H-form and the Na-form resin in the aqueous solution of each metal nitrate, which contained the appropriate quantity of the metal ion. They were washed and dried in a similar manner as H-form resin. The ion-exchange capacity of H-form resin measured by the usual column method with Na ion was 4.11 mEq/g of the dry resin (10). The concentration of the cations on the resins were determined by EDTA analysis of the original solutions and the residual solutions after washing.

Reaction

The isomerization of 1-butene was carried out in a conventional circulating reactor of a closed type. The products in the gas phase were analyzed by means of a gas chromatograph equipped with a propylene carbonate-alumina column. Every catalyst, 20–1000 mg for each run, has evacuated at 120°C for 2 hr, prior to use. The initial pressure of 1-butene was about 400 mm Hg.

RESULTS

Ion Exchange of Na⁺ with Fe³⁺

During our study of the ion-exchange properties of the acidic resin, it was found that the polyvalent cations, like La³⁺, Fe³⁺ and Th⁴⁺, can be taken up by either H-form or Na-form resin to higher extents than the expected values from their ion-exchange capacities (11). This fact is exemplified in Fig. 1. It is obvious that

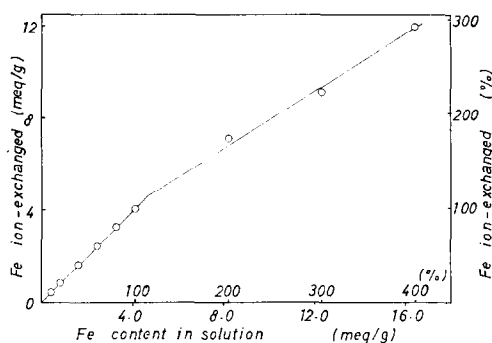


FIG. 1. Ion-exchange curve for H-form resin the hydrogen of which was ion-exchanged with Fe³⁺ in a solution of Fe(NO₃)₃. Percentage of ion exchange was expressed by H-form resin base (4.11 mEq/g of dry resin).

the equivalent amount of Na⁺ on Na-form resin could be almost completely substituted for Fe³⁺ from the dilute solution, up to the equivalent concentration to the ion-exchange capacity. Moreover, when an excess of the polyvalent cation was added into the initial solution, the further uptakes could occur proportionally to the excess amount of the cation in the solution.

The Isomerization of 1-Butene Over H-Fe-Form and Na-Fe-Form Series Catalysts

The rate of the isomerization reaction of 1-butene could apparently be expressed by the first order rate equation as to the reac-

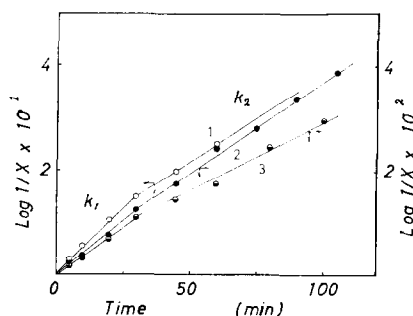


FIG. 2. Plots of the first order rate expression. Catalyst: Na-Fe form resin (Fe content, 98.4%). Catalyst size and the reaction temperature: (1) 1000 mg, 70°C, (2) 204 mg, 60°C, (3) 410 mg, 40°C. X: conversion of the reactant 1-butene, t: reaction time (min).

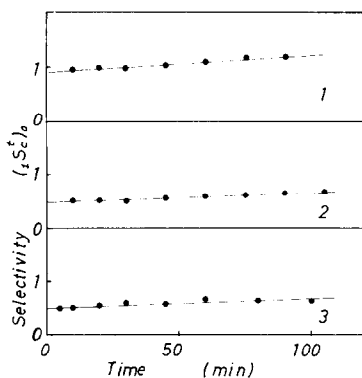


FIG. 3. Selectivity curve for Na-Fe form resin. The reaction temperature (1) 70°C, (2) 60°C, (3) 40°C.

tant of 1-butene. However, as shown in Fig. 2, the plot of $1/X$ vs t , consists of two straight lines of the first order rate processes. From this type of plots the two rate constants, k_1 and k_2 , were obtained corresponding to the initial stage and the later stage of the reaction. When the reaction temperatures were relatively low or the poisoned catalyst was used, the plot provided a simple linear line in several cases. On the other hand, the stereoselectivity represented by the ratio of the two products, *trans*-2-butene/*cis*-2-butene, was monotonously increased as the reaction proceeded irrespectively of the characteristic change of the rate constants. Some examples for the selectivity change are given in Fig. 3. The initial values of the selectivity which were obtained by the extrapolation of the plot for the second stage† to the zero-conversion, $(S_c^t)_0$, were rather small and they indicate to have the strong preference for *cis*-2-butene formation. These tendencies were quite different from the results on the typical protonic acid catalyst, such as H-form resin of the same type structure (10, 11). In Fig. 4, the dependence of the catalytic activities on the concentrations of Fe ion was shown with the result for H-Na form resins.

† The selectivity values obtained by the extrapolation for the first stage usually gave similar values.

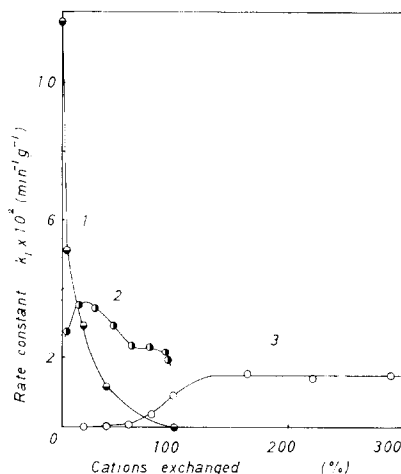


FIG. 4. Effect of the cation exchange with Fe^{2+} or Na^+ on the catalytic activity. (1) H-Na forms [reaction at 70°C cited from Ref. (10)]; (2) H-Fe forms (at 70°C); (3) Na-Fe forms (at 60°C).

The Isomerization of 1-Butene Over Na-M Form Catalysts

The results for the variously cation-exchanged acidic resin catalysts are listed in terms of the catalytic activities and the selectivities in Table 1. It is evident that the higher-valent cation-exchanged resins enhanced the more activities for the reaction, though no activity was detected for monovalent cation-exchanged resin. Moreover, the observed selectivities seemed to be strongly dependent on the valence or the acidity of the cation. In other words, the higher-valent cation-exchanged resin catalysts have relatively lower selectivity for the double bond migration than for the *cis*-*trans* isomerization of 1-butene. It should be noticed that over several metal salt-type resin catalysts, induction period was clearly observed as shown in Fig. 5. The first order rate constants for the induction periods, k_{ind} , were also ranged similarly to the rate constant, k_1 , for the succeeding rate process.

DISCUSSION

Catalytic activities of acidic resins for various reactions have hitherto been ascribed to the hydrogen on the functional groups, since no catalytic activities were

TABLE 1
CATALYTIC PROPERTIES OF VARIOUSLY CATION-EXCHANGE ACIDIC RESIN

Catalyst form Na-M	Valence of M	Ion exchanged with M		Activity selectivity	
		mEq-% exchanged	mmol ^a /g Na-M form	$k_1 \times 10^3$ min ⁻¹ mmol ⁻¹ ^a	(iS^t) ₀
Na-Ca	2	89.7	3.69	Null	—
Na-Mn	2	77.4	3.18	Null	—
Na-Cu ^b	2	70.9	2.91	0.100	0.46
Na-Ni ^b	2	70.0	2.88	0.113	0.40
Na-Zn ^b	2	84.0	3.45	0.116	0.20
Na-Co ^b	2	46.3	1.79	0.290	—
Na-Ga	3	91.2	3.75	1.74	0.63
Na-V ^b	3	61.2	0.796	3.11	0.70
Na-Cr	3	83.5	2.56	3.58	0.70
Na-Fe	3	98.4	4.04	7.94	0.90
Na-Th	4	99.6	4.09	5.82	0.70

^a mmol of polyvalent cation M.

^b The catalyst observed induction period in the reaction.

found on the alkali metal salt-type resins with Li, Na, K, and Rb (3, 4, 7, 8, 10). However, now it is confirmed by the present results that some of the metal salt form resins can also enhance the remarkable activities in the gas phase reaction. These resin catalysts whose activities are directly depending on the properties of the metal ion on the resin matrix can be considered as a new type of polymer catalyst.

The unexpected behavior in the cation exchange as shown in Fig. 1 were also ob-

served for other polyvalent cation-exchanged resin systems, H-Fe form, H-La form, H-Th form (11). The excess of the polyvalent cation on these resins may be present in different states from the charge valenced form, $(R-SO_3)_n-M^{n+} \cdot XH_2O$, in the dilute solutions. One of the possible states that allows excess content of cations may be a partially hydroxylated complex in such a form as $(R-SO_3)_m-M^{n+}(OH)^{-n-m} \cdot XH_2O$, ($n - m \geq 1$), which seems to be more probable for the higher valent cations.

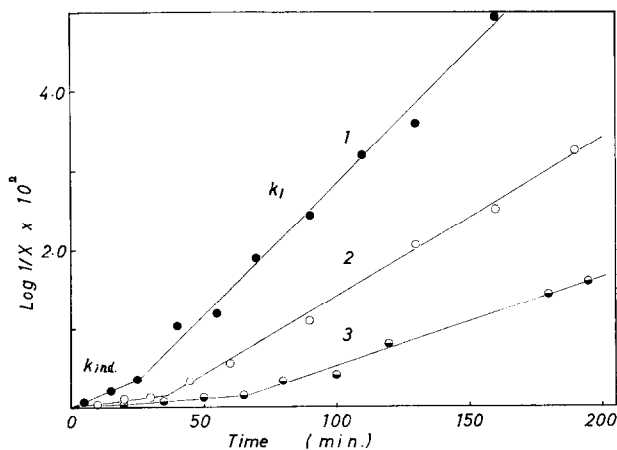


FIG. 5. Examples of the induction period observed. The rate constant for the induction period, k_{ind} , and that for the later stage, k_1 , are calculated from the each slope. Catalyst: Na-V form. The reaction temperature: (1) 80°C, (2) 70°C, (3) 60°C.

The presence of a hydroxylated complex was also suggested for H-Mg form resin in the previous work (10). These hydrated complexes may easily be converted to the more active dehydrated form by the pre-treatment of evacuation. Another possible state may be simple solute ions in the polyelectrolyte solution contained in the channels or the pores in the resin matrix. These ions may be difficult to be completely removed by simple washing. The activity changes for Na-Fe form resins, shown in Fig. 6, however, indicate that these excess cations, if present, have little contribution either to the catalytic activity or to the selectivity.

The functional groups of the resin can be considered to have homogeneous activities for ion exchange, since the ion-exchange curves usually show the proportional replacement of the cations (Fig. 1). However, the results shown in Fig. 4 suggest that the catalytic activities are not simply proportional to the numbers of the active sites on the resin which are consistent with the reported results for the decomposition of methanol and *t*-butanol over various H-alkali metal form resins (7, 8). In the case of Na-Fe form resins, the catalytic activities for the butene isomerization were found to depend exponentially on the

concentration of Fe ion, i.e., the concentration of the active sites, and the selectivities were also affected with their increase (Fig. 6). These results support the previous interpretation that the active sites of the functional groups on the resin are not catalytically equivalent and the heterogeneity is induced by the interactions between the functional groups and/or the adsorbed molecules (10).

There is another evidence for these interactions. The result in Fig. 4 shows that the appropriate ratio of H-form and Fe-form groups is most desirable for the higher activity. The behavior of this curve of the activity change may well be explained by the assumption that both of the active sites due to H and Fe on the resin are cooperating in the catalytic process in a similar manner as the concerted mechanism which was postulated for the isomerization of butenes on *p*-toluene sulfonic acid crystals (19). This is also consistent with the proposed mechanism for the decomposition of formic acid, methanol and *t*-butanol which involves the concerted actions of two, three and four $-\text{SO}_3\text{H}$ groups (7-9).

From the results shown in Table 1 and Fig. 8, it should be noticed that Na-metal form resin can enhance the remarkable catalytic activities in spite of no $-\text{SO}_3\text{H}$ groups contained. This fact may insist that

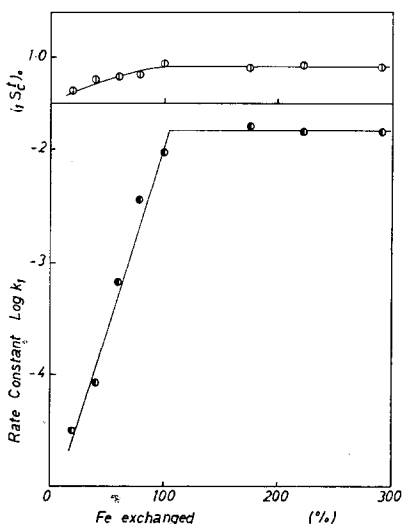


FIG. 6. Dependence of the catalytic properties on the concentration of Fe on Na-Fe form resins.

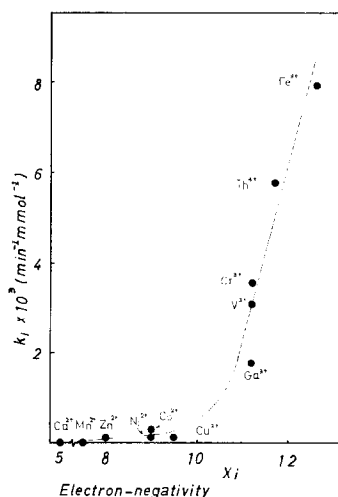


FIG. 7. Correlation of the catalytic activity and the electron negativity of the cation on the resin.

the acidic metal cations on the resin are responsible for the catalytic activities as well as the protonic hydrogens on H-form resin. In Figs. 7 and 8, the catalytic activities represented by the first order rate constant k_1 and the selectivities for the isomerization of 1-butene, $(1S_c^f)_0$, are plotted against the electron negativities of the cations, X_i (16, 17). It is obvious from these features that the order of the catalytic activities and the selectivities are strongly correlated to the electron negativities, in other words, the relative strengths of the Lewis acidity of the metal ions. Similar results have been reported for series of inorganic ion-exchangers, cation-exchanged x-zeolites (13) and metal sulfates (18). In the former case, however, the selectivity for *trans*-2-butene formation decreased with increase of the electron negativity which imply some difference in the catalytic mechanism.

There is another possible active site that should be referred to. The hydrated water molecules or the hydroxy groups coordinated to metal cations have very frequently been pointed out to act as protonic sites, e.g., cation-exchanged zeolites (13, 14), metal sulfates (18) and cation-exchanged silica (15). The numbers of the hydrated water molecules were found to correspond to 4.7 and 2.9 for each functional group on the evacuated resins of H-form and Na-form, respectively (10). The water contents of conventional gel-type resins of various transition metal form were reported to range 1.7–2.5 for a functional group on the evacuated resins. The several types of the

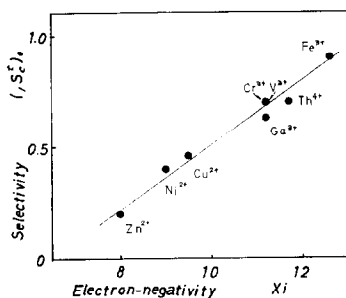


FIG. 8. Correlation of the stereoselectivity to the electron negativity of the cation on the resin.

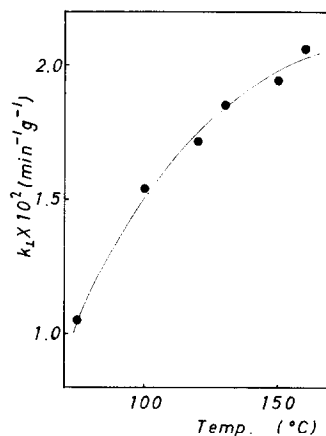


FIG. 9. Effect of the evacuation temperature on the catalytic activity. Catalyst: Na-Fe form resin (Fe content, 175.4%).

polyhydrated complexes with hydrogen bonds have been observed by ir method (21, 22). On the metal salt form resins used in the present work, similar hydrations are expected.

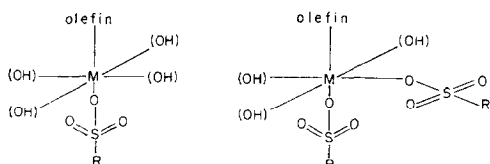
After a prolonged evacuation at high temperatures, most of the hydrated molecules were removed so that the catalytic activities appeared with temperature increased (Fig. 9). It should be noticed that the hydroxy groups coordinated to the cations might have survived the treatment employed and they were possibly acting as protonic sites. However, they are supposed to be weaker acid sites than the Lewis acid sites of the cations, and the low values of the selectivities compared with those for the typical protonic sites on H-form resin, suggest to be ascribable to the Lewis acid sites. Therefore, the protonic hydrogen of the hydroxy group may probably take a less important role as the active sites for the reaction than the Lewis acid sites of the metal cations.

A fine compensation effect was observed between the preexponential factors and the activation energies of the reaction over the various metal salt-type resins, as was reported for the hydrogen-alkali metal form resin in the butene isomerization (10) and the methanol decomposition (7).

This fact suggests that the isomerization of butenes may proceed without much al-

ternation of the catalytic mechanism via a similar intermediate complex.

The induction periods observed for several metal salt-type resins are considered to correspond to the process of the complex formation. The strong correlation of the catalytic properties to the metal ions on the resin may lead to a postulation of the complex as a directly bonded metal-olefin complex as pictured,



Similar type of olefin complex was reported for the transition metal on silica catalysts by Anderson (23, 24). It must be pointed out now that the apparent energy of activation and the selectivity for the isomerization of 1-butene were fairly well correlated to the number of the 3d electron of the cations on the resin (Uematsu, T., and Tsukada, K., unpublished data). We will discuss, in a later paper, the properties of the transition metal complex formed on the resin catalysts in terms of the electron negativity and the stabilization by the ligand field of the complex.

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