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Studies on Isomerization of *n*-Butenes and 3,3-Dimethyl-1-butene over Cobalt-Exchanged Zeolite X

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Isomerization of *cis*-2-butene, 1-butene, and 3,3-dimethyl-1-butene was studied over CoX zeolites, degassed at various temperatures. Activity of these catalysts was found to be affected by the degree of exchange of Na^+ for Co^{2+} ions. The initial rise in the Co^{2+} ion content in the zeolite lattice is accompanied by a very small increase in catalytic activity. It is only after the exchange of Na^+ for Co^{2+} has exceeded ~28% that the catalytic activity increases rapidly, in a nearly direct relation to the degree of exchange. Also, the catalytic activity of the zeolites proved to be in a clear-cut correlation with the "concentration" of tetrahedral-coordinated Co^{2+} ions in the zeolite lattice. It was postulated that, in the systems investigated, the active centers consist of the hydroxyl groups that arise by residual water molecules being split on the tetrahedral-coordinated Co^{2+} ions, $Co(OH_2)^{2+} \rightleftharpoons CoOH^+ + H^+$, and subsequently lattice oxygen atoms being immediately protonated to reconstitute new hydroxyl groups. A mechanism has been suggested involving a secondary carbonium-ion intermediate.

INTRODUCTION

In the course of our studies of the electronic spectra of cobalt zeolites (*1*), the coordination of cobalt ions was found to vary with the zeolite degassing temperature. In the zeolites degassed at 473 K, tetrahedrally coordinated cobalt ions were the most prevalent. The cobalt ions are believed to occupy positions I′, II′, and II in the structure in which they acquire tetrahedral symmetry by interacting with three lattice oxygen atoms and with the hydroxyl group. The spectrum attributable to the tetrahedral cobalt decreased in intensity as the degassing temperature was raised. This, together with the associated dehydroxylation, were thought to be explicable in terms of migration of the cobalt ions to position I within the hexagonal prisms (to acquire therein octahedral symmetry) and of formation of Co–O–Co groupings.

In the present work, we have studied effects associated with the localization of cobalt ions including the nature of the arising centers on the catalytic properties of CoX zeolites. Isomerization of *n*-butenes and 3,3-dimethyl-1-butene was chosen as the model reaction, the mechanism and kinetics of which have been extensively explored. Isomerization of 3,3-dimethyl-1-butene has been investigated over aluminosilicates (*4*) and zeolites X containing various cations (*2,3*). Isomerization of *n*-butenes has been studied over a number of acidic (*4*) and basic oxide catalysts (*10–12*) and over zeolites in both the sodium form and forms containing other cations (*13–17*). As far as the authors are aware, there are no reports on isomerization of butenes in the presence of cobalt zeolites.

EXPERIMENTAL METHODS

Materials. The starting material for preparing catalysts was a 13NaX zeolite (Inowrocław Soda Works, Matwy, Poland), silicon-to-aluminium ratio 1.27 ± 0.02, powder form free of binder. Several series of cobalt zeolites differing in Co^{2+} ion content were prepared by the ion exchange process as described in the preceding paper (*1*).

The degree of exchange, expressed as the percentage of original Na^+ ions replaced by Co^{2+} ions and designated by n in CoX (n), was determined by analyzing cobalt chloride solutions before and after the exchange. The additional elimination of Na^+ ions from the zeolite framework, caused by preliminary reduction of the pH of the reaction medium to 6.20, was established by a parallel analysis for sodium in the blank solution. The amount of sodium determined in the solution after the exchange was consistent with the total quantity of Na^+ ions replaced by Co^{2+} ions and those found in the blank test, in which 13.6% of the original Na^+ ions underwent hydrolysis. Fluka's "purum" grade 1-butene, *cis*-2-butene, and 3,3-dimethyl-1-butene were used as the reactants. In a few experiments *trans*-butene was used, too.

Before being used, the reactants were degassed and purified by repeated bulb-to-bulb vacuum distillations.

Apparatus and procedure. Isomerization was carried out in a static system using a cylindrical glass reactor (2.35×10^{-4} m^3 in capacity) attached to a conventional vacuum line, which permitted degassing of the catalyst and admitting of measured reactant quantities.

In each experiment a fresh catalyst was used, in the hydrous form, viz, 3 and 1 dg in the reactions of *n*-butenes and 3,3-dimethyl-1-butene, respectively. The catalyst was degassed initially at room temperature to a pressure of 10^{-2} N m^{-2} and subsequently heated in a thermostated electric furnace. After the required temperature had been attained, the catalyst was activated for 2 hr at a pressure of $\sim 10^{-3}$ N m^{-2}. Temperature was maintained constant to within ±2 K. Each catalyst was activated before the reaction at a standard temperature, i.e., 473 or 673 K. Then the catalyst was allowed to cool to reaction temperature and after the conditions had become established (in ~30 min), the reactant was fed into the reactor by opening the valve of a calibrated holder equipped with a manometer, containing a measured quantity of *n*-butene or 3,3-dimethyl-1-butene in a mixture with argon (the olefin content in the mixture was 14 mole%). The total pressure in the reactor was equal to 2.67×10^4 or 3.34×10^4 N m^{-2}, respectively.

The composition of the reaction mixture was determined by glc using dimethylsulfolane (20%)-on-Chromosorb P columns operated at 323 K. In analyzing *n*-butenes and in separating dimethylbutenes, the columns used were 3 and 1 m long, respectively. Samples, ~0.5% of the reaction mixture, were withdrawn from the reactor by using gastight syringes at varying time intervals. On isomerization of *n*-butenes at initial reaction stages, samples were withdrawn every 20 s and, as the reaction proceeded, sampling intervals were progressively protracted. With the *n*-butenes, the reaction was carried out at a standard temperature of 373 or 423 K; and with 3,3-dimethyl-1-butene, at 348 K. In addition to the series of cobalt catalysts, the starting zeolite NaX and NaHX (with 13.6% of Na^+ ions protonated) were used as catalysts.

RESULTS

Isomerization of n-butenes. In each of the cases investigated, isomerization was found to proceed selectively. The samples analyzed were found to contain *n*-butenes only.

The catalyst specimens of identical Co^{2+} contents and degassed preliminarily at 473 K were found to be much more active than those degassed at 673 K. With the zeolites NaHX and NaX, the catalytic activity was found to be affected by the degassing temperature in an analogous manner but to a lesser extent. When used at 423 K, the NaX exhibited only slight catalytic activity, and at 373 K it was practically inactive (an attempted 2-hr reaction led to nothing but trace amounts of products). The NaHX catalyst was found to be as active as was the CoX (9.6) catalyst which had been degassed under analogous conditions.

For each sample analyzed, the ratio of the two resulting isomers was calculated and plotted against percentage conversion of the starting isomer. The ratio was found to vary with the extent of reaction until equilibrium was ultimately achieved.

The products ratio at zero conversion was established by extrapolation. With isomerization of 1-butene, neither the degassing temperature nor the reaction temperature was found to have any effect on the product ratio at zero conversion; in individual experiments, the value was oscillating around unity (Table I). With the CoX (n) catalysts, the *cis–trans* ratio was equal to, or slightly higher than, unity; with the NaHX, the ratio was lower than unity. On the other hand, in isomerization of 2-butenes the product ratios 1-Bu/*trans* and 1-Bu/*cis* were distinctly dependent on both the reaction temperature and catalyst degassing temperature. Furthermore, when the reaction was carried out at a temperature of 373 K, the 1-Bu/*trans* and 1-Bu/*cis* ratios progressively diminished as the reaction was advancing; whereas at 423 K they initially (up to 3–4% conversion) rose and then fell.

When evaluated from the CoX (35.2)-catalyzed reactions of the individual isomers, the product ratios were found to conform well to the relation (*cis*/*trans*) (*trans*/1-Bu) (1-Bu/*cis*) = 1, which indicates that the reactions following the general scheme

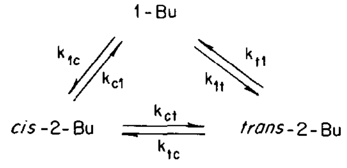

TABLE 1

RELATIVE RATE CONSTANTS FOR ISOMERIZATION OF n-BUTENES OVER CoX(n), NaHX AND NaX

Catalyst			Initial product ratio			Relative rate constants					
Na⁺ for Co²⁺ exchd (%)	Degass. temp (K)	Reaction temp (K)	*cis*/*trans*	1-Bu/*trans*	1-Bu/*cis*	k_{1c}	k_{c1}	k_{1t}	k_{t1}	k_{ct}	k_{tc}
CoX (18.5)	673	373	0.99	3.94	—	1.00	0.249	1.01	0.108	0.063	0.027
	473	373	0.80	3.00	—	1.00	0.249	1.25	0.134	0.083	0.036
	673	423	1.12	2.50	—	1.00	0.343	0.893	0.151	0.137	0.068
	473	423	1.00	1.89	—	1.00	0.343	1.00	0.169	0.181	0.089
CoX (27.8)	673	373	1.33	4.21	—	1.00	0.249	0.753	0.081	0.059	0.025
	473	373	1.44	3.28	—	1.00	0.249	0.694	0.074	0.076	0.028
	673	423	1.27	2.55	—	1.00	0.343	0.787	0.133	0.134	0.066
	473	423	1.19	2.20	—	1.00	0.343	0.840	0.142	0.156	0.077
CoX (35.2)	673	373	1.00	4.00	3.96	1.00	0.249	1.00	0.107	0.062	0.027
	473	373	1.27	3.00	2.42	1.00	0.249	0.787	0.084	0.083	0.036
	673	423	1.28	2.60	2.10	1.00	0.343	0.781	0.132	0.132	0.065
	473	423	1.10	2.34	2.15	1.00	0.343	0.909	0.154	0.146	0.072
CoX (43.5)	673	373	0.94	4.00	—	1.00	0.249	1.06	0.114	0.062	0.027
	473	373	1.25	3.40	—	1.00	0.249	0.80	0.086	0.073	0.031
	673	423	1.32	2.80	—	1.00	0.343	0.757	0.128	0.122	0.060
	473	423	1.10	2.20	—	1.00	0.343	0.909	0.154	0.156	0.077
NaHX	673	373	0.73	1.50	—	1.00	0.249	1.37	0.147	0.166	0.072
	473	373	0.88	1.75	—	1.00	0.249	1.14	0.122	0.142	0.061
	673	423	0.85	1.50	—	1.00	0.343	1.18	0.199	0.229	0.113
	473	423	0.90	1.60	—	1.00	0.343	1.11	0.188	0.214	0.106
NaX	473	423	1.00	2.60	—	1.00	0.343	1.00	0.169	0.132	0.065
Equilibrium product ratios (22)		373	0.408	0.10	0.245						
		423	0.466	0.166	0.358						

are all of the same order and the initial product ratios are equal to the ratios of corresponding rate constants. On the basis of the initial products ratio and equilibrium data (*18*), relative rate constants were calculated, characteristic of formation of individual isomers over the catalysts employed (Table 1). The isomerization was assumed to be a first-order reaction and the kinetic data obtained were plotted according to the equation $\log(X_e - X) = -kt + \log X_e$, X_e and X being the conversions, respectively, at equilibrium and at time *t* at the experimental temperature. The log $(X_e - X)$ vs *t* plots were linear (within the range of 1-butene conversions of 60–70% (Fig. 1) and *cis*-Bu-2 conversions of 30–60%) and passed through the point log X_e. Reasons for the much faster disappearance of linearity in the reaction of *cis*-Bu-2 carried out at the lower temperature (cf. Figs. 2 and 3) have not yet been explained.

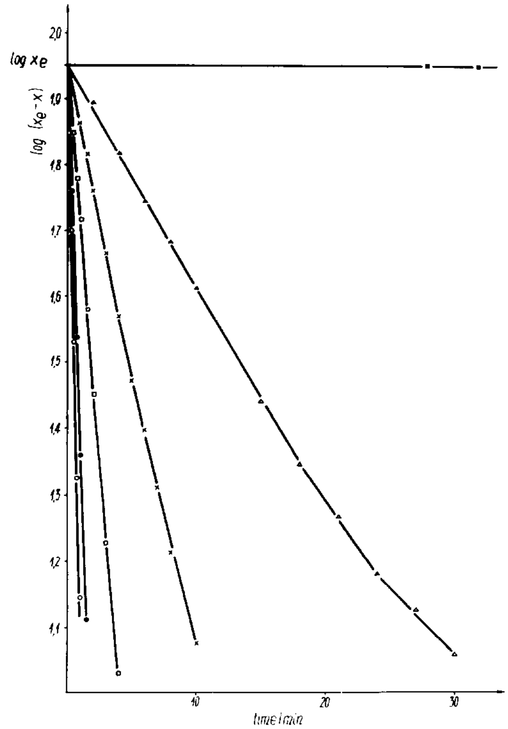

FIG. 1. A plot of the first-order equation for disappearance of 1-butene at 423 K over catalysts degassed at 473 K. (○) CoX (43.5); (●) CoX (35.2); (□) CoX (27.8); (x) CoX (18.5); (△) NaHX; (■) NaX.

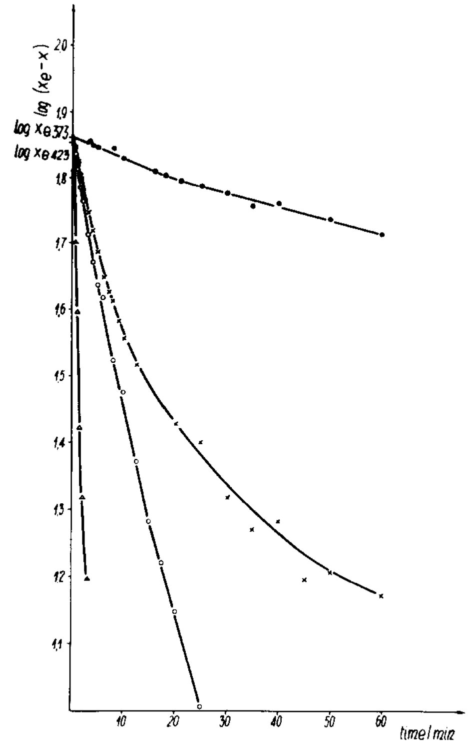

FIG. 2. A plot of the first-order equation for disappearance of *cis*-2-butene over CoX (43.5) catalyst. (△) degassing temperature, 473 K; reaction at 423 K; (○) degassing temperature, 673 K; reaction at 423 K; (x) degassing temperature, 473 K; reaction at 373 K; (●) degassing temperature, 673 K; reaction at 373 K.

Nevertheless, the results obtained made it possible to evaluate the initial reactant disappearance rate constants as observed in the presence of individual catalysts. The constants k_1 and k_c (% $\min^{-1}$) were recalculated into absolute units (molecules s^{-1} dg^{-1}) (Table 2). Plots of the reactant disappearance rate constants, k_c and k_1, as functions of percentage exchange of Na^+ for Co^{2+} ions in the zeolite (Fig. 4) illustrate the variation of the catalyst activity with the Co^{2+} content in the catalyst and also the effect of temperature at which the catalysts were preliminarily degassed. The values marked on the ordinate axis represent the reactant disappearance rate constants observed in the presence of NaHX.

Isomerization of 3,3-dimethyl-1-butene. The compound was isomerized at 348 K because at higher temperatures (over the

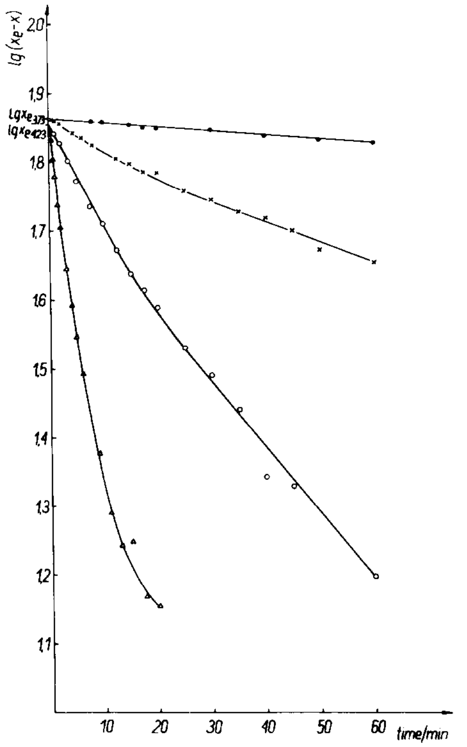

FIG. 3. A plot of the first-order equation for disappearance of *cis*-2-butene over CoX (27.8). (△) degassing temperature, 473 K; reaction at 423 K; (○) degassing temperature, 673 K; reaction at 423 K; (x) degassing temperature, 473 K; reaction at 373 K; (●) degassing temperature, 673 K; reaction at 373 K.

TABLE 2

KINETIC DATA ON ISOMERIZATION OF 1-BUTENE AND *cis*-2-BUTENE OVER CoX(*n*), NaHX AND NaX CATALYSTS

Catalyst			Reactant disappearance rate constant (molecule s^{-1} dg^{-1})	
Na^+ for Co^{2+} exchd (%)	Degass. temp (K)	Reaction temp (K)	$k_1 \times 10^{15}$	$k_c \times 10^{15}$
CoX (4.8)	473	423	—	0.55
CoX (9.6)	473	423	—	0.983
CoX (18.5)	673	373	0.114	0.017
	673	423	2.85	0.916
	473	373	0.814	0.123
	473	423	8.11	2.33
CoX (27.8)	673	373	0.388	0.0691
	673	423	3.41	1.17
	473	373	2.32	0.454
	473	423	20.6	5.23
CoX (35.2)	673	373	1.04	0.17
	673	423	7.30	2.66
	473	373	6.39	1.25
	473	423	45.6	11.2
CoX (43.5)	673	373	2.04	0.312
	673	423	13.7	3.66
	473	373	12.7	3.34
	473	423	77.1	22.0
CoX (51.2)	673	423	—	4.78
	473	423	—	27.2
NaHX	673	373	0.0483	0.0189
	673	423	1.20	0.80
	473	373	0.0824	0.0474
	473	423	2.82	0.983
NaX	473	423	0.0067	0.0033
	473	423	0.0108	0.0042

catalysts with the higher percentage of Na^+ exchanged for Co^{2+} ions and degassed at 473 K), in addition to 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, methylpentenes were also produced. At 348 K, the isomerization was selective but, when applied in these conditions, the zeolites NaX, NaHX and CoX (18.5) (degassed at 673 K) proved to be practically inactive. With CoX (27.8), CoX (35.2) and CoX (43.5), catalyst activity was found to be affected by the degree of exchange of Na^+ for Co^{2+} and by the degassing temperature, as with isomerization of *n*-butenes. As is evident from Fig. 5, the catalysts degassed at 473 K were found to be much more active than those having identical cobalt ion contents and degassed at 673 K.

An inspection of Fig. 5 shows that formation of 2,3-dimethyl-2-butene was distinctly favored. The ratio of 2,3-dimethyl-2-butene to 2,3-dimethyl-1-butene remained practically constant at about 4.5 throughout the whole experiment. The product ratio was not affected by the degassing temperature nor by the Co^{2+} ion content in the zeolite, which suggests that the products may well have formed in the equilibrium ratio.

DISCUSSION

Inspection of the plots presented in Figs. 4 and 5 reveals that the zeolites CoX (*n*) degassed at 473 K are much more catalytically active toward isomerization of 1-butene, *cis*-2-butene and 3,3-dimethyl-1-butene than are those degassed at 673 K. A comparison of these results with the electronic spectrum data (1) allows us to infer that there exists a distinct correlation

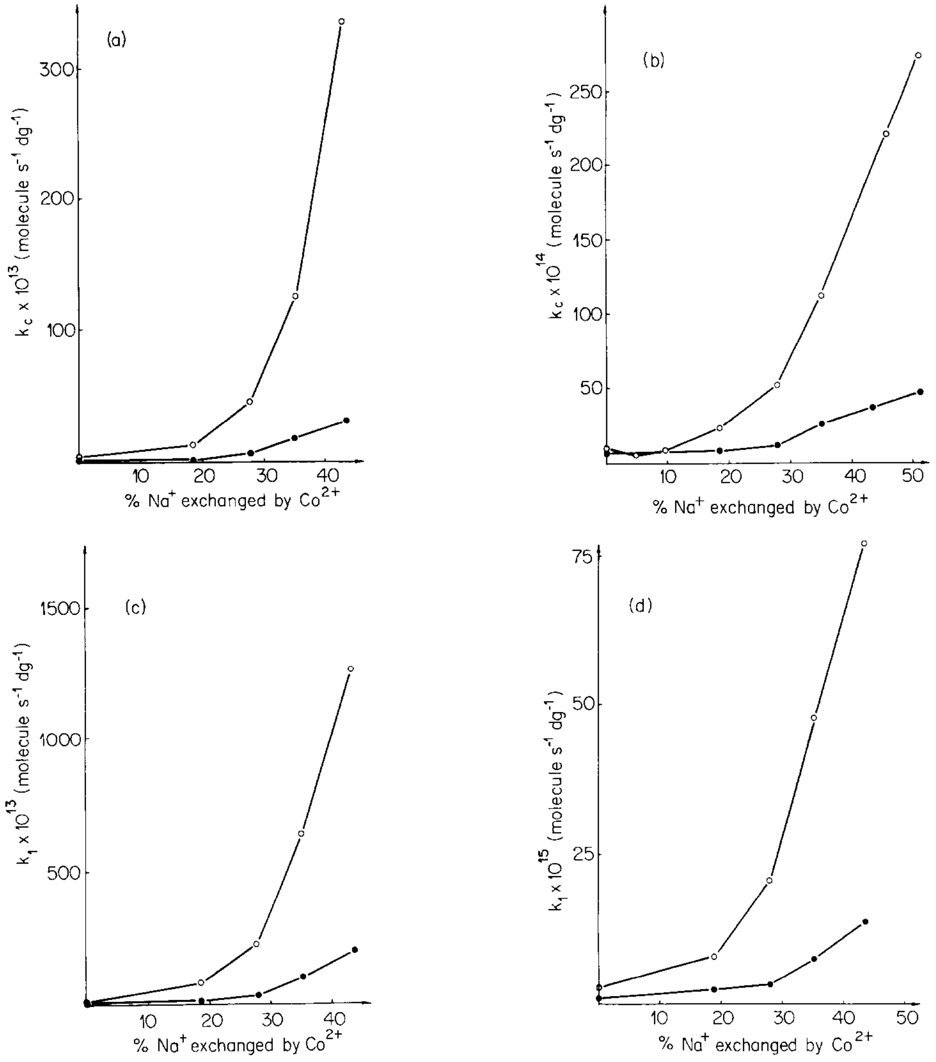

FIG. 4. The effect of the extent of exchange of Na^+ for CO^{2+} and degassing temperature on catalytic activity: (a) isomerization of *cis*-2-butene at 373 K, (b) at 423 K; (c) isomerization of 1-butene at 373 K, (d) at 423 K((○) degassing temperature, 473 K; (●) degassing temperature, 673 K.

between the catalytic activity of CoX (*n*) and the "concentration" of tetrahedrally coordinated cobalt ions in the zeolite lattice. In faujasite-type zeolites, cobalt ions are believed to assume tetrahedral symmetry in positions I′, II′ and II provided that, in addition to interactions with three oxygen atoms, there occurred also interactions between the oxygen atoms and either the residual water molecules or hydroxyl groups formed therefrom by dissociation according to the scheme $Co(OH_2)^{2+} \rightleftharpoons Co(OH)^+ + H^+$, with the simultaneous addition of H^+ to the adjacent oxygen atom in the lattice. Infrared spectral studies carried out in this Laboratory on CoX (*n*) zeolites (*19*) degassed at temperatures within the range 423–673 K have borne out our earlier hypothesis (*1*). It was found that in the CoX (*n*) zeolites degassed at temperatures higher than 423 K, the bands attributable to deformation vibrations of water molecules at ~ 1655 cm^{-1} completely disappear and, instead, there ap-

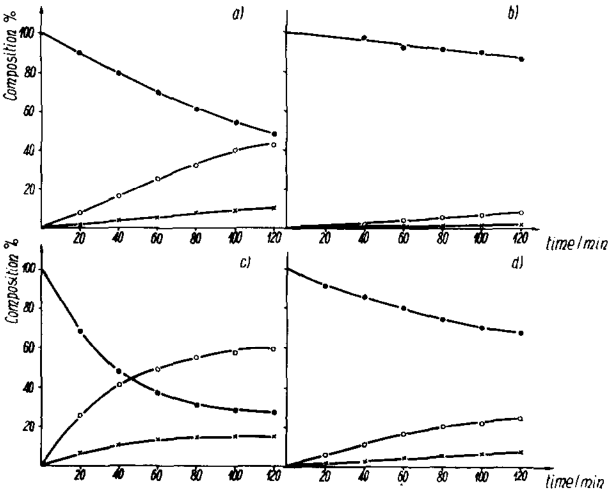

FIG. 5. Isomerization of 3,3-dimethyl-1-butene (a) over CoX (35.2) degassed at 473 K; (b) over CoX (35.2) degassed at 673 K; (c) over CoX (43.5) degassed at 473 K; (d) over CoX (43.5) degassed at 673 K.

pear absorption maxima within the range 3500–3750 cm^{-1} assignable to vibrations of free hydroxyl groups, whose intensity diminishes as the degassing temperature is increased above 473 K. With the zeolites degassed at 673 K, the ~ 3660 cm^{-1} band disappeared almost completely.

While proceeding a step further, one may suppose that the centers responsible for the catalytic activity of CoX (*n*) zeolites in isomerization of 1-butene, *cis*-2-butene and 3,3-dimethyl-1-butene are the hydroxyl groups formed by cleavage of residual water molecules under the action of Co^{2+} ions.

The curves shown in Fig. 4 (representing the variation of the activity of the catalysts degassed at 473 K with the rising content of Co^{2+} ions in the zeolite) indicate that incorporation of small quantities of Co^{2+} ions into the zeolite lattice (exchange <28%) results in only slightly enhanced catalytic activity, but as the Co^{2+} ion content is further increased, the activity goes up rapidly and follows a nearly linear pattern. This behavior appears to be explicable in terms of nonequivalent distribution of the tetrahedral cobalt and acid hydroxylic groups formed by addition of protons to adjacent lattice oxygen atoms $[\equiv Co(OH_2)^{2+} \rightleftharpoons \equiv Co{-}OH^+ + H^+]$, as may be seen from the viewpoint of accessibility of reactant molecules. At low exchange degrees, Co^{2+} ions are likely to become localized in positions I′ and II′ inside the sodalite cages and only after their proportion has increased do they occupy positions II on the walls of the supercages, a fact associated with the effective rise in catalytic activity. The marked drop in catalytic activity of the zeolites degassed at 673 K is thus attributable to dehydroxylation proceeding under the prevailing conditions and the accompanying migration of Co^{2+} ions to position I inside the hexagonal prisms, or the formation of Co–o–Co groupings.

Studies on product ratios in catalyzed isomerization of *n*-butenes have been undertaken by numerous investigators (*8,20*) who demonstrated that the product ratios are closely dependent upon the nature of the active centers at the catalyst surface.

Basic catalysts have been found to be conspicuously favorable to migration of the double bond rather than to *cis–trans* isomerization (with 2-butenes) as the result of hindered rotation of the resulting intermediate carbanion. In isomerization of 1-

butene, formation of the *cis*-isomer is favored in the initial course of the reaction.

On the other hand, in the presence of acid catalysts unobstructed rotation in the carbonium ion makes *cis–trans* isomerization occur more easily than the displacement of the double bond (in 2-butenes) and formation of *cis*-butene from 1-butene is less conspicuously favored.

The *cis–trans* ratios obtained among the products formed over the CoX (*n*) catalysts (Table 1) are typical of the reactions proceeding in the presence of acid catalysts. On the other hand, the ratios found in isomerization of *cis*-2-butene differ considerably from those obtained over aluminosilicates (*4–7*) and metal salts (*8*) as also from the ones predictable on the basis of thermodynamic stabilities (Table 1). They bear considerable resemblances to the data obtained by Dimitrov and Leach (*17*) with zeolites CuX (*n*) (of the higher Cu^{2+} contents) and Lombardo and Hall in their study on zeolites NaY (*15–16*).

Based on the noticeable induction period, the former investigators have suggested a radical mechanism to explain the results obtained; whereas the latter investigators, pointing to the nonexistence of any temperature effect (within the range below 533 K), have adopted the mechanism involving a secondary carbonium ion to explain the high 1-Bu/*trans* ratios by the lack of differences in the energy barrier between the carbonium ion and the individual products formed over zeolites NaY. Assumption of such a model implies a value of (1-Bu/*trans*) = 3.

With the zeolites CoX (*n*), but not with NaHX, the reaction temperature has had a well-defined effect on the selectivity ratio.

The occurrence of neither the induction period (Figs. 1, 2, and 3) nor any signals in the EPR spectra for the *cis*-2-butene/473 K-degassed CoX system and of only very weak signals in the *cis*-2-butene/673 K-degassed CoX system (which with CeX zeolites (*21,23*) were easily noticeable already at room temperature), permitted us to disregard the radical mechanism in the systems under investigation.

Additional evidence in support of the mechanism involving the secondary carbonium ion was obtained from the studies on isomerization of 3,3-dimethyl-1-butene.

It was found that 3,3-dimethyl-1-butene is readily isomerized over proton-donating catalysts (*2–4*) according to the generally

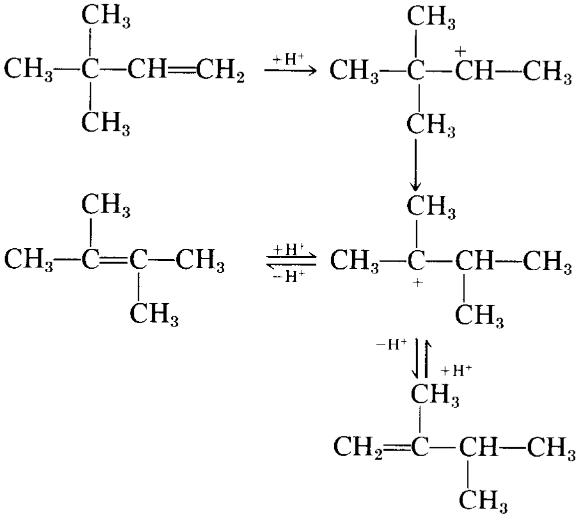

FIG. 6. Scheme of isomerization of dimethylbutenes.

adopted scheme (Fig. 6) but much less readily over catalysts like magnesium oxide (*2*).

The results presented in Fig. 5 clearly illustrate suppression of acidic properties in the catalysts CoX (35.2) and CoX (43.5) degassed at 673 K. The formation of methylpentenes observed (in the presence of the above catalysts degassed at 473 K) at higher reaction temperatures also points to the presence of strong acidic centers.

Summing up the results obtained, we believe that isomerization of 3,3-dimethyl-1-butene and also of n-butenes over the CoX (*n*) catalysts used proceeds through the secondary carbonium ion as an intermediate stage. Favored migration of the double bond with respect to *cis–trans* isomerization, reported also by numerous investigators for zeolite catalysts (*13–15*), may well be associated with the obstructed rotation of the carbocation in the pores of the zeolite lattice.

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