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Contribution to the Understanding of the Reaction Chemistry of Isobutane and Neopentane over Acid Catalysts, I

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The reaction chemistry for the cracking of neopentane was compared with that for isobutane in steady-state flow experiments over silica–alumina catalysts and HY zeolites. The activity for isobutane cracking changed only slightly as it lined out. In contrast, the neopentane reaction was self-poisoning; coking was nearly 10 times as fast as that with isobutane. In addition, the principal reaction pathway with neopentane was the primary unimolecular demethylation step forming CH_4 and C_4 hydrocarbons as products. With both substrates paraffins were formed extensively on the more active catalysts. At low conversions with isobutane this was largely due to H^- transfer from the reactant; with neopentane, the surface residues furnished the required hydrogen. Further dehydroxylation of silica–alumina catalysts effected by raising the pretreatment temperatures from 500 to 650°C was found to decrease the conversion rates by about a factor of 2, suggesting that the primary reaction events are Brønsted acid catalyzed. Replacing such sites in Y-zeolites with Na^+ ions also drastically reduced the catalytic activity, but the observed effects resulted from changes in the strength (intensive factor) of the sites, not just from the decrease in their number (extensive factor). Interestingly, the nearly 10^2 increase in rates obtained on removing Na^+ was not accompanied by a change in selectivity at constant temperature when the conversion was maintained constant at 2.33% by increasing the space velocity. The effects of adding small amounts of olefins into an isobutane feed stream were also investigated. Ethene inhibited the reaction somewhat, but otherwise had little effect. Propene and isobutene additives enhanced both the conversion and paraffin formation. The way these results amplify our understanding of these simple reactions and make them more useful for catalytic studies is briefly discussed.

INTRODUCTION

In recent years, considerable interest in the cracking of small paraffin molecules has developed. A variety of substrate molecules has been studied (*1*), but most notably *n*-hexane and isobutane. The former has been used for many years as a standard test reaction by workers at the Mobil Laboratories (*2*) and the latter by McVicker and co-workers (*3*), who have pointed out that the relatively stable *t*-butyl cation cannot undergo β-scission, thus greatly restricting the products which may be formed and making data interpretation tractable. Neopentane can be used to generate the same *t*-butyl ion (*4*) and might be expected to undergo similar chemistry. However, isobutane contains a tertiary hydrogen which is labile for H^- transfer, whereas neopentane has only primary CH bonds. Consequently, although the primary initiation steps may be the same, the secondary chemistry would be expected to be quite different.

Before proceeding, the reader's attention should be called to a matter of semantics or perspective. In our work (*4–9*) we have adopted the terminology "*primary reactions, primary events and/or primary processes*" to mean the result of the *monomolecular initiation reactions* in which the initial carbenium ions are formed. Similarly,

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we have termed all the subsequent *bimolecular processes* (mainly involving carbenium ion chain reactions carried by H^- transfer, but also including oligomerization and subsequent cracking by β-scission) as "*secondary processes*." This usage is distinct from "*primary products*" vs "*secondary products*" as used by Wozciechowski and coworkers (*1*, *22*). Their assignments are based on the shapes of their "optimum performance envelopes" and thus depend upon the relative rates of formation of identifiable products. In this context it follows that a *primary product* may result from *secondary* chemistry. This happens for example when the adsorbed reactant molecule goes through a series of steps before releasing a product, as invariably occurs with H-mordenites. Thus, we hae not *assumed* that H^- transfer is a secondary process; we have so defined it.

Objectives of our recent work (*4–9*) have been to develop diagnostic tools for the study of catalyst acidity and to define how this property controls product selectivity. This work, much of which was carried out using the pulse technique, led to generally similar conclusions using either reaction, in spite of the fact that the data showed no evidence of reaction of neopentane by H^- transfer. In the catalytic cracking of isobutane and neopentane, the gross reaction chemistry is generally understood. With the former, it is convenient to consider the overall process in terms of a generalized chain reaction. *Initiation* occurs following first-order kinetics (*3*) by chemistry described by Olah and co-workers (*10–12*), viz.,

$$(CH_3)_3CH + H^+ \rightarrow [C_4H_{11}]^+ \begin{array}{ll} \nearrow H_2 + (CH_3)_3C^+ & \quad (1a) \\ \searrow CH_4 + (CH_3)_2C^+H, & \quad (1b) \end{array}$$

where $[C_4H_{11}]^+$ is the (undetected) pentacoordinated carbonium ion intermediate. The chain-carrying steps follow second-order kinetics (*3*) and involve transfer of the tertiary hydrogen of the isobutane reactant to existing carbenium ions, forming the corresponding paraffins (and regenerating the original $(CH_3)_3C^+$ cation, i.e.,

$$(CH_3)_3CH + [C_nH_{2n+1}]^+ \rightarrow (CH_3)_3C^+ + C_nH_{2n+2}. \quad (2)$$

Among these, the sec-butyl carbonium ion (formed by isomerization of the *t*-butyl ion) and isopropyl cation formed in Reaction (1b) are most important, especially in the low conversion limit; i.e.,

$$(CH_3)_3C^+ \rightarrow CH_3C^+HCH_2CH_3 \xrightarrow{iC_4H_{10}} nC_4H_{10} + (CH_3)_3C^+. \quad (3)$$

Chain termination involves decomposition of the carbenium ions into olefins which either undergo oligomerization or are desorbed as products. With neopentane the 12 primary hydrogens do not participate in the H^- transfer reactions so that a self-sustaining chain reaction is not possible and olefin desorption would appear inevitable. However, paraffins are formed and it has been shown that the required hydrogen is furnished by residues held by the catalyst (*4*, *5*).

In the present work, we have used steady-state flow experiments carried out at low conversions to make careful comparisons of these two reactions and this has given us a more detailed understanding of the processes involved. Interestingly, with neopentane only paraffins are released from the strongest acid catalysts (*4*, *5*) in spite of the fact that olefin formation seems unavoidable. A possible scenario for the chemistry has been presented previously (*9*).

The mechanism of the primary reactions remains controversial. Garten (*13*) suggested that dehydrogenation was an essential step in the isomerization of isopentane and *n*-pentane over silica–alumina cracking catalysts, and that the resulting pentenes then become protonated at nearby Brønsted sites. Brenner and Emmett (*14*) concluded that this dehydrogenation activity was an intrinsic property of the catalyst and not the result of trace impurities. Others (*15–17*) have suggested that this dehydrogenation function may be carried out by Lewis acids. McVicker and co-workers (*3*) postulated the formation of cation radicals at electron acceptor sites (supposedly intrinsic to the catalyst) and that these decomposed into H_2 and CH_4, and the corresponding olefins, i.e., the same result obtained from Reactions (1), or from thermal cracking of these compounds. Haag and co-workers (*18, 19*), on the basis of results obtained in the cracking of *n*-hexane and isopentane, proposed the direct protonation of hydrocarbons forming pentacoordinated carbonium ions which in turn decomposed into H_2 or smaller paraffins and the corresponding carbenium ions as described above. We have preferred this interpretation over all of the others for reasons outlined earlier (*7*).

There is general agreement among all of the aforementioned workers that two mechanisms coexist, viz., primary monomolecular steps leading to formation of H_2, CH_4 (or other smaller paraffin molecules) together with conjugate carbenium ions, and the classical carbenium ion chain reactions. The former initiate the chains which carry the latter.

EXPERIMENTAL

Catalysts. The catalysts used and their properties are listed in Table 1. Houdry M-46 amorphous silica–alumina was a nonzeolitic preparation obtained from the manufacturer over 25 years ago. It was taken from the same batch used in many of our earlier studies requiring such a catalyst. The N-631-L, an amorphous silica–alumina, was obtained as a gift from Professor K. I. Segawa; it was provided by the NIKKI Chemical Co., Japan.

Two dealuminated H-Y zeolites were prepared. The starting material (LZ-Y62) was heated to 540°C in a static muffle furnace for 2 h before twice treating under reflux with 0.9 *M* NH_4NO_3 and calcining for 2 h to 815°C. This thermally treated zeolite (TT-HY) was washed at 60°C with 1.0 *M* HCl for 2 h to remove extraneous alumina expelled from the lattice in the previous thermal treatment. This was labeled H-Y(8.1).

LZ-210(12.0) and LZ-210(6.0) were supplied by Linde. They were treated at 90°C with 1.0 *M* ammonium acetate to reduce sodium content. After drying at 120°C these samples were calcined at 500°C for 5 h. LZ-Y82 was from the same source, but used without modification.

Apparatus and procedures. As described previously (*8*), the catalytic tests were carried out in the steady-state flow mode under atmospheric pressure in a quartz U-tube (8 mm i.d.) reactor. The downflow side served as a preheater and the catalyst was packed into a 2.0-cm-long bed held between plugs of quartz wool in the upflow side. The reactor was held at temperatures constant to ± 0.2°C inside an electrically heated furnace. The temperature was monitored by a thermocouple placed externally near the center of the catalyst bed. The flow rate of the reactant gas was kept constant and adjusted by using Brooks flow controllers.

The catalysts were given a standard pretreatment. The powder was pressed into pellets without binder, crushed, and sieved. An aliquot of the 20–40 mesh fraction (0.425–0.85 mm) was heated in an open quartz crucible to 500°C for 5 h. After being covered with a lid, the catalyst was cooled and 400 mg weighed on a Mettler balance. This aliquot was packed into the reactor. After attachment to the flow system, the catalysts were again heated in a stepwise fashion to, and then held overnight at, 500°C in flowing dry O_2. Finally, the reactor was flushed (at 60 cm^3/min) with dried prepurified grade N_2 and cooled to the preselected reaction temperature.

The reactants were 10% isobutane in N_2 (Matheson, instrument grade, which contained 0.2% propane and 0.3% *n*-butane impurities) and neopentane (Columbia Organic Co., nominal purity 98%). The neopentane

TABLE 1

Physicochemical Properties of Catalysts[a]

	M-46 Houdry	N-631-L NIKKI	TT-HY[b]	H-Y(8.1)[c]	LZ-210 (12.0)	LZ-210 (6.0)	LZ-Y82
Chemical analysis							
SiO_2 wt%	87.5	87.0	75.5	90.2	87.3	78.8	75.7
Al_2O_3 wt%	12.5	13.0	23.7	9.3	12.7	21.2	24.1
Na_2O wt%	nd	nd	<0.3	<0.3	0.1	0.02	0.46
[Al atoms (total)/g] $\times 10^{20}$	14.8	15.4	27.9	10.9	14.9	23.3	25.7
[Framework Al atoms/g] $\times 10^{-20}$	Na	Na	12.2	6.7	14.3	22.8	16.2
Si/Al (chemical)	5.9	5.7	2.7	8.1	5.9	3.1	2.9
Si/Al (framework)[d]	Na	Na	6.2	13.2	6.0	3.4	5.2
Pore volume (cm^3/g)	0.2	Na	0.28	0.30	0.33	0.33	0.32
Surface area (m^2/g)	270	500	Na	Na	Na	Na	Na

Note. Na not applicable or not available.

[a] The chemical analyses were furnished by the suppliers or determined in house.

[b] Made from Linde LZ-Y62 by steaming at 815°C; see text.

[c] Made from TT-HY by acid extraction; see text.

[d] Determined by MASNMR of ^{29}Si.

was diluted with N_2 in a ratio of 1 : 9 by using a Brooks dual channel mass flow controller unit. Before entering the latter the N_2 was passed through a molecular sieve drier and the neopentane was led through a trap filled with Ag_2SO_4/H_2SO_4 on pumice stone to remove any possible olefinic impurities (*17*). No impurities were detectable downstream by GLC. In some experiments small amounts of olefins were added to the isobutane feed stream; a mixture of 10% isobutane in N_2 was mixed with a stream containing 0.1% ethylene, propene, or *i*-butene in N_2 (Matheson). The final ratios of olefin to isobutane were 0.006.

The reaction was started by switching the reactor from nitrogen to the reactant mixture stream. The effluent gas was sampled and analyzed by on-line GLC. Two columns were connected in series, and N_2 was used as carrier gas. In the first, hydrogen was separated and determined on a 5-Å molecular sieve column at 0°C using a thermal conductivity detector. In the second, hydrocarbons were separated and determined after passing over two packings in series at 0°C (dibenzylamine and propylene carbonate on Chromosorb) using a flame ionization detector. Satisfactory separation of all C_1 to C_5 hydrocarbons was obtained. The composition of effluent was calculated as the mole fractions (X_i) of the total product (including isobutane) after making corrections for impurities in the feed.

Treatment of the data. As before (*8*), differential reaction rates were taken as the initial slopes of plots of X_i vs (W/F), or, at low conversions, as $C_i = X_i(F/W)$, where (F/W) is the entering reactant calculated as moles per gram per second. Thus, the data recorded in Tables 2 to 8 give the differential reaction rates for formation of the individual products. Moreover, the total conversion rate of reactants is given by $(1/n)\Sigma_i jC_i$, excluding isobutane, where j is the number of carbon atoms in each of the i components of the product and n is 4 for isobutane and 5 for neopentane. This defines the rate, Conversion B. For comparison the rate, Conversion A, was calculated as the sum of the rates of the two processes by which isobutane may be reacted, i.e., by protonation (primary) and by H^- transfer (secondary). Thus, Conversion A = $[C_{H_2} + C_{CH_4} + \Sigma C_{\mathrm{paraffin}}]$ provided that the overall percentage conversion is sufficiently low that virtu-

TABLE 2

Rates of Product Formation from Reaction of Isobutane or Neopentane over M-46 Silica–Alumina and TT-HY Zeolite, at 520°C[a]

Catalyst:	M-46		TT-HY	
Reactant:	Isobutane	Neopentane	Isobutane	Neopentane
H_2	25.9	0	10.9	0
CH_4	9.5	74.0	6.8	10.9
C_2H_6	0		0	0
C_2H_4	0	0.6	0	1.8
C_3H_8	0	0	0	0
C_3H_6	8.0	1.5	5.5	1.4
i-C_4H_{10}	R	0.6	R	0
n-C_4H_{10}	1.2	0	0	0
i-C_4H_8	21.5	74.5	11.2	9.1
n-C_4H_8	3.7	18.2	0	5.3
C_5H_{12}	0	0	0	0
$(H_2 + CH_4)$	35.4	74.0	17.7	10.9
Σ_2^5 (Paraffins)	1.2	0.6	0	0
Conversion A[b]	36.6	74.6	17.7	10.9
Conversion B[c]	34.8	90.6	17.0	15.3
TOF B[d]	7.73	20.13	8.36	1.52
% Conversion	0.61	1.60	0.30	0.27
% Primary[e]	97	99	100	100

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used; the flow rate, F/W, was 5.7×10^{-6} mol g^{-1} s^{-1}.

[b] Conversion A = $(H_2 + CH_4) + \Sigma_2^5$ paraffin.

[c] Conversion B = $(1/n) \Sigma_1^5 jC_i$ where $n = 4$ for isobutane and $n = 5$ for neopentane, and j is the number of carbon atoms in each of the i products.

[d] TOF B is given as 10^9 molec. cm^{-2} s^{-1} for amorphous silica/alumina and as 10^{-6} molec. Al_F^{-1} s^{-1} for zeolites.

[e] % Primary reaction was calculated as: $[(H_2 + CH_4)/\text{conversion A}] \times 100$.

ally all collisions involve isobutane (so that the only source of CH_4 and H_2 is in the decomposition of this molecule and all paraffins are formed by H^- transfer from this molecule).

RESULTS

Isobutane and neopentane cracking experiments were carried out on M-46 amorphous silica–alumina and TT-HY zeolite. Under the experimental conditions, no reaction was detected below 460°C. Typical results are collected in Table 2. Blank tests showed that less than 5% of the reported products could have been formed by thermal cracking.

Only hydrogen + i-butene and methane + propene resulted from the cracking of isobutane over TT-HY. Dehydrogenation was favored over demethanation by roughly a factor of 2. This catalyst, which contained a large amount of extra-lattice aluminum, was found to be less active than amorphous silica/alumina, presumably because of a dearth of Brønsted sites. On M-46 relatively small amounts of both n-butene and n-butane appeared in the products. On both catalysts Conversion A was in good agreement with Conversion B.

For neopentane cracking CH_4 and i-C_4H_8 were the anticipated products. Even on the less active TT-HY, however, C_2H_4, C_3H_6, and n-C_4H_8 were produced. Most notable was that while the i-butene was in fair agreement with the methane formed, n-butene was also formed in comparable quantities. Thus, the sum of butenes exceeded considerably the amount of methane formed and Conversion Rate B greatly exceeded Conversion Rate A. It is therefore evident that some reaction in addition to the anticipated primary initiation by protonation occurred during the decomposition of neopentane.

The results obtained from neopentane cracking over Catalyst M-46 exhibited similar features. Interestingly, a small amount of i-C_4H_{10} was formed as well as excess n-C_4H_8, even though the primary hydrogens of neopentane are unlikely to have participated in the H^-transfer process. Moreover, no C_5 hydrocarbons were detected in the product. Activation by H^- transfer from neopentane should cause the formation of the 2-methylpentyl ion (*12*) and thus the formation of isopentene. On amorphous silica/alumina, the percentage conversion of neopentane was notably higher than that of isobutane, while on TT-HY this was not true. Possibly the zeolite catalyst is less effective for reacting the bulkier neopentane because of molecular sieve effects.

Under otherwise identical reaction conditions, lower reaction temperatures were required to reach comparable conversion levels with the remaining zeolite catalysts. Interestingly, H-Y(8.1), which was prepared from TT-HY by acid extraction to remove much of the extraneous alumina, was much more active for paraffin cracking (Table 3) than the parent catalyst. The main products were no longer hydrogen + butenes and methane + propene from isobutane, but propane, i-pentane, and n-butane. The contribution of primary reactions (calculated as the sum of hydrogen and methane) was only about 30% of the total conversion rate (calculated from the sum of primary products and paraffins).

The conversion rate of neopentane was much lower on H-Y(8.1) than that of isobutane. In addition to methane, isobutane was the single largest product. With isobutane, good agreement was again found for the conversion rates calculated by the two methods (A and B); in the case of neopentane, however, such agreement could not be expected because the paraffins produced are not equivalent to neopentane molecules reacted by H^- transfer. In contrast with the data given in Table 2, conversion levels calculated by Method A were about twice those calculated by Method B, suggesting that a considerable amount of carbon remained on the catalyst. Particularly notable was the small amount of C_4 olefins produced, relative to the methane formed. In this respect the present results, which were obtained in the steady-state flow mode, differed markedly from those from the pulse mode (*3*) for this catalyst.

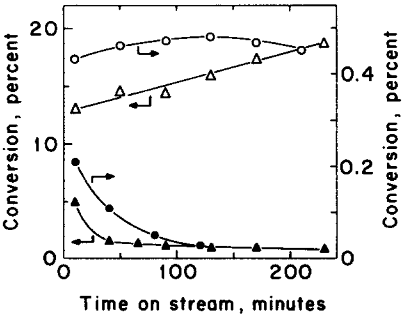

FIG. 1. Percent conversion of isobutane (open symbols) and neopentane (solid symbols) over catalyst LZ-210(6.0)[0.1] at 330°C (○, ●) and 430°C (△, ▲) as a function of time on stream; 400 mg of catalyst was used; $F/W = 5.7 \times 10^{-6}$ mol g^{-1} s^{-1}.

Very little extra-lattice aluminum was present (Table 1) in zeolite LZ-210 (12.0)[0.1].[3] On this catalyst the conversion rate and turnover frequencies for isobutane were much higher (Table 3) than those for H-Y(8.1). With increasing conversion, the contribution of primary reactions dropped to 8% of the total. Because of the relatively high percentage conversion (18.5%), a close agreement between the conversion rates (A

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[3] The (SiO_2/Al_2O_3) ratio is given in parentheses and the [% Na_2O] in brackets.

TABLE 3

Rates of Product Formation from Reaction of Isobutane or Neopentane over H-Y(8.1) and LZ-210(12.0)[0.1] Zeolites at 430°C[a]

Catalyst:	H-Y(8.1)		LZ-210(12.0)[0.1]	
Reactant:	Isobutane	Neopentane	Isobutane	Neopentane
H_2	25.1	0	66.9	3.0
CH_4	19.4	35.1	85.6	131.0
C_2H_6	0	0	3.6	1.0
C_2H_4	1.3	1.9	33.2	9.5
C_3H_8	23.8	0.6	533.7	5.5
C_3H_6	14.6	4.6	74.0	14.2
i-C_4H_{10}	R	15.1	R	62.1
n-C_4H_{10}	57.5	0	756.5	0
i-C_4H_8	22.0	3.0	43.6	6.5
n-C_4H_8	14.2	3.9	41.9	7.6
i-C_5H_{12}	24.2	0	412.4	3.7
(H_2 + CH_4)	44.5	35.1	152.5	134.0
Σ_2^5 (Paraffins)	105.5	15.7	1706.2	72.3
Conversion A[b]	150.0	50.8	1858.7	206.3
Conversion B[c]	158.3	28.4	1699.3	106.9
TOF B[d]	37.1	15.6	713.0	44.9
% Conversion	2.79	0.5	18.5	1.2
% Primary[e]	30	—[f]	8	—[f]

[a] Rates are given as 10–9 mol g^{-1} s^{-1}; 400 mg of each catalyst was used; the flow rate, F/W, was 5.7×10^{-6} mol g^{-1} s^{-1}.

[b] Conversion A = (H_2 + CH_4) + Σ_2^5 paraffin. With isobutane it could be assumed that the second term evaluates the rate of reaction by transfer of its tertiary hydrogen to form paraffins, e.g., by Reactions (2) and (3). With neopentane this is inappropriate as residue furnishes the hydrogen for paraffin formation. Nevertheless the calculation was carried out to emphasize the different behavior of the two molecules.

[c] Conversion B = $(1/n)\,\Sigma_1^5 jC_i$, where $n = 4$ for isobutane and $n = 5$ for neopentane, and j is the number of carbon atoms in each of the i products.

[d] TOF B is given as 10^{-6} molec. Al_F^{-1} s^{-1}.

[e] Percentage primary reaction was calculated as: [(H_2 + CH_4)/Conversion A] × 100.

[f] The paraffins produced cannot be taken as equivalent to neopentane reacted by H^{-1} transfer. Hence the secondary reactions cannot be approximated as the sum of the paraffins produced.

and B) was not expected because secondary cracking of oligomer and surface residue has distorted the product distribution. The rate of neopentane cracking did not increase as drastically on this catalyst [compared with H-Y(8.1)] as did that of isobutane. Here again the largest single product in addition to methane was isobutane.

The dependence of the percentage conversion of these two paraffins with time on stream is shown in Fig. 1 for LZ-210(12.0)[0.1] at two temperatures. The percentage conversion of isobutane increased with time on stream; at 430°C the increase was steady even after 4 h in spite of the relatively high conversion level. In contrast, the percentage conversion of neopentane dropped quickly with time on stream at both temperatures as the catalyst lined out. This suggested that rapid coking had occurred with neopentane but not with isobutane. In most cases, after reaction of isobutane there

TABLE 4

Rates of Conversion of Isobutane on M-46 and N-631-L Amorphous Silica–Alumina Pretreated at Different Temperatures (Reaction Temperature was 500°C[a])

Catalyst:	M-46		N-631-L	
Pretreatment temp.:	500°C	650°C	500°C	650°C
H_2	19.3	10.7	22.0	16.1
CH_4	4.8	2.4	9.8	4.0
C_2H_6	0	0	0	0
C_2H_4	0	0	0	0
C_3H_8	0	0	0	0
C_3H_6	4.1	2.0	7.7	4.0
$n\text{-}C_4H_{10}$	0	0	0	0
$i\text{-}C_4H_8$	17.4	10.0	17.6	15.9
$n\text{-}C_4H_8$	1.2	0	3.9	0
C_5H_{12}	0	0	0	0
$(H_2 + CH_4)$	24.1	13.1	31.8	20.1
Σ_2^5 Paraffin	0	0	0	0
Conversion A[b]	24.1	13.1	31.8	20.1
Conversion B[c]	22.9	12.1	29.7	19.9
TOF B[d]	5.09	2.69	3.56	2.39
% Conversion	0.20	0.11	0.27	0.18
% (Primary)[e]	100	100	100	100

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used; the flow rate, F/W, was 1.1×10^{-5} mol g^{-1} s^{-1}.

[b] Conversion A = $(H_2 + CH_4) + \Sigma_2^5$ paraffin.

[c] Conversion B = $\frac{1}{4}\Sigma_1^4 jC_i$, where j is the number of carbon atoms in each of the i products.

[d] TOF B is given as 10^9 molec. cm^{-2} s^{-1}.

[e] % Primary reaction was calculated as: $[(H_2 + CH_4)/\text{Conversion A}] \times 100$.

was no or only slight coloration of the catalyst, whereas after reaction of neopentane the catalyst was always more or less dark. Coke formation on this catalyst after 4 h on stream at 430°C was determined for both reactants by combustion and measurement of the combustion products (*4, 5*). From the CO_2 and H_2O formed it was determined that 32 mg of coke (H/C = 1.2) had been removed from 400 mg of catalyst after the reaction of neopentane, but only 2.5 mg (H/C = 1.5) after reaction of isobutane. The much larger quantity of hydrogen-deficient coke formed from neopentane affords an explanation for the rapid decay of the catalyst activity in neopentane.

Isobutane cracking experiments were carried out on the two silica–alumina catalysts pretreated in flowing dry O_2 overnight at either 500 or 650°C. As shown previously (*20*), treatment at higher temperatures resulted in further dehydroxylation of catalyst, resulting in a decrease in the Brønsted/Lewis acid site ratio. As shown in Table 4, the conversion of isobutane was lower on both catalysts after pretreatment at 650°C than after 500°C treatment. When the catalyst pretreated at 650°C was contacted with air at room temperature and then again given the 500°C pretreatment, the resulting catalyst returned to its initial activity. These two silica–aluminas from two very different sources behaved similarly. Dehydrogenation of isobutane was favored over demetha-

TABLE 5

Rate of Isobutane Conversion at 430°C on LZ-210(6.0) Zeolite with Different Concentrations of Na_2O[a]

Na_2O (wt %) Na/Al	2.03 0.17	0.45 0.04	0.02 0.002
H_2	8.2	22.7	41.3
CH_4	12.8	34.8	54.0
C_2H_6	0	0	0.4
C_2H_4	0	1.2	5.2
C_3H_8	7.9	24.4	73.8
C_3H_6	8.8	16.9	32.1
n-C_4H_{10}	10.5	51.5	167.9
i-C_4H_8	5.1	20.3	32.6
n-C_4H_8	0	9.5	32.9
i-C_5H_{12}	0	6.7	48.6
(H_2 + CH_4)	21.0	57.5	95.3
Σ_2^5 Paraffin	18.4	82.6	290.1
Conversion A[b]	39.4	140.1	385.4
Conversion B[c]	31.3	135.0	389.6
TOF B[d]	9.93	37.0	102.5
% Conversion	0.28	1.21	3.48
% (Primary)[e]	53	41	25
Chain length[f]	0.9	1.4	3.0

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used; the flow rate, F/W, was 1.1×10^{-5} mol g^{-1} s^{-1}.

[b] Conversion A = (H_2 + CH_4) + Σ_2^5 paraffin.

[c] Conversion B = $\frac{1}{4}$ $\Sigma_1^5 jC_i$, where j is number of carbon atoms in each of the i products.

[d] TOF(B) is given as 10^{-6} molec. $(Al_F - Na^+)^{-1}$ s^{-1}.

[e] Percentage primary reaction was calculated as: [(H_2 + CH_4)/Conversion A] × 100.

[f] Molecules reacted by H^- transfer/molecules reacted by Brønsted sites (primary reaction).

TABLE 6

Rates of Product Formation from the Reaction of Isobutane at 430°C and 2.33% Overall Conversion Level on LZ-210(6.0); Effects of Different Concentration of Na_2O; the Conversion was Maintained Constant by Varying F/W[a]

Na_2O (wt %) Na/Al F/W(mol g^{-1} s^{-1}) × 10^6	2.03 0.17 0.12	0.45 0.04 1.0	0.02 0.002 8.2
H_2	0.3	2.3	18.7
CH_4	0.4	3.0	24.4
C_2H_6	0	0	0
C_2H_4	0	0.3	2.7
C_3H_8	0.5	4.0	32.7
C_3H_6	0.2	1.7	13.7
n-C_4H_{10}	1.2	10.3	84.5
i-C_4H_8	0.3	2.2	17.7
n-C_4H_8	0.3	2.3	19.1
i-C_5H_{12}	0.4	3.3	27.3
(H_2 + CH_4)	0.7	5.3	43.1
Σ_2^5 Paraffin	2.1	17.6	144.8
Conversion A[b]	2.8	22.9	187.9
Conversion B[c]	2.8	23.1	191.1
TOF B[d]	0.89	6.33	50.2
% Conversion	2.33	2.33	2.33
% (Primary)[e]	25	23	23
Chain length[f]	3.0	3.3	3.4

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 600 mg of each catalyst was used.

[b] Conversion A = (H_2 + CH_4) + Σ_2^5 paraffin.

[c] Conversion B = $\frac{1}{4}$ $\Sigma_1^5 jC_i$, where j is the number of carbon atoms in each of the i products.

[d] TOF B is given as 10^{-6} molec. $(Al_F - Na^+)^{-1}$ s^{-1}.

[e] Percent primary reaction was calculated as: [(H_2 + CH_4)/Conversion A] × 100.

[f] Molecules reacted by H^- transfer/molecules reacted by Brønsted sites (primary reaction).

nation. The rate of H_2 formation approximately equaled the sum of the rates of formation of the butenes, and the methane formation rate was in fair agreement with that of propene. No paraffin formation was observed with these catalysts; i.e., only the primary reaction occurred, suggesting that the intermediate carbenium ions were not stabilized long enough for secondary reactions to occur.

Cracking of isobutane was studied on LZ-210(6.0) with different amounts of residual sodium. The results obtained at 430°C are presented in Table 5. As reported previously (*21*), decreasing the sodium content increased the percentage conversions (and the rates of formation of all of the products) much more effectively than could be accounted for by the incremental increase in the number of Brønsted sites (taken as the lattice Al concentration). The turn-over frequencies increased by approximately an order of magnitude. This behavior was reminiscent of the effects of poisoning with NH_3

TABLE 7

Rates of Product Formation from the Reaction of Isobutane at 2.33% Overall Conversion; Effects of Different Concentrations of Na_2O; $F/W = 1.1 \times 10^{-5}$ mol g^{-1} s^{-1} on LZ-210 (6.0)[a]

Na_2O (wt%) Na/Al Temp (°C)	2.03 0.17 480	0.45 0.04 442	0.02 0.002 415
H_2	78.8	40.2	25.9
CH_4	91.4	52.9	33.7
C_2H_6	0	0	0
C_2H_4	3.2	3.7	0
C_3H_8	31.5	43.8	45.2
C_3H_6	66.2	32.4	18.9
n-C_4H_{10}	47.3	91.3	116.9
i-C_4H_8	47.3	34.7	24.5
n-C_4H_8	53.6	36.5	26.4
i-C_5H_{12}	6.3	21.9	30.2
(H_2 + CH_4)	170.2	93.1	59.6
Σ_2^5 Paraffin	85.1	157.0	192.3
Conversion A[b]	255.3	250.1	251.9
Conversion B[c]	261.0	261.0	261.0
TOF B[d]	82.8	71.5	68.7
% Conversion	2.33	2.33	2.33
% (Primary)[e]	67	37	24
Chain length[f]	0.5	1.7	3.1

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used; the flow rate, F/W, was 5.7×10^{-6} mol g^{-1} s^{-1}.

[b] Conversion A = (H_2 + CH_4) + Σ_2^5 paraffin.

[c] Conversion B = $\frac{1}{4}\Sigma_1^5 jC_i$, where j is the number of carbon atoms in each of the i products.

[d] TOF B is given as 10^{-6} molec. $(Al_F - Na^+)^{-1}$ s^{-1}.

[e] Percentage primary reaction was calculated as: [(H_2 + CH_4)/conversion (A)] × 100.

[f] Molecules reacted by H^- transfer/molecules reactedby Brønsted sites (primary reaction).

(*8*, *9*). Thus, as the poisoning was removed, the acid strength of the catalyst increased along with a concomitant increase in the total conversion and an increase in the selectivity for formation of paraffins. The chief products in each case were n-butane and propane. Pentane formation (oligomerization) became important and, when present, was exclusively isopentane; its concentration was always lower than that of propane.

At constant temperature an increasing conversion will increase the partial pressure of all intermediate species. This should lead to a higher probability for secondary reactions and this factor should be at least partly responsible for the observed effects. In order to test this point, the total conversion level was maintained constant at 2.33% over the same catalyst at 430°C by increasing the space velocity, and the results are presented in Table 6. Interestingly the same large increases in rate and TOF were observed, but without a change in selectivity. The percentage primary reaction remained constant as did the length of the carbenium ion chains.

The results of Tables 5 and 6 may be compared with those of Table 7 where the conversion was maintained constant at constant flow rate by changing the temperature. In these experiments the yield of each product was plotted against the total conversion obtained at temperatures required to overlap 2.33%. The values presented in Table 7 were interpolated from curves corresponding to this conversion. The remarkable feature of these results was that while the absolute rates of the primary reactions decreased with lowering the temperature (in spite of the increasing acidity) the absolute rates of reaction of isobutane by H^- transfer actually increased, leading to higher paraffin concentrations in the products. Similar behavior has been observed previously (*8*, *18*).

The effects of olefins on the cracking of isobutane and on the product distribution were studied by addition of small amounts of olefins to the feed (olefin/isobutane = 0.006). The results of experiments carried out over LZ-Y82 at 370°C are given in Table 8. The data showed a continuous utilization of the olefin added, and this increased in the sequence $C_2H_4 \ll C_3H_6 < i$-C_4H_8. The rate of hydrogen formation was not significantly influenced by olefin addition, although the rate of methane formation was diminished. Ethylene addition decreased the percentage conversion, but propene and i-butene addition increased it. With the latter two, much of the added olefin appeared as the corre-

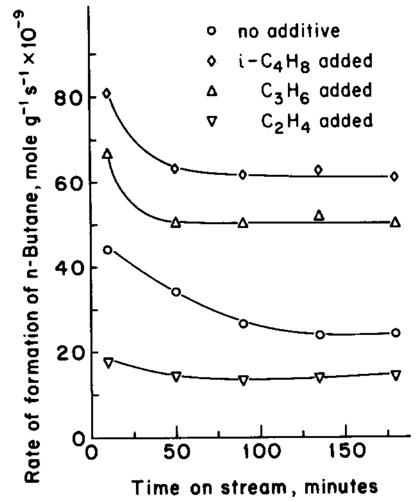

FIG. 2. Dependence of the rate of formation of *n*-butane on time on stream over LZ-Y82 at 370°C; the feed rate of *i*-butane was 5×10^{-6} mol g^{-1} s^{-1} and that of added olefin was 3×10^{-8} mol g^{-1} s^{-1}.

sponding paraffin, but the formation of *n*-butane and isopentane was also enhanced. Thus, the olefins influenced the product distribution in different ways. Without additives, propane and *i*-pentane formed in approximately equimolar quantities. Ethylene suppressed, while *i*-butene accelerated, *i*-pentane formation more significantly than propane formation. Propylene, however, understandably enhanced propane formation more than *i*-pentane formation. As can be deduced from the data of Table 8, the increase in rate of propane formation was higher than the net rate of propene consumption. Similar conclusions can be reached with *i*-butene, but the opposite effect was found with ethylene. Ethylene lowered the percentage conversion of isobutane, but had little effect on the percentage primary reaction. The other two olefins very much enhanced the activation of isobutane by H^- transfer. Similar effects have been reported recently (*22*) for methylpentanes.

Figure 2 shows the dependence of the *n*-butane yield on time on stream with and without olefin additives. Similar results were obtained for propane. The presence of olefins in the feed decreased the time required to line out the catalyst into a steady-state conversion.

On catalysts where paraffin formation was low, dehydrogenation always exceeded demethanation; on catalysts where significant paraffin formation occurred, the reverse was true. This could not be attributed to utilization of H_2 by direct hydrogenation of olefins. In an experiment carried out under otherwise identical conditions with 1% propene in excess hydrogen over LZ-210(6.0)[0.02], no indication of propane formation was found.

DISCUSSION

Since isobutane has a tertiary hydrogen while neopentane does not, it was anticipated that the former would establish carbenium ion chain reactions in the secondary chemistry while neopentane could not. This was established experimentally. The data presented in Tables 2 and 3 were obtained under comparable conditions. At low conversions over the weak acids (Table 2) very little secondary reaction occurred; the rates of formation of C_3H_6 and C_4H_8 from isobutane corresponded fairly well with those of CH_4 and H_2, respectively. Conversion A agreed fairly well with Conversion B, and the contribution of the primary reactions approached 100%. Paraffin formation was small and no C_5 products were observed, confirming that contributions from secondary reactions were negligible.

Similarly the *i*-C_4H_8 produced from neopentane agreed fairly well with the CH_4 formation, and no paraffins or C_5 isomers were detected. There was, however, one significant difference: the rate, Conversion B, significantly exceeded Conversion A, and this corresponded to the extra *n*-C_4H_8 which must have resulted from reactions of neopentane which did not produce CH_4 (as did the production of C_2H_4 and C_3H_6). It is tentatively suggested that reactions involving surface residue, perhaps with CH_3 transfer, are responsible for this extra conversion.

TABLE 8

Rates of Product Formation from Isobutane over LZ-Y82 at 370°C with Different Olefins Added to the Feed (Flow Rates were 5 × 10^{-6} mol *i*-Butane g^{-1} s^{-1} + 3 × 10^{-8} mol Olefin g^{-1} s^{-1})[a]

Additives	None	C_2H_4	C_3H_6	*i*-C_4H_{10}
H_2	1.4	1.4	1.3	1.3
CH_4	5.6	2.4	2.4	2.4
C_2H_6	0	0	0	0
C_2H_4	0	(−1.0)	0.8	0.8
C_3H_8	4.7	3.3	40.5	29.5
C_3H_6	1.2	0.7	(−12.4)	8.3
n-C_4H_{10}	24.3	14.1	50.3	60.6
i-C_4H_8	2.9	1.8	8.3	(−14.5)
i-C_4H_8	0	0	1.4	1.5
2-C_4H_8	0	0	4.9	6.2
i-C_5H_{12}	4.6	0	24.2	37.3
n-C_5H_{12}	0	0	1.0	1.4
H_2 + CH_4	7.0	3.8	3.7	3.6
Σ_2^5 Paraffin	3.6	17.4	116.0	128.8
Conversion A[b]	40.6	21.2	119.7	132.4
Conversion B[c]	38.8	19.6	118.6	131.5
TOF B[d]	14.6	1.4	44.8	49.6
% Conversion	0.78	0.39	2.38	2.63
% (Primary)[e]	17	18	3.1	2.7
$C_3H_8/\Sigma C_5H_{12}$	1.02	∞	1.61	0.76

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of catalyst was used.

[b] Conversion A = (H_2 + CH_4) + Σ_2^5 paraffin.

[c] Conversion B = $(\frac{1}{4}) \Sigma_1^5 jC_i$, where *j* is the number of carbon atoms in each of the *i* products.

[d] TOF B is given as 10^{-6} molec. Al_F^{-1} s^{-1}.

[e] Percentage primary reaction was calculated as: [(H_2 + CH_4)/Conversion A] = 100.

Over more active Y-zeolite catalysts (Table 3), the overall conversion rates of isobutane were much higher than those of Table 2, even at much lower temperature. Nevertheless, similar underlying trends were detected and these were dominated by secondary H^- transfer processes. The two largest single products were now *n*-C_4H_{10} and C_3H_8. The former resulted from isomerization of the *t*-butyl to the sec-butyl cation followed by H^- transfer from the parent isobutane, thus establishing a carbenium ion chain reaction [see Eq. (3)]; C_3H_8 was formed similarly by H^- transfer to the isopropyl cation formed either in the primary step or as a product of cracking of a C_8 oligomer. With neopentane these processes did not occur because the primary hydrogens of this molecule are inactive for H^- transfer, even though the same *t*-butyl ion was formed in the initiation step.

With these catalysts isopentane was an important product of the isobutane reactions. This suggested that oligomerization followed by skeletal isomerization and cracking occurred and that the lifetime of the metastable carbenium ions was sufficient to make these bimolecular processes possible. Interestingly, comparable amounts of C_3 products were produced when account was taken of that formed as a result of the primary reaction (measured by CH_4).

The results with neopentane as reactant were quite different. The products were mainly C_4-hydrocarbons together with small amounts of C_3. Conversion B was only about half Conversion A measured by the CH_4 produced. This suggested that a considerable portion of the i-C_4H_8 formed in the primary reaction was retained by the catalyst as a surface residue. This was confirmed by the data of Fig. 1, which shows the rapid decay in catalytic activity in the flow reactor (and the much higher coking rate recorded) when neopentane was the feed in contrast with the nearly stable activity and much lower coking rate with isobutane. A small amount of H_2 was produced in the reaction over the most active LZ-210(12.0)[0.1]. This was approximately balanced by isopentane. Olah *et al.* reported that the isopentyl ion and H_2 resulted from reaction of neopentane in magic acid (*16*).

Some years ago, the effects of pretreatment temperature on the rates of isomerization of cyclopropane and the *n*-butenes (*20*) were investigated over Catalyst M-46. The rates fell by about an order of magnitude as the catalyst was dehydroxylated, i.e., as the hydrogen content was reduced. Since the mechanisms of these reactions require Brønsted protons, it was concluded that the surface concentrations of these were diminished by dehydroxylation. In the present work, we have used this approach in the study of the cracking of isobutane. The results presented in Table 4 responded as before, thus supporting the view that the primary decomposition of isobutane is catalyzed by Brønsted acids. This additional evidence should be added to the reasons already presented (*7*) in support of this chemistry.

Alternative ways to reduce the acidity of zeolites include replacement of Brønsted sites with Na^+ or NH_4^+ cations. It is already known (*8, 9, 21*) that this lowers catalytic activity much more than expected from the change in the extensive factor of the acidity (Brønsted sites/g). In the present work the effect of residual Na^+ was studied further to document effects on selectivity. These experiments were carried out in three different ways. As expected, in all cases the activity increased markedly as the Na^+ concentration was lowered. When the temperature and flow rate were held constant (Table 5), the percentage conversion and TOF increased by about an order of magnitude as the Na/Al ratio was decreased from 0.17 to 0.002, i.e., as the last 17% of the sites were freed. The rates of both the primary and secondary processes increased, the former by a factor of about 5 and the latter by a factor of 15; the fraction reacted by the primary reaction pathway fell from 53 to 25%. These huge rate increases cannot be explained by the modest 17% increase in the extensive factor alone; the intensive factor must also have increased, either by increasing the strength of all of the sites or by creating a small fraction of hyperactive sites as claimed by Fritz and Lunsford (*21*). Thus, it might be concluded that not only were *chains* being initiated faster, but also that the resulting *t*-butyl carbenium ions became more stable (longer lived) as the residual Na^+ content was decreased. Another aspect must be considered, however, viz., that because the percentage conversion increased, higher concentrations of all reactive species were present and this may have enhanced the rates of the secondary reaction processes. This was substantiated by the results of experiments carried out at the same temperature, but with the conversion held constant at 2.33% by varying F/W. The results (Table 6) showed that while the overall conversion rates increased by nearly two orders of magnitude, the fraction reacted in the primary process, and the length of the carbenium ion chains remained constant. Indeed, the individual products all were formed in about the same proportion on all three catalysts. Presumably this is the result of a nearly constant gas-phase composition over the catalysts brought about by adjusting the space velocity to maintain a constant percentage conversion. It follows, therefore, that removal of Na^+ greatly increased both the rates of chain initiation (the primary formation of the *t*-butyl and isopropyl cations) and the rates of the secondary reactions (isomerization, hydride transfer, and oligomerization). The acidity was enhanced by the removal of Na^+ and its strength was increased, but this was not reflected by an increase in carbenium ion stability. When the gas-phase composition was not held constant, the contribution of secondary processes varied with the conversion level (see % Primary, Table 5.) In all of these experiments, *n*-butane was the single largest product and usually more C_3H_8 than C_3H_6 was formed. These two paraffins accounted for the major portion of the H^- transfer activity.

Experiments were made in which the same 2.33% conversion was maintained at constant flow rate by varying the temperature and these results are presented in Table 7. Under these conditions the overall conversion rate was constant [Conversions A and B], but the selectivity changed. As the catalyst activity increased corresponding to the removal of Na^+, lower temperatures were required and the contribution from secondary reactions increased. These changes probably reflected increasing stability of the intermediate carbenium ions at lower temperature, and vice versa, because the rates of the primary reaction ($H_2 + CH_4$) decreased as expected as the temperature was lowered. This decrease was, however, almost exactly compensated by an increase in the rates of reaction by hydride transfer and in chain length, both of which increased together with decreasing temperature (*n*-C_4H_{10} and C_3H_8) as did oligomerization (C_5H_{12}). These reactions between gas molecules and carbenium ions would be accelerated by an increased lifetime of individual carbenium ions at lower temperature. Thus, the selectivity for the primary monomolecular step increased with temperature as reported previously (*8*, *18*). The Na^+ poisoning experiments confirm and amplify the related findings of Fritz and Lunsford (*21*) for *n*-hexane cracking. Moreover, it now seems evident that poisoning the catalyst with small amounts of NH_3 (which reacts with Brønsted sites forming NH_4^+) is another manifestation of the same phenomenon. The result is a weakening of the remaining Brønsted sites with a concomitant decrease in the rates of the primary monomolecular initiation reaction and in the resulting steady-state concentration of metastable carbenium ions.

The data presented in Tables 5–7 provide food for further thought. As described above, each set of data is internally consistent and the observations are as expected. Problems arise, however, when cross-comparisons of these data are made to further delineate the mechanism. For example, for *each* catalyst at fixed temperature XF/g = constant in the limit of differential reaction conditions ($X \rightarrow 0$). Values of 3.1, 13.3, and 38.3 × 10^{-8} mol g^{-1} s^{-1} may be deduced for the catalysts of Table 5 containing 0.17, 0.04, and 0.002 Na/Al, respectively. The corresponding values from Table 6 are 0.3, 2.3, and 19.0 mol g^{-1} s^{-1}. The disagreement is accentuated when it is recalled that the latter values were obtained at lower flow rates than that used for the experiments of Table 5, i.e., longer contact times producing lower rates. Further, if the gross kinetics are first order for the primary initiation steps, $R_1 = k_1P_{iC_4H_{10}}$, and second order for the secondary (mainly H^- transfer) reactions, $R_2 = k_2P_{iC_4H_{10}}$, then it follows that $R_2/R_1 \approx$ constant in the limit of low conversion, independent of space velocity. Values deduced from Table 5 are 0.85, 1.6, and 3.1 while from Table 6, 3.0, 3.3, and 3.4 are obtained. Clearly, further study will be necessary to clarify these points.

Recently Abbot and Wojciechowski (*22*) reported on the effects of small amounts of added olefins on the cracking of both linear and branched chain paraffins. The reaction of linear paraffins was found to proceed via protonation of the feed molecules on Brønsted sites. Such molecules have only primary and secondary hydrogens and so H^- transfer is slow. As a consequence, the reaction was inhibited by the competition for the same sites by olefin molecules. Branched chain hydrocarbons, on the other hand, contain tertiary hydrogens and once the reaction has been initiated by the protonation on Brønsted sites, the resulting carbenium ions can act as hydride acceptor sites for the reactant paraffin. Thus, during the subsequent course of the reaction, cracking of the branched feed molecules occurred predominantly by the classical carbenium ion chain mechanism. Related results for isobutane are presented in Table 8 and may be similarly interpreted. Both C_3H_6 and i-C_4H_8 enhanced the conversion of isobutane, but C_2H_4 inhibited it slightly. The former two olefins are readily protonated and the resulting carbenium ions can accept hydride ions from isobutane as discussed above. This then forms the dominant pathway with the percentage primary reaction falling to about 3% (from 17%). This did not occur with C_2H_4, which is not easily protonated. Interestingly, carbenium ions formed on Brønsted centers may be regarded as Lewis acid sites and hydride transfer may then be regarded as H^- abstraction by this Lewis acid. This is the only case where convincing evidence exists for this process.

In the present work these ideas were pushed to the extreme by comparison of the reactions of isobutane, which has a facile tertiary hydrogen, with those of neopentane, which has only inactive primary hydrogens. The former behaved as expected, as did the latter in the primary step in which methane and the same t-butyl cation were produced. Since the latter had no ready source of H^-, desorption of olefins would seem inevitable. This occurred with silica–alumina. However, olefins are not easily released from the surfaces of stronger acids such as HY and HM. With these the products obtained were rich in paraffins, isobutane being the single largest product. Our data suggest that the olefins retained by the zeolites have undergone oligomerization and reactions leading to a hydrogen-deficient conjunct polymer. The way this process leads to the formation of relatively large quantities of isobutane has been described previously (*9*). This surface residue both furnishes the hydrogen required for release of the paraffins and forms the coke which rapidly poisons the Brønsted sites. When isobutane is the reactant, its tertiary hydrogen acts to keep the surface clean from this strongly held "poison."

In the present work catalyst TT-HY contained more extra lattice than lattice Al atoms. It was relatively inactive compared with H-Y(8.1) which was prepared from it by acid extraction to remove extraneous alumina. This was contrary to the results of Haag (*23*) and of Beyerlein *et al.* (*3*), who reported that extra-lattice aluminum enhanced catalytic activity. Evidently more than one kind of extra-lattice aluminum exists and generalizations cannot be made.

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