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The Nature of Active Sites in the Isomerization of 1-Hexene on Cracking Catalysts

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The molar ratio of *cis/trans* 2-hexene isomers formed from 1-hexene on NaY zeolites exchanged to various levels with protons or lanthanum ions can be explained by assuming that two types of sites are active for the 1-2 isomerization reaction. The first gives both isomers, while the second gives only the *cis* isomer. In HY zeolite, active sites for the isomerization reaction can be produced by substitution of the most easily replaced sodium ions, either by simple washing with water, or by calcination of a partially exchanged ammonium form. The catalyst activity and the observed ratio of *cis/trans* isomers formed on a partially exchanged LaY zeolite, has been found to depend on the degree of hydration of the catalyst. Ratios of *cis/trans* 2-hexene are closer to their equilibrium value when the reaction is carried out on ZSM-5, mordenite and amorphous silica–aluminas rather than on Y zeolite. This is explained in terms of the proportion of each type of site present, although diffusional limitations within the narrower pore structures of ZSM-5 and mordenite may also play a role. © 1984 Academic Press, Inc.

INTRODUCTION

It is generally accepted that the catalytic activity exhibited by solid acid catalysts in many types of hydrocarbon transformations is attributable to the acidity of the structural OH groups (*1*). One test reaction which has received particular attention in studies of acid catalyst activity is the isomerization of olefins. The isomerization of 1-butene, 1-pentene, and 1-hexene have been investigated over silica gel (*2*), alumina (*3*), amorphous silica–alumina (*3, 4*), and zeolites (*5, 6*). These studies have shown the stereoselective nature of the solid-acid-catalyzed reaction, reflected by a higher ratio of *cis*-2-ene/*trans*-2-ene than the equilibrium value obtained by experiment. The isomerization of butenes on solid acid catalysts has been extensively studied by Hall and co-workers (*7–10*), who have proposed a model based on the formation of a *sec*-butyl carbonium ion to explain the observed *cis/trans* 2-butene ratios. In this model it is postulated that the relative heights of activation energy barriers between the metastable intermediate and the three isomers control the product distribution.

Unfortunately it is often difficult to compare results from these various studies because of the different experimental conditions used by various authors. In the present work, the isomerization of 1-hexene (1H) to isomers of 2-hexene (2H) was studied on a variety of acid catalysts under the same conditions, allowing differences in stereoselectivity to be observed, and further elucidating the nature of the active sites on these catalysts.

THEORY

A theoretical treatment of the decline in the concentration of active sites with time-on-stream, t, has enabled three classes of catalyst decay to be defined according to the value of a decay parameter, N (*11*). Each class gives characteristic curves when the integral reactant conversion, $\overline{X}_R$, is plotted against run duration, t_f. Class I catalysts ($N < 1$) give complete integral conversion at sufficiently long time-on-stream for any

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constant catalyst-to-reactant ratio. Class II catalysts ($N = 1$) give different limiting values of integral conversion at long times-on-stream at various ratios of catalyst to reactant. Maximum integral conversion is observed at a certain time on stream for each catalyst-to-reactant ratio for class III catalysts ($N > 1$).

For each reaction product, the time average yield sampled from $t = 0$ to t_f can be plotted against $\overline{X}_R$. These plots can be enveloped by a single curve, the optimum performance envelope (OPE), which describes the selectivity behavior of a product as t_f approaches zero. This allows the behavior of six types of product to be described by characteristic curves, illustrated in Fig. 1. A product is regarded as primary if its formation has not been preceded by any intermediates in the gas phase, although many intermediate species may have existed on the catalyst surface. A secondary product is derived from a primary product in a similar sense. The initial selectivity of a product, given by the slope of the OPE at zero conversion, is non-zero for a primary product and zero for secondary or subsequent products.

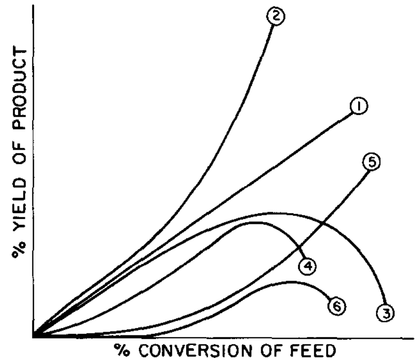

FIG. 1. Theoretical optimum performance envelope (OPE) curves of various products for all three classes of catalyst. The OPEs shown refer to the products: (1) stable primary product; (2) stable primary plus secondary product; (3) unstable primary product; (4) unstable primary plus secondary product; (5) stable secondary product; (6) unstable secondary product.

EXPERIMENTAL

1H of 97.78% purity obtained from Aldrich was used without further purification. The major impurity, 2-ethyl-1-butene, has previously been found (*12*) to produce isomers of 3-methyl-2-pentene on solid acid catalysts at 200°C, and does not contribute to the production of 2H isomers.

Repeated exchange of NaY (Linde Co. Lot No. 45912, SK 40) with 0.5 *N* ammonium nitrate solution (*13*) followed by calcination at 500°C gave HY at various levels of exchange. LaY was similarly prepared from NaY by exchange from aqueous solution containing La^{3+} ions. The partially exchanged LaY had 29% of the Na^+ ions replaced by La^{3+} and protons, while the fully exchanged LaY zeolite had all the sodium ions replaced by either La^{3+} ions (86%) or protons from the solution (14%). Atomic absorption was used to determine the sodium content of the samples.

H-ZSM-5 (Sample 1) was prepared from ZSM-5 (Si/Al ratio = 80) by repeated exchange followed by calcination until no more replacement of Na^+ could be detected. H-ZSM-5 (Sample 2) was provided by Mobil Corporation in the ammonium form and was calcined at 500°C before use.

Hydrogen mordenite was obtained from Strem Chemicals. All experiments were performed using an integral, fixed bed, gas phase, plug flow reactor with an independently controlled three-zone heater. The experimental apparatus and procedures were similar to those described in previous studies (*14*).

The liquid and gaseous products were, respectively, analyzed by a Varian Model 3700 and a Carle SX 1156 gas chromatograph, using conditions described previously (*12*).

Regeneration of catalysts was carried out by passing air through the reactor for 24 h at 500°C.

RESULTS AND DISCUSSION

HY Zeolite

(*a*) *Fully exchanged.* Figure 2 shows the integral conversion of 1H as a function of

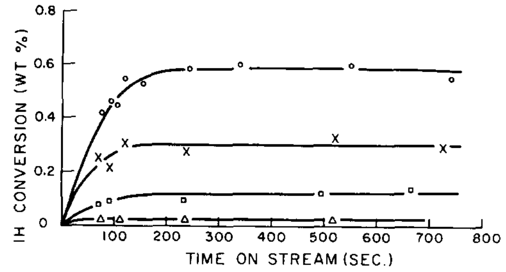

FIG. 2. Integral conversion of 1H on HY at 200°C. Catalyst-to-reactant ratio: (△) 0.00179; (□) 0.00618; (×) 0.024; (○) 0.049.

time-on-stream at 200°C. It was found that the catalyst regained its original activity following a regeneration period of 24 h, so that each curve was generated from results obtained after a series of runs at the same catalyst/reactant ratio on the same sample of zeolite. The integral conversions were calculated allowing for the fact that 1H was only present as 97.78% of the original feed by subtracting the amount of 1H remaining after reaction. Figure 3 shows the OPE curves for *cis*-2H and *trans*-2H. It is evident that both isomers are unstable primary products at this temperature. Their initial formation can be represented by mechanism a (Fig. 4) and the equilibrium between the 2H isomers can be neglected at low conversion. If this interconversion were important (mechanism b) selectivity behavior typical of a primary + secondary product would be revealed (Fig. 1).

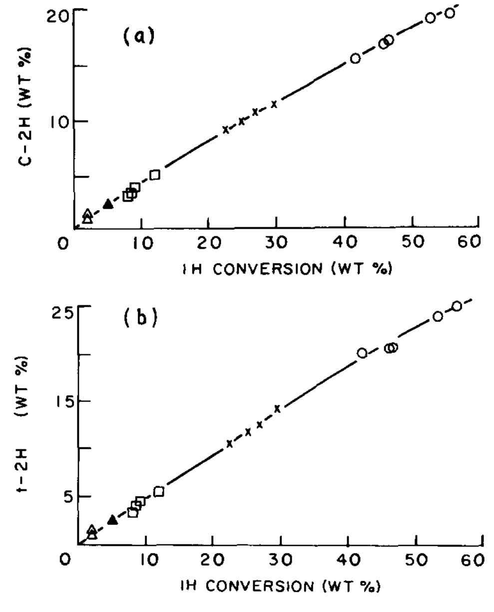

FIG. 3. OPE curves. (a) *cis*-2H. (b) *trans*-2H. Catalyst-to-reactant ratio: (△) 0.00179; (▲) 0.00225; (□) 0.00618; (×) 0.024; (○) 0.049.

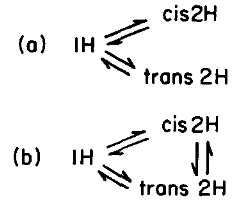

FIG. 4. Mechanisms for formation of 2-hexene isomers.

Initial selectivities for the 2H isomers can be calculated from the initial slopes of their selectivity curves. The ratio of these slopes gives the initial ratio *cis*-2H/*trans*-2H formed on the catalyst, and the value obtained (0.83) is significantly above the equilibrium value (0.4). This ratio can also be found from a plot of *cis*-2H/*trans*-2H against 1H conversion. Figure 5 indicates that extrapolation to the *Y*-axis also yields a value of 0.83. It should be noted that the slope of this plot is small over the region (0–30%) conversion, and that equilibrium is approached only at very high conversion.

(*b*) *Partially exchanged.* As has been reported by other authors (*15, 16*), unexchanged NaY zeolite was found to have no measurable activity in the 1,2 double-bond shift reaction, and no Brønsted acidity can be detected (*17*). In this work, care was taken to eliminate possible activity due to the presence of Ca^{2+} ions (*15*), which are reported to be present as an impurity in Linde catalysts, by repeated exchange of the raw material with sodium acetate. The NaY sample was not washed with distilled water before use, to avoid possible decationization (*15, 18*).

Simple washing of NaY zeolite with distilled water has been found to remove so-

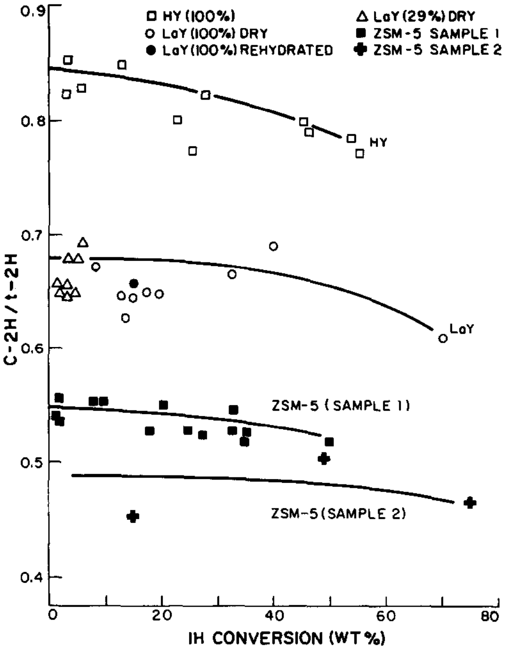

FIG. 5. The variation in the ratio of *cis*/*trans* 2-hexene isomers with total conversion on various zeolites.

dium ions, forming Brønsted sites capable of catalyzing the isomerization of 1-butene (*15, 16*). It has been reported (*18*) that 20% of the total sodium ions in NaY can be removed in this way. Table 1 shows that appreciable catalytic activity can be imparted to NaY by prolonged washing with distilled water at room temperature. It would seem reasonable to assume that sodium ions are replaced by protons from the water, but in a selective manner depending on the strength of the acid sites concerned. The values of the *cis*-2H/*trans*-2H ratios for the washed samples (Table 1) also indicate that the active sites thus formed are very similar to those active for this reaction in fully exchanged HY.

Samples of NaHY, obtained by calcination of the partially exchanged ammonium forms were also found to regain their activity after a period of regeneration at 500°C. Results from several series of experiments are given in Table 2, which again shows that the value of *cis*-2H/*trans*-2H at low conversion is very similar to that found on fully exchanged HY.

Studies of acid strength properties of the faujasites (*19*) show that the exchange of protons in NaY begins with the elimination of the cations associated with the weakest sites. The strong acid sites are exchanged

TABLE 1

Isomerization of 1H on Proton-Exchanged Zeolites Formed by Washing with Distilled Water and by Calcination of $Na(NH_4)Y$

Catalyst[a]	Exchange level (%)	Total conversion[b] (%)	*cis*-2H / *trans*-2H
NaY (unwashed)	0	0	—
NaHY (12th exchange)	98	18.63	0.79
NaY (1st washing)[c]	2	4.35	0.79
NaY (2nd washing)[d]	11	13.37	0.78

[a] Catalyst (0.20 g) used in each case. Temperature 200°C, time-on-stream 225 sec, weight of feed 13.4 g. Only first-run experiments reported. Exchange level (1–12) refers to exchange from NH_4NO_3 solution.

[b] Total conversion was calculated allowing for 97.78% 1H present in the feed.

[c] Washing with distilled water for 24 h at room temperature.

[d] Washing with distilled water for 6 days at room temperature.

TABLE 2

Isomerization of 1H on Proton-Exchanged Zeolites Formed by Calcination of $Na(NH_4)Y$

Catalyst[a]	Exchange level (%)	Time-on-stream (sec)	Conversion (%)	*cis*-2H / *trans*-2H
NaHY (1st exchange)		41	6.72	0.89
		45	7.24	0.91
		48	7.92	0.87
		71	8.92	0.80
		220	15.92	0.87
NaHY (3rd exchange)	68	47	11.05	0.86
		49	9.02	0.78
		212	13.29	0.77
		448	12.85	0.82
NaHY (5th exchange)	86	37	7.58	0.85
		48	11.28	0.81
		90	10.70	0.84
		201	12.31	0.84
		400	17.80	0.76
NaHY (12th exchange)	98	33	17.25	0.84
		48	20.09	0.83
		146	18.00	0.79
		213	18.63	0.79
		510	22.65	0.80

[a] Temperature 200°C, weight of feed 13.4 g.

only when there are no more sodium ions linked to weak acid centers. The "weaker" sites were reported to account for ≈30% of the total number of protonic sites present in HY. It has been previously suggested (*20*) that the more easily replaced acid sites in NaY are active in the double-bond shift reaction, and our results give support to this observation.

Exchange with La

Crystallographic studies (*21*) have shown that by exchange from aqueous solution, rare earth cations can be exchanged for the sodium within the large cavities of X and Y zeolites. Dehydration, by heating to 350°C, leads to migration of the rare earth cations into the sodalite cage cavities. Further evidence for ion migration is provided by Auger spectroscopic studies (*22*) on rare earth- and transition metal-exchanged Y zeolites. These studies show that heating the hydrated, fully exchanged zeolite leads to migration of the cations, and this cannot be reversed by rehydration of the sample. These observations are consistent with the observation that heat treatment of rare earth-exchanged zeolites causes stronger binding of the multivalent cation to the structure, while the residual sodium ions become more easily exchanged. Titration studies (*23*) with LiAlH on 75% exchanged LaY zeolite show that on drying LaY, acidic OH groups are formed within the supercavities of the zeolite. An equilibrium of the type (*24*)

$$\mathrm{La^{3+} + H_2O + O\text{–}Zeolite \rightleftarrows La(OH)^{2+} + HO\text{–}Zeolite} \quad (1)$$

have been proposed to account for the generation of active Brønsted sites.

It has been shown that Brønsted sites in HY zeolite do not appear to be lost unless the sample is heated above (550°C) (*25*, *26*). Beyond this temperature the Brønsted sites are converted into Lewis acid sites and catalytic activity falls dramatically for many reactions (*27*). The situation is rather different in lanthanum-exchanged Y zeolites. Titration studies with $\mathrm{LiAlH_4}$ (*23*) have indicated that on heating La-exchanged Y zeolite from 120 to 400°C water is lost, and the total number of Brønsted sites decreases to ≈10% of the number found at 120°C. This would account for the steady decline in the cracking activity for *n*-heptane as the activation temperature of LaY is increased from 350 to 500°C (*26*). This deactivation may result from a shifting of Eq. (1) to the left.

TABLE 3

Isomerization of 1H on Lanthanum-Exchanged Y Zeolite

Weight of catalyst[a] (g)	Time-on-stream (sec)	Conversion (%)	*cis*-2H / *trans*-2H
0.2	222	4.91	0.67
1.0	224	14.42	0.64
1.0	222	14.48	0.66
1.0	48	8.3	0.63
1.0	486	17.83	0.66
1.0 (Hydrated)	223	14.68	0.66
2.5	225	48.14	0.69
2.5	320	40.37	0.69
2.5	49	13.94	0.65
4.5	222	67.9	0.61

[a] Temperature 200°C, weight of feed 13.4 g.

The activity of fully exchanged LaY was also found to be restored by regeneration for a 24-h period at 500°C. Table 3 shows results for several catalyst/reactant ratios at various times-on-stream.

Figure 5 shows the ratio *cis*-2H/*trans*-2H plotted against total 1H conversion for HY zeolite and lanthanum-exchanged Y zeolites. Also included here are results for a partially exchanged LaY zeolite using several catalyst/reactant ratios and times-on-stream between 58 and 500 sec. Points for both fully exchanged LaY and 29%-exchanged LaY appear to fall along the same curve when all the samples have been preheated to 500°C and maintained in the dehydrated state. This curve falls significantly below that representing this ratio of isomers obtained on HY.

To explain these observations, first con-

TABLE 4

Isomerization of 1H on Partially Exchanged LaY Zeolites

Catalyst[a]	Rehydration at 200°C	Run number	Time-on-stream (sec)	Conversion (%)	$\frac{cis\text{-}2H}{trans\text{-}2H}$
LaY (29%)	No	1	223	3.93	0.66
	No	2	58	2.64	0.65
	No	3	433	2.30	0.66
LaY (29%)	Yes	1	225	38.16	0.74
	Yes	2	220	13.01	0.75
	Yes	5	223	9.88	0.77

[a] Catalyst (1.0 g) used; temperature 200°C, weight of 1H—13.4 g.

[b] Rehydration carried out by rapidly passing 5 ml distilled water through the reactor at 200°C, and purging for 1h with nitrogen flow.

sider the fully exchanged zeolite, in which all sodium ions have been replaced either by La^{3+} or H^+ ions. Let us suppose that the active sites for the isomerization in Y zeolites, which are assumed to be the OH groups in the supercavities, are of two types. The first, type A, can give both the *cis* and *trans* 2H isomers. The second, type B, can give only the *cis* 2H isomer due to steric constraints, i.e., the activated complex leading to the *trans* isomer cannot form on B sites because of the steric configuration in the vicinity of the double bond. It is then reasonable to conclude that the proportion of type B sites is smaller on LaY than HY.

A reduction in the proportion of type-B sites in LaY could occur because, as stated earlier, there is a reduction in Brønsted sites on lanthanum-exchanged zeolites as the activation temperature is increased. It is possible that type-B sites are preferentially removed, giving rise to the observed decrease in *cis*/*trans* ratio.

Effect of Hydration

Table 3 shows that hydration of the fully exchanged LaY zeolite had no effect on the activity or *cis*-2H/*trans*-2H ratio.

Hydration of the partially exchanged LaY zeolite produces a large increase in activity as shown in Table 4. Not only does the activity increase, but the *cis*-2H/*trans*-2H ratios obtained from experiments with the hydrated catalyst do not fall along the same line as for the dehydrated zeolite. Figure 6 shows this ratio plotted against 1H conversion, and includes results obtained at a time-on-stream of 225 sec for both the first run on a catalyst and subsequent runs. Experiments at times-on-stream between 45 and 500 sec also gave *cis*-2H/*trans*-2H ratios which fell on the curve in Fig. 6. Although the activity of a hydrated catalyst cannot be fully restored by regeneration alone, the *cis*-2H/*trans*-2H ratio appears to fall along the same line for all hydrated catalysts. This line has been moved upward

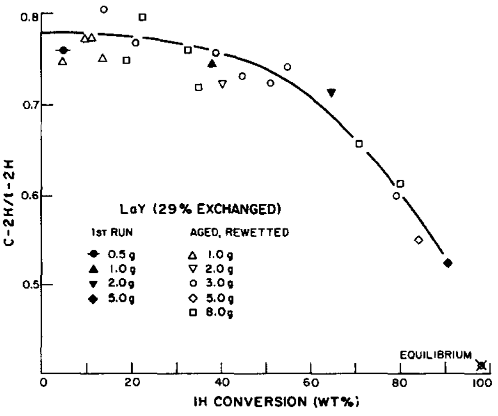

FIG. 6. The variation in the ratio of *cis*/*trans* 2-hexene isomers with total conversion on partially exchanged (29%) LaY zeolite.

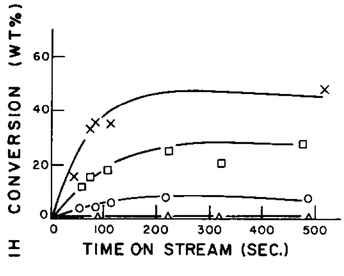

FIG. 7. Integral conversion of 1H on ZSM-5 at 200°C. Catalyst-to-reactant ratio: (△) 0.026; (○) 0.075; (□) 0.195; (×) 0.386.

with respect to the dehydrated lanthanum results (Fig. 5) and lies just beneath results for HY. To account for this it is suggested that in the partially exchanged LaY zeolite, at sites which are in close proximity to sodalite cages occupied by La^{3+} ions, OH groups are essentially equivalent to those in the fully exchanged LaY zeolite. However, there must also be some exchange of Na^+ ions by protons from the acidic $LaCl_3$ solution producing sites which are similar to those present in partially exchanged NaHY zeolite. It is the activity of these sites which is enhanced and made dominant in the hydrated samples, as demonstrated by the large increase in activity, and therefore the *cis*-2H/*trans*-2H ratio is raised to a position similar to that for NaHY. These sites are partly lost during regenerations at 500°C whereas in pure HY zeolite significant loss of similar Brønsted sites does not occur until a temperature of 550°C is reached. The fate of the sites associated with lanthanum ions is unclear. They seem to either be eliminated by the hydration or to be transformed to HY-type sites.

The Effect of Other Zeolite Structures and Amorphous Silica–Alumina

Figure 7 shows the integral conversion of 1H as a function of time-on-stream at 200°C for a ZSM-5 catalyst (Si/Al = 80). As for HY zeolite, the full activity of the catalyst was restored by regeneration at 500°C. Figure 8 shows the OPE curves for *cis*-2H and *trans*-2H, and again it is clear that these isomers are unstable primary products. The ratio of initial selectivities for these isomers (determined from the initial slopes in Fig. 8) gives a value of 0.54. This can also be determined from the plot of *cis*-2H/trans-2H against 1H conversion in Fig. 5. Results from a second sample of ZSM-5 were also found to produce low ratios of *cis*-2H/*trans*-2H at all 1H conversions.

Both ZSM-5 (Fig. 5) and mordenite (Fig. 9) produce a *cis*-2H/*trans*-2H ratio lower with respect to the curve for HY. In both cases, this may be due to a smaller intrinsic proportion of type-B sites or due to diffusional limitations within the narrower pore structures of these zeolites (*28–30*).

Ratios of *cis*-2H/*trans*-2H obtained on amorphous silica–alumina are also included in Fig. 9. Various catalyst to reactant ratios were used, and TOS was varied between 45 and 500 sec. Well defined pore structures do not exist within the amorphous materials, so the observed *cis*-2H/*trans*-2H ratios are probably the result of some statistical abundance of type-A and type-B sites.

CONCLUSION

Our results have shown that the introduc-

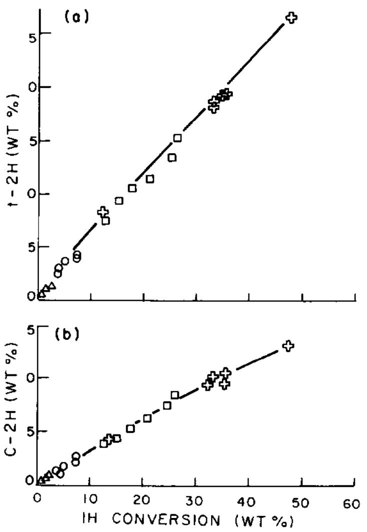

FIG. 8. OPE curves. (a) *cis*-2H. (b) *trans*-2H. Catalyst-to-reactant ratio: (△) 0.026; (○) 0.075; (□) 0.195; (✣) 0.386.

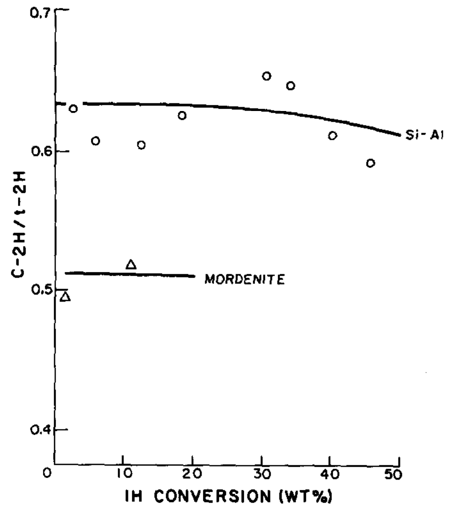

FIG. 9. The variation in the ratio of *cis*/*trans* 2-hexene isomers with total conversion on silica–alumina and mordenite.

tion of different ions into the same zeolite framework produces a variation in the ratio of *cis*-2H/*trans*-2H formed by isomerization of 1H. This variation can be explained by assuming two types of active site for this reaction: the first gives both *cis* and *trans* isomers, while the second gives only the *cis* isomer. Differences in the relative proportion of these sites may also explain the ratio of isomers formed on other zeolites and on amorphous silica–aluminas. Diffusional limitations may also have an important influence by promoting equilibration when the pore diameters of a zeolite approach the kinetic diameter of the reactant molecules.

The model proposed by Hall (*9*, *10*) explained the *cis*/*trans* ratios produced by isomerization of 1-butene on solid acid catalysts in terms of the relative heights of activation energy barriers between the intermediate carbonium ion and the three isomers. In the original form of this model (*9*), it was suggested that initial *cis*/*trans* 2-butene ratios close to unity were generally obtained experimentally because formation of either isomer depended on loss of one or other of the two methylene hydrogen atoms from the three-carbon atom of the carbonium ion, and these were equally probable events. More recent studies (*10*, *31*) of 1-butene isomerization on a variety of solid acid catalysts have revealed that initial *cis*/*trans* ratios close to unity are not always obtained. These results have led to a modification of the model (*10*) in which the intermediate carbonium ion is not an identical species on all surfaces. Interactions may exist which affect energetic factors causing the barriers between the intermediate and the product 2-butene molecules to be different. It was proposed that steric factors may cause a difference in the ease of abstraction of the two methylene hydrogens, resulting in different activation energies for formation of the *cis* and *trans* isomers.

In terms of our two site model, it is suggested that the energy barriers between the intermediate species and the *cis* or *trans* 2-hexene isomers are of the same order of magnitude for the type-A of site. On the type B, however, steric constraints create a very large energy barrier leading to the *trans* isomer, compared to that yielding the *cis* isomer. Consequently only the *cis* isomer is formed on this site.

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