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The Conversion of Butanes in HZSM-5

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The distribution of products from the conversion of iso- and normal butane on HZSM-5 has been determined from 300 to 550°C over a wide range of conversions. The results clearly indicate that the nature of the products changes significantly in altering both the temperature and conversion conditions. High temperatures and low conversions favor low molecular weight products expected from a protolytic or radical attack on the butane. Reverse conditions favor C_3 and higher hydrocarbons. These products are indicative of a classical carbenium ion mechanism. As conditions were changed the transition in mechanism was indicated by the amount of methane produced. For the first time H_2 was detected as a primary product in the conversion of normal butane indicating that a tertiary C–H bond is not required for its production.

INTRODUCTION

Despite the fact that paraffin cracking on solid acid catalysts has been studied for many years it is still the subject of controversy (*1–17*). Until recently the reaction products were rationalized by the classical carbenium ion mechanism where initially formed carbenium ions underwent chain reactions via processes such as hydride transfer, oligomerization, and β cracking. Usually the main products were C_3 to C_6 paraffins and olefins with smaller hydrocarbons and hydrogen being distinctly absent. While many paraffin–catalyst systems gave these products (*12–21*), the reported detection of hydrogen, methane, and ethane as major products by a number of workers (*1–7, 22–26*) as well as unexpected values of paraffin/olefin ratios (*3*) necessitated the revision of the original carbenium ion mechanism.

Guided by the fact that small product molecules are typical of gas phase radical decomposition McVicker *et al.* (*2*) suggested that feed paraffin molecules combine with electron acceptor sites (*27*) on solid acid catalysts to form radical ions which decompose to small alkanes or hydrogen and alkenes. The latter may then form carbenium ions which may isomerize, oligomerize, and crack. Haag and Dessau (*1*) and Corma *et al.* (*3*) proposed an alternative mechanism based on Olah *et al.*'s interpretation of paraffin reactions in superacids (*29, 30*), where small product molecules are also obtained. The initial step of this mechanism is the direct protonation of a paraffin to form a nonclassical pentacoordinated carbonium ion. This decomposes to form a small alkane or hydrogen and a carbenium ion which deprotenates to an olefin. By assuming that both this "protolytic" mechanism and the classical carbenium ion mechanism operated in varying proportions Haag and Dessau were able to account for the mix of products for 3-methyl pentane and hexane on silica–alumina and zeolite catalysts. Their results indicated that high temperatures and low conversions favored the protolytic mechanism.

More recently Lombardo and Hall (*5*) have proposed a single mechanism to account for the observed product distribution of neopentane and isobutane on silica–alu-

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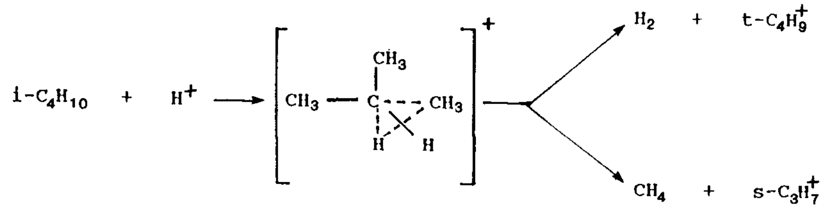
mina and zeolite catalysts of varying acid strength. The initial step, identical to that of Haag and Dessau, is the direct protonation of the paraffin to form the carbonium ion which decomposes to form a carbenium ion and an alkane or hydrogen. For isobutane



The *t*-butyl cation equilibrates with its isomerized forms and subsequently an equilibrium is established between all carbenium ions and their corresponding alkenes.

$$\begin{array}{llll} s-C_3H_7^+ & +A^- \rightleftharpoons C_3H_6 & & +HA \\ t-C_4H_9^+ & +A^- \rightleftharpoons i-C_4H_8 & & +HA \\ \quad\upharpoonleft\downharpoonright & & & \\ n-C_4H_9^+ & +A^- \rightleftharpoons n-C_4H_6 & & +HA \end{array}$$

According to Lombardo and Hall the key point is the lifetime of the carbenium ions. If the solid is a weak acid equilibrium lies far to the right, the lifetime of these ions is short, and the above reactions along with the initial formation of the carbenium ion constitute the complete mechanism. For convenience the reactions leading to alkenes can be considered to be primary. For these catalysts the only products to be expected are hydrogen, methane, propene, and butenes.

For strong acid catalysts or under the right reaction conditions the equilibrium lies far to the left and the carbenium ion lifetime is long. The ions may then undergo secondary reactions that comprise the classical carbenium ion mechanism: oligomerization, rearrangements, β scission, and hydride transfer. For isobutane as the feed this results in propane, *n*-butane, pentanes, and higher hydrocarbons. Any product distribution can then be explained by postulating intermediate lifetimes for the C_3 and C_4 carbenium ions and hence a differing proportional contribution of the primary and secondary reactions. This single mechanism, composed of primary and secondary reactions with a well-defined set of products for each, neatly encompasses the two separate mechanisms proposed by Haag and Dessau.

A similar mechanism for *n*-butane would result in hydrogen, methane, ethane, and their corresponding carbenium ions, $s-C_4H_9^+$, p-$C_3H_7^+$, and $C_2H_5^+$. Depending on the lifetime these latter ions can form the corresponding alkenes or oligomerize and crack. For weak acid catalysts the expected products would be hydrogen and butenes, methane and propene, and ethane and ethylene while for strong acids the products would be mainly propane, isobutane, and higher hydrocarbons.

The mechanisms by McVicker *et al.* and Lombardo and Hall differ only in the step leading to the initial formation of the carbenium ions. Overall both mechanisms predict the same distribution of products so that they cannot be differentiated by this means. The evidence for radical ion species in catalytic conversion is equivocal at the present time. Lombardo and Hall have noted that if electron acceptor sites are involved, oxidative and reductive treatments of catalysts and the inclusion of hydrogen in the feed should have a significant effect on radical ion formation and hence on the amount of products. Such procedures, however, have not resulted in different product distributions for the case of neopentane and isobutane on HZSM-5 (*4*, *5*).

Some investigators have suggested that the methoxyl methyl radical is important in the conversion of methanol to gasoline (*8*,*9*) but Hunter *et al.* (*10*) have provided evidence against the involvement of radicals in this reaction. In their study of the effect of oxygen on the conversion of light paraffins on HZSM-5 Centi and Golinelli (*11*) concluded that radical ions are of minor importance in the methanol conversion but that they may play a more critical role in alkane conversion. It is clear from the available data that the role of ion radicals, if any, remains obscure and as Hall *et al.* (*7*) have pointed out neither mechanism has yet been proved to be correct.

In this paper we report results on the cracking of iso- and normal butane on HZSM-5 from 300 to 550°C. In addition to the temperature variation we are particularly interested in a detailed examination of the change in product distribution with conversion at each temperature. Very few investigations emphasize this aspect when attempting to correlate product distributions to reaction mechanisms. We hope that our results will clarify the regime under which the primary reactions leading to alkenes and secondary reactions (classical carbenium ion mechanism) leading to alkanes dominate.

METHODS

Catalytic reactions were carried out in a fixed-bed flow reactor consisting of a 0.63-mm stainless-steel tube whose temperature was monitored and controlled by two thermocouples. Temperatures selected were 300, 400, 450, 500, and 550°C. The flow rate was varied to change the contact time and hence the conversion. These ranged from well below 1% to greater than 30%. At lower temperatures approximately 100 mg of catalyst was used but at high temperatures it was necessary to reduce this to 10 mg to decrease the contact time to the low values required for conversion under 10%.

The feed at 1 atm pressure consisted of 10% butane in a dried nitrogen stream and was preheated prior to entry into the reactor or the gas chromatograph. The butanes obtained from Matheson were 99.7% pure with propane and the butane isomer being the only detectable impurities. These were determined prior to each run and taken into account in calculating product distributions.

A procedure by Ball and Stewart (*42*) was used to synthesize Zeolite ZSM-5 (Si/Al = 14). The ammonium form (*43*) was calcined in air at 550°C.

Each zeolite sample in the reactor was ramped over a 2-h period to 115°C in a nitrogen stream, held for 1 h, ramped to 350°C over 4 h, ramped to 550°C, and held at that temperature for 16 h. The temperature of the catalytic run was then set to the desired value. In carrying out the runs the temperatures were selected in a random fashion.

Product detection was accomplished with a Varian 6000 gas chromatograph equipped with TCD and FID detectors. The reactor output was fed into the GC via a short section of tubing and control valve both of which were heated to ensure that all products would remain in the gas phase. In order to detect hydrogen the product stream was split into two parts. The first passed through a 1.3 m × .3 mm i.d. molecular sieve 13 packed column linked to the TCD where hydrogen and methane were detected. The columns were then backflushed to prevent column clogging by high molecular weight material. The electronics were switched and the FID monitored as the second part was fed into a 50 m × 0.32 mm i.d. PLOT–Al_2O_3 capillary column which could separate all butene and pentane isomers in addition to the standard resolution of C_1 to C_7 aliphatics and aromatics.

Initial time on stream studies revealed very little change in product distribution with time at any particular flow rate. Conversion rates remained relatively constant with time. While coke determinations were not carried out a visual examination of the catalyst showed very little darkening even after many runs.

Prior to catalytic runs the contribution by thermal cracking was determined under conditions which gave the maximum conversions when the catalyst was present, i.e., high temperature and low flow rates. The maximum converison at 550°C and the lowest flow rate possible was 0.1%. The corresponding conversion with zeolite present was 35%. The products from isobutane were hydrogen, methane, propene, and isobutene. No butene isomers or normal butane were obtained. With normal butane as the feed the products were hydrogen, methane, ethane, ethylene, propene, and the three normal butenes. No isobutane or isobutene was detected. These products are precisely those to be expected from free radical reactions which do not favor isomerizations.

RESULTS AND DISCUSSION

Isobutane

Tables 1–5 show the product selectivities at 300 to 550°C over a wide range of conversion. Also shown at the bottom of each table are (a) the sum of hydrogen and methane, (b) the sum of all C_3 and C_4 products, (c) the paraffin/olefin ratio for C_3 and C_4 products, and finally (d) the total mass of the products as a check on the product distribution. Since selectivities are given for 100 mol of isobutane converted the total mass of the products should equal 5800 g.

Initial molar selectivities obtained by extrapolating product selectivity plots to zero converison are given in Table 7. These are useful in determining the initial reactions leading to products.

If the reaction is purely primary both (a) and (b) should equal the total amount of isobutane converted (100 mol) and the amount of H_2 formed should equal the amount of C_4 while the same should be true for the values for C_1 and C_3 products. Since hydride transfer does not occur for primary reactions no C_3 or C_4 alkanes are expected. If, on the other hand, oligomerization followed by β cracking is a contributory path the total C_3 plus C_4 products should be less

TABLE 1

Mol Product per 100 Mol of Butane Converted (Isobutane–HZSM-5 at 300°C)

Conversion mol%	0.23	0.87	1.8	7.6	11.3
Hydrogen	—	—	—	—	1.8
Methane	—	—	—	—	1.1
Ethane	—	—	—	—	0.9
Ethylene	9.3	6.5	5.2	4.0	3.1
Propane	43.5	49.0	54.2	57.0	59.8
Propene	13.8	10.3	8.7	5.0	3.6
n-Butane	19.5	20.7	21.3	17.5	14.9
trans-Butene	3.1	1.5	1.3	0.5	0.4
1-Butene	—	—	—	—	0.2
Isobutene	7.8	4.3	3.6	2.0	1.0
cis-Butene	—	—	1.0	0.7	0.3
Σ Butenes	10.9	5.8	5.9	3.2	1.9
Branched pentanes	18.1	17.1	13.6	13.0	21.6
n-Pentane	—	4.1	5.1	5.9	2.8
Pentenes	—	—	—	0.2	0.2
Hexane/hexene	—	—	—	2.0	1.3
Aromatics	—	—	—	0.5	0.2
$H_2 + C_1$	—	—	—	—	2.9
$C_3 + C_4$	87.7	85.5	90.1	90.5	80.2
C_3/C_3^{2-}	3.2	4.8	6.2	11.0	17.0
C_4/C_4^{2-}	1.8	3.6	3.6	5.5	7.8
Total mass	5797	5821	5798	5796	5791

TABLE 2

Mol Product per 100 Mol of Butane Converted (Isobutane–HZSM-5 at 400°C)

Conversion mol%	0.22	1.4	5.9	14.2	28.6
Hydrogen	25.6	8.2	3.5	1.7	1.4
Methane	21.6	5.7	2.4	1.3	1.3
Ethane	—	—	0.6	0.9	1.0
Ethylene	13.9	11.1	6.0	3.6	2.1
Propane	19.1	51.1	62.4	69.5	83.9
Propene	26.3	16.2	8.4	4.7	2.5
n-Butane	27.5	19.4	18.9	18.8	17.0
trans-Butene	4.6	2.2	1.1	0.7	0.3
1-Butene	—	0.8	0.4	0.3	0.1
Isobutene	14.7	5.0	2.6	1.5	0.7
cis-Butene	3.9	1.7	0.7	0.4	0.2
Σ Butenes	23.2	9.7	4.8	2.9	1.3
Branched pentanes	—	7.0	11.1	10.5	8.1
n-Pentane	—	3.9	3.2	3.0	1.8
Pentenes	—	—	0.9	0.3	—
Hexanes/hexenes	—	—	0.1	1.6	—
Aromatics	—	—	—	—	0.1
$H_2 + C_1$	47.2	13.5	5.9	3.0	2.7
$C_3 + C_4$	95.8	96.4	94.5	95.9	105.
C_3/C_3^{2-}	0.7	3.2	7.4	15.	34.
C_4/C_4^{2-}	1.2	2.0	3.9	6.5	13.
Total mass	5768	5800	5798	5789	5781

TABLE 3

Mol Product per 100 Mol of Butane Converted (Isobutane–HZSM-5 at 450°C)

Conversion mol%	.69	1.4	4.3	10.6	16.5	28.6
Hydrogen	36.1	23.2	14.0	10.1	9.0	5.2
Methane	35.0	26.1	13.4	8.7	7.4	5.9
Ethane	—	—	1.0	1.4	1.8	2.5
Ethylene	15.0	19.4	20.7	14.7	13.1	8.7
Propane	16.1	27.6	53.5	61.8	67.2	78.8
Propene	41.5	38.2	23.7	16.4	14.4	9.6
n-Butane	11.4	12.6	12.8	13.6	13.2	13.5
trans-Butene	7.5	5.9	2.5	1.9	1.7	1.1
1-Butene	3.1	2.8	1.0	0.9	0.7	0.5
Isobutene	14.7	10.1	5.3	4.1	3.3	2.3
cis-Butene	4.7	3.7	1.7	1.3	1.2	0.7
Σ Butenes	30.0	22.5	10.5	8.2	6.9	4.6
Branched pentanes	—	—	1.5	4.7	3.2	3.5
n-Pentane	—	—	1.5	1.7	1.6	1.3
Pentenes	—	—	0.7	1.0	1.1	0.7
Hexane/hexene	—	—	—	0.5	0.6	0.6
Aromatics	—	—	—	—	0.2	0.3
$H_2 + C_1$	71.0	49.3	27.4	18.8	16.4	11.1
$C_3 + C_4$	99.0	101.	101.	100.	102.	107.
C_3/C_3^{2-}	.39	.72	2.3	3.8	4.7	8.2
C_4/C_4^{2-}	.38	.56	1.2	1.3	1.9	2.9
Total mass	5850	5817	5797	5774	5714	5803

TABLE 4

Mol Product per 100 Mol of Butane Converted (Isobutane–HZSM-5 at 300°C)

Conversion mol%	1.3	1.6	5.5	13.4	21.7	35.1
Hydrogen	35.5	21.1	27.2	20.2	17.0	13.9
Methane	53.4	45.2	33.7	25.5	18.0	14.6
Ethane	—	0.7	0.8	1.6	2.5	3.5
Ethylene	2.9	13.9	25.2	33.7	25.8	19.8
Propane	1.7	8.7	25.1	38.0	51.4	61.0
Propene	59.4	52.0	47.6	34.2	24.6	18.8
n-Butane	0.4	3.8	5.8	6.5	8.6	9.1
trans-Butene	10.0	8.1	3.2	2.8	2.3	1.9
1-Butene	5.5	5.1	2.3	1.6	1.3	1.0
Isobutene	17.5	12.3	8.1	5.5	4.4	3.6
cis-Butene	6.9	6.8	2.9	2.4	1.3	1.2
Σ Butenes	39.9	32.3	16.5	12.3	9.3	7.7
Branched pentanes	—	0.7	0.9	1.0	1.8	2.3
n-Pentane	—	—	0.2	0.3	0.7	0.8
Pentenes	—	—	1.0	1.3	1.6	1.3
Hexane/hexene	—	—	—	—	0.4	1.0
Aromatics	—	—	—	—	0.5	1.3
$H_2 + C_1$	88.9	77.3	60.9	45.7	35.0	28.5
$C_3 + C_4$	101.	96.8	95.0	91.0	95.1	96.6
C_3/C_3^{2-}	.03	.17	.53	1.1	2.1	3.2
C_4/C_4^{2-}	.01	.12	.35	.53	.92	1.2
Total mass	5855	5842	5840	5794	5821	5813

TABLE 5

Mol Product per 100 Mol of Butane Converted (Isobutane–HZSM-5 at 550°C)

Conversion mol%	7.8	12.3	15.5	36.9	35.7
Hydrogen	32.5	27.5	30.4	31.3	32.7
Methane	62.0	59.7	57.0	54.8	51.5
Ethane	—	—	0.2	0.5	1.0
Ethylene	3.8	7.1	10.7	20.4	31.9
Propane	2.2	3.4	3.8	4.5	8.6
Propene	68.9	67.0	64.7	63.2	57.2
n-Butane	1.1	1.2	1.1	0.9	1.2
trans-Butene	6.2	6.1	6.3	5.3	4.3
1-Butene	4.9	4.8	5.0	4.3	3.4
Isobutene	11.9	10.9	10.9	9.5	7.3
cis-Butene	4.6	4.5	4.6	4.4	3.3
Σ Butenes	27.6	26.3	26.9	23.5	18.3
Branched pentanes	1.3	1.7	1.3	0.8	0.8
n-Pentane	—	0.1	0.2	0.4	0.1
Pentenes	—	—	0.1	0.1	0.4
Hexane/hexene	—	—	—	—	—
Aromatics	—	—	—	—	0.4
$H_2 + C_1$	94.5	87.2	87.4	86.2	84.2
$C_3 + C_4$	99.8	97.9	96.5	92.1	85.3
C_3/C_3^{2-}	.03	.05	.06	.07	.15
C_4/C_4^{2-}	.04	.05	.04	.04	.07
Total mass	5851	5841	5845	5836	5832

TABLE 6

Paraffin/Olefin Ratio: Dependence on Conversion and Temperature

Conversion			Temperature (°C) Isobutane C_3/C_3^{2-}		
mol %	300	400	450	500	550
1	4.7	2.2	.53	0	.025
5	130	5.5	2.4	.51	.031
10	—	12	3.5	.82	.036
20		40	5.8	1.9	.054
			C_4/C_4^{2-}		
1	3.0	1.8	.46	0	.033
5	22	3.6	1.3	.19	.034
10	45	4.5	1.6	.46	.036
20	—	8.5	2.2	.89	.040
			Normal butane C_3/C_3^{2-}		
mol %	300	400	450	500	550
1	37	4.5	1.5	.071	—
5	59	9.8	4.1	.88	.18
10	140	11	4.7	2.1	.20
20	190	18	6.0	3.2	.23
			C_4/C_4^{2-}		
1	31	2.6	.27	.004	—
5	30	2.6	1.1	.083	.019
10	35	2.8	1.6	.31	.049
20	45	4.0	2.3	.16	.062

than 100 mol and significant amounts of C_5 products should be detected.

Since paraffin/olefin ratios provide a measure of the extent of hydride transfer and secondary reactions these are given for C_3 and C_4. The larger the value of this ratio the greater the importance of these bimolecular hydrogen transfer processes.

The results clearly show that there is a dramatic change in the product distribution not only with temperature but also, in most cases, with the extent of conversion. The implication is that any discussion of the product distribution should be based on as complete a knowledge of the variation of the distribution with both the temperature and conversion. In particular, comparison of product distributions obtained in different laboratories for the same systems may be invalid unless both the temperature and the conversion are the same.

The nature of the mechanism for the conversion is most apparent at the two extremes of temperature. As shown in Table 5 at the highest temperature, 550°C, the major products hydrogen and butenes, and methane and propene, are precisely those expected from the primary mechanism. It is noteworthy that at this temperature there is realtively little change in the amounts of these products as the conversion increases to 35.7%. The sums of H_2 and C_1, and C_3 and C_4 match reasonably closely and are almost the same as the amount of isobutane converted; the amounts of hydrogen and total butenes are similar in value as well. The same is true for methane and propene. At the same time the amounts of products expected from hydride transfer, propane, *n*-butane, and pentanes, are quite modest even at high conversions.

Paraffin/olefin ratios are very small, much less than 0.10 in almost all cases, indicating that hydride transfer and oligomerization are not significant although they do occur to a small extent as indicated by the presence of isopentane.

Fig. 1 shows the change in the four major products with conversion. As this approaches zero the amounts of hydrogen and butenes approach each other as do methane and propene. Extrapolation of product distributions to zero conversion leaves only the above four products. This shows most clearly that at low conversion only the primary reactions are operative. At 550°C this is mainly true even at high conversion. This agrees with the scheme of Lombardo and Hall(5) which implies that when the contact time is very short and thus conversion low the lifetime of the C_4 and C_3 carbenium ions is too short to permit secondary oligomerization reactions so that only the corresponding olefins are formed from these species.

At the other temperature extreme, 300°C, as shown in Table 1, the product distribution clearly indicates that the primary mechanism is not a factor in its determination even at the lowest conversion. No hydrogen or methane is detected and aside from some C_2 the main products are C_3, C_3, $n - C_4$, some butenes which quickly decrease with conversion, and substantial amounts of branched pentanes, an obvious product of oligomerization. At high conversions there are essentially only three products, all paraffinic, propane, *n*-butane, and branched pentanes which are compatible with an oligomerized intermediate and a dominant hydride transfer mechanism. The paraffin/olefin ratios, in comparison to the very low values at 550°, are in excess of 1 even at very low conversions and rise to large values again indicative of enhanced hydride transfer.

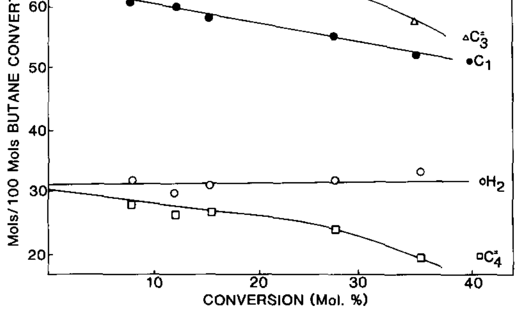


FIG. 1. Distribution of products for 100 mol of isobutane converted at 550°C. (△) C_3^{2-}; (●) C_1; (○) H_2; (□) C_4^{2-}.

Between these two extremes of temperature and mechanisms the broad picture is that of an ever increasing contribution by the primary mechanism as the temperature rises and conversion decreases. In both the schemes by Lombardo and Hall (5) and Dessau and Haag (*1*) this is to be expected since increased temperature will shift the endothermic reaction

$$t - C_4^+ + A^- \rightleftharpoons i - C_4 + HA$$

to the right. This results in a decrease of the lifetime of the carbenium ion and therefore its participation in oligomerization and hydride transfer. This situation is also realized when the contact time is reduced and the conversion decreased.

Table 2 shows that at 400°C very substantial amounts of hydrogen and methane are detected at very low conversion. At 0.10% conversion the sum of these two products is 95 mol indicating that the primary reactions are almost completely dominant. As the conversion increases, however, these products decrease dramatically. When the conversion has reached 15% the sum is already down to 13.5 mol, there is evidence of oligomerized C_5 products, and propane is again the major product.

Since paraffins always increase with conversion while olefins decrease the P/O ratio increases with conversion at each temperature. Table 6 shows the behaviour of the P/O ratio as a function of both the temperature and conversion. These values were obtained from plots of P/O ratios vs conversion at each temperature. Representative values of 1, 5, 10, and 20% conversions were chosen. While in the case of Lombardo and Hall(*5*) the P/O ratio for HZSM-5 showed no trend as a function of temperature, the results for our sample are unequivocal at each conversion. They decrease as expected since high temperature favors primary reactions rather than hydride transfer. It is clear, however, that in looking for P/O trends with temperature, values at the same conversion must be chosen.

The behavior of methane is of interest since it is comparatively unreactive and unlikely to be involved in secondary reactions once formed. It should serve as a diagnostic molecule (*31*). Figure 2 shows the wt% selectivity of methane as a function of wt% conversion over the temperature range covered. Ko and Wojciechowski (*32*) have shown that the nature of the product can be inferred from the shape of these plots and in particular that an initial linear section indicates that the product is primary. At 550°C the plot is linear over the range of conversion shown but as the temperature is lowered the plots show an initial linear section, whose length decreases with temperature, followed by a section with a lower slope. Normally the latter is indicative of a secondary reaction but in the case of methane it is much more likely that this definite change in slope signifies a change in the rate of production of methane or a change in the mechanism responsible for its production. Since at 550°C primary reactions are dominant over the entire conversion range the initial linear section can be identified with the primary mechanism. As the temperature decreases the initial linear section is shortened and the slope decreases as the conversion rises. This is to be expected if the primary mechanism becomes less significant compared to the secondary classical carbenium ion reactions since the latter do not produce methane. At 400°C the initial section ends at a low conversion, about 0.2%, at the same point where the amount of propane, the main product of the secondary reactions, begins to increase very quickly. The data for methane, therefore, are entirely consistent with the view of the two mechanisms and their relative contributions as the temperature and conversion change. A similar decrease in the slope of methane selectivity is seen in the cracking of propane over HZSM-5 (*24*).

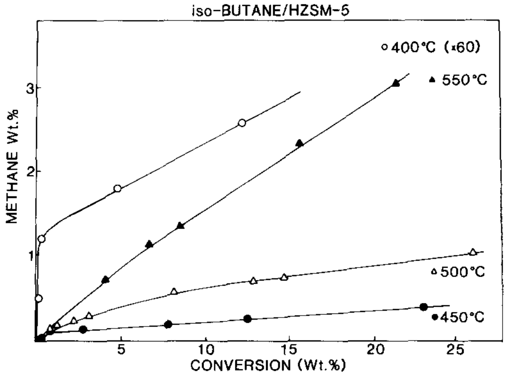


FIG. 2. Weight percent methane produced for the conversion of isobutane at different temperatures. (○) 400°C × 60; (●) 450°C; (△) 500°C; (▲) 550°C.

Table 7 gives the initial molar selectivities obtained by extrapolating product selectivities to zero conversion. Plot of weight selectivities versus conversion were used to determine whether, in the language of Wojciechowski and co-workers (*25,32*), products were primary or secondary and stable or unstable. Generally, paraffins were found to be primary and stable products while olefins were primary and unstable. Ethylene was unusual in that it changed from a primary to secondary product at high temperatures. For some species such as methane as discussed already, however, the results were equivocal because the shape of the plots were determined by the differing proportions of the two contributing mechanisms rather than whether species were stable or unstable.

At 300°C the initial product distributions

TABLE 7

Initial Molar Selectivities for 100 Mols of Butane Converted

Temperature	300	400	450	500	550
			(a) Isobutane)		
Hydrogen	—	28.8	48.5	42.0	31.2
Methane	—	25.6	44.5	60.0	65.0
Ethane	—	—	—	—	—
Ethylene	12.5	14.2	8.2	—	—
Propane	41.3	—	—	—	—
Propene	15.0	28.7	45.1	59.5	69.5
n-Butane	18.9	34.0	10.5	—	—
Butenes	12.9	34.5	40.9	45.0	30.1
Pentanes	18.9	—	—	—	—
Total weight selectivity	1.03	1.03	1.01	1.04	0.98
			(b) *n*-Butane		
Hydrogen	—	7.4	12.3	17.0	25.1
Methane	—	18.3	38.2	39.0	32.0
Ethane	—	26.2	45.6	45.0	41.5
Ethylene	—	21.7	49.8	49.0	42.5
Propane	85.0	11.0	—	—	—
Propene	—	9.7	17.5	29.0	29.8
n-Butane	21.5	30.0	—	—	—
Butenes	—	28.0	32.2	28.5	27.5
Pentanes	9.8	—	—	—	—
Total weight selectivity	.98	1.02	1.02	1.08	1.00

$$\text{Total weight selectivity} = \frac{\Sigma\ \text{molar selectivity} \times \text{molecular weight}}{5800}$$

indicate that the reactions in the limit of zero conversion must involve the formation of C_8 oligomers which subsequently crack to C_2 to C_5 products. As the temperature increases the contribution of the protolytic/radical mechanism increases so that at 400°C both mechanisms contribute to product formation. At 450°C and above only the latter contributes. The initial reactions can be summarized as

$$\begin{array}{llll}
H_2 + C_4^{2-} \leftarrow & iC_4 \rightarrow & [C_8] & \rightarrow C_3 + C_5 \\
C_1 + C_3^{2-} \leftarrow & & & \rightarrow C_4 + C_4 \\
 & & & \rightarrow C_4 + C_2 + C_2 \\
 & & & \rightarrow C_3 + C_3 + C_2
\end{array}$$

The detection of significant amounts of ethylene and its change from a primary to secondary product merit some discussion. At lower temperatures, where the carbenium ion mechanism dominates, ethylene is found to be a primary product. This must result from the cracking of oligomers despite the fact that it requires the formation of a small and energetically unfavorable primary carbenium ion. At 550°C, however, ethylene behaves as a secondary product which increases with conversion and becomes a major product in a regime where the carbenium ion mechanism and oligomer formation play a minor role. At these high temperatures, however, the barrier to primary carbenium ion can be more easily overcome so that any oligomers formed could result in ethylene formation. Lombardo *et al.* also obtain large amounts of a C_2 product (whether this is ethane, ethylene, or a combination is not indicated) for HZSM-5 (*35*) for both isobutane and neopentane (*4*, *5*).

The fact that ethylene becomes a secondary product at high temperature suggests another explanation, namely that it results from a protolysis of two of the main primary products, propane and *n*-butane. However, this was rejected on the following basis. Kitagawa *et al.* (*24*) have shown that at high temperature the main products from the catalytic conversion of propane by HZSM-5 are methane and ethylene. This would mean that as the amount of ethylene rose as in the case at 550°C there should be a corresponding rise in methane. In fact, the reverse occurs. Similarily if the ethylene resulted from the ethyl carbenium ion produced from the protolytic or radical attack of *n*-butane an equal or larger amount of ethane would be expected. However, this is the one product which was consistently absent or present in very small amounts.

Product distributions show that isomerization of isobutane to *n*-butane occurs to a significant extent except at the highest temperatures. On the other hand butane isomerization in superacids occurs with difficulty. Reports in the literature vary on this point with respect to zeolites (*2*, *5*, *22*, *23*, *33*, *35*) and appear to depend on the activity of the catalyst. Lombardo and Hall only observe a small amount of isomerization at 350°C on their HZSM-5 (*35*) sample that was pretreated at 500°C (Table 6 in Ref. (*5*)). On the other hand at 340°C Hall *et al.* (*40*) detected large amounts of *n*-butane on their HZSM-5 (*15*) sample that had been pretreated at a slightly higher temperature 550°C. *n*-Butane was the second most abundant species after propane. Their results for the isomerized products are similar to those obtained in this work. Butene isomers, however, were a common finding. In our results, as with the findings of McVicker *et al.* on faujasites (*2*), the butenes appeared to be in thermodynamic equilibrium.

With regard to the production of normal butane and butenes from isobutane there are at least two mechanisms leading to these isomerized products. The simplest and most direct path would be the isomerization of the *t*-butyl to the *s*-butyl carbenium ion which would either undergo hydride abstraction to form *n*-butane or deprotenate to desorb as one of the *n*-butenes. This pathway, however, requires the formation of a primary carbenium ion. For reactions in superacids the transition from a *t*-butyl to a primary butyl carbenium ion requires an activation energy greater than 32 kcal/mol (*37*). On the other hand the isomerization of the *t*-pentyl to the *s*-pentyl carbenium ion only requires approximately 10 kcal/mol. This difference satisfactorily explains why *n*-pentane, which can avoid primary carbenium ion formation, isomerizes easily in superacids while *n*-butane cannot. In light of this fact, for the case of isobutane on solid acids some authors (*21*, *35*, *38*) have favored the more indirect path involving the formation of C_8 oligomers which can undergo relatively facile isomerizations without the formation of primary carbenium ions. Among the products of the subsequent β scission are the *s*-butyl carbenium ion and *n*-butenes which can then account for the isomerized C_4 products. It has been noted, however, that activation energy values on solid surfaces are not known and although the speculation is that they would be higher, little or no account of the solvating effect of the zeolite lattice has been taken into account (*15*).

Our results at the highest temperature, 550°C, may be explained by the scheme of Lombardo and Hall if it is assumed that at temperatures above 400°C the *t*-butyl to *s*-butyl carbenium ion isomerization may be facile despite the high activation energy. Additionally, where hydride transfer is limited the only products to be expected from the butyl carbenium ions are butenes rather than butanes. This is exactly what is observed. What is not so easily rationalized, however, is the temperature dependence of the butene production. If the large activation barrier between isobutyl carbenium and *n*-butyl carbenium ions were the only factor controlling the amount of *n*-butenes produced there should be a very substantial difference in the total amount of *n*-butenes at 400 and 550°C. In fact, at 400°C the total amount of *n*-butenes extrapolated to zero conversion is approximately 12 mol while at 550°C the value is only slightly higher at about 17 mol. The reason that there is not a large difference may be that there are two competing effects. High temperature increases the rate of overcoming the isomerization barrier but it also decreases the lifetime of the isobutyl carbenium ion and hence its rate of isomerization to *n*-butenes.

At low temperatures direct isomerization should be severely hindered. In this case the production of *n*-butane and *n*-butenes would likely result from oligomerization. As seen from Table 1, *n*-butane production at 300°C is accompanied by substantial amounts of isopentane, a clear sign of oligomerization.

N-Butane

There are very few reports of the detection of molecular hydrogen as a primary product from the cracking of linear paraffins on zeolites. Haag and Dessau detected hydrogen for *n*-hexane on HZSM-5 (*1*) as an initial product but Abbot and Wojciechowski (*25*) found that on HY zeolite, *n*-hexane and higher paraffins only gave hydrogen as a secondary product and that the feed paraffin required a tertiary C–H bond in order to obtain hydrogen initially. Lombardo *et al.* (*41*) agree with this position. Bizreh and Gates (*23*) in their work on *n*-butane conversion on HZSM-5 did not have the capability to detect hydrogen but there is little doubt that it was present as a primary product. This can be implied from an analysis of their products. For low conversions they detected equal amounts of methane and propene, and ethane and ethylene. They also found significant quantities of butenes. The only missing product from the list expected from primary reactions for *n*-butane and which is coupled to butene production is hydrogen, which must have been present.

The product distributions for *n*-butane in this work are shown in Tables 8–12 while the initial selectivities as a function of temperature are given in Table 7(b). The presence of hydrogen as a major and primary product is shown unequivocally at temperatures from 400 to 550°C. This demonstrates that if a secondary C–H bond is present hydrogen can be formed as a primary product. Lombardo *et al.* (*4*) have shown, however, that hydrogen is not produced when only a primary C–H bond is present.

In general, the product distributions are in agreement with the main points discussed with respect to isobutane. At 550°C there is little evidence of oligomerization and hydride transfer. The products can be accounted for by primary reactions. As well as hydrogen and butenes, and methane and propene, the additional pair ethane and ethylene is obtained, as might be expected from a protolytic/radical attack on the middle C–C bond of *n*-butane. These are the only products which approach nonzero values as the conversion approaches zero. Thus the primary mechanism can account for the product distribution for *n*-butane at high temperatures and low conversion.

As in the case of isobutane at 550°C extrapolation to zero conversion reveals that each product of a pair approaches a definite limit. These indicate the selectivity at zero conversion and must be related to the tendency for protolytic cleavage or radical attack for the various types of bonds involved. The approximate values and the types of bond cleaved are given.

Conversion Over H-ZSM-5 at 550°C

Reactant Product pair	Selectivity at zero conversion	
	n-butane	Isobutane
Hydrogen and butenes	26 Mol (sec C–H)	31 Mol (tert C–H)
Methane and propene	21 Mol (end C–C)	67 Mol (C–C)
Ethane and ethylene	42 Mol (middle C–C)	

TABLE 8

Mol Product per 100 Mol Butane Converted (Normal Butane–HZSM-5 at 300°C)

Conversion mol%	.10	1.3	6.0	14.7	19.7	23.2
Hydrogen	—	—	—	—	—	—
Methane	—	—	—	—	—	—
Ethane	—	1.4	0.2	0.2	0.2	0.1
Ethylene	—	3.4	0.7	0.4	0.2	0.1
Propane	85.8	83.6	86.5	86.6	85.1	78.0
Propene	—	2.2	1.3	0.7	0.3	—
Isobutane	22.9	18.9	20.2	18.3	19.9	24.2
trans-Butene	—	—	0.3	0.2	0.1	0.1
1-Butene	—	—	—	—	—	—
Isobutene	—	—	0.3	0.3	0.1	0.1
cis-Butene	—	—	—	0.1	0.1	—
Σ Butenes	—	—	0.6	0.6	0.3	0.2
Branched pentanes	—	2.4	2.9	3.9	4.6	5.4
n-Pentane	9.7	8.5	6.5	6.1	5.7	5.5
Pentenes	—	—	—	—	—	0.4
Hexane/hexene	—	—	0.5	1.1	1.3	1.5
Aromatics	—	—	—	0.4	0.2	—
$H_2 + C_1 + C_2$	—	1.4	0.2	0.2	0.2	0.1
C_2/C_2^{2-}	—	0.41	0.29	0.50	1.0	1.0
C_3/C_3^{2-}	—	38	67	124	284	—
C_4/C_4^{2-}	—	—	67	61	66	121
Total mass	5798	5796	5796	5796	5810	5825

TABLE 9

Mol Product per 100 Mol Butane Converted (Normal Butane–HZSM-5 at 400°C)

Conversion mol%	.23	1.0	1.9	4.9	9.6	29.0
Hydrogen	6.5	5.5	2.5	1.2	1.1	0.8
Methane	16.2	14.6	6.4	2.8	2.3	1.2
Ethane	24.6	14.5	12.9	4.7	4.0	2.3
Ethylene	21.1	18.2	15.7	8.4	7.7	3.0
Propane	21.0	41.5	51.3	75.9	83.2	95.5
Propene	9.7	7.9	8.5	8.6	7.0	3.2
Isobutane	26.6	27.4	25.1	12.9	10.8	12.2
trans-Butene	6.6	2.5	2.1	1.6	1.2	0.5
1-Butene	2.0	0.6	0.7	0.6	0.5	0.2
Isobutene	11.9	4.8	3.4	2.6	2.0	0.9
cis-Butene	3.3	2.1	1.2	0.9	0.7	0.3
Σ Butenes	23.8	10.0	7.4	5.7	4.4	1.9
Branched pentanes	—	1.0	1.1	2.2	2.1	2.3
n-Pentane	—	3.7	3.7	5.0	3.9	2.6
Pentenes	—	—	0.5	0.9	0.7	0.4
Hexane/hexene	—	—	—	0.3	0.6	0.7
Aromatics	—	—	—	—	0.5	0.3
$H_2 + C_1 + C_2$	47.3	34.6	21.8	8.7	7.4	4.3
C_2/C_2^{2-}	1.2	.80	.82	.56	.52	.77
C_3/C_3^{2-}	2.2	5.3	6.0	8.8	12.	30.
C_4/C_4^{2-}	1.1	2.7	3.4	2.3	2.5	6.4
Total mass	5806	5838	5793	5800	5794	5790

TABLE 10

Mol Product per 100 Mol Butane Converted (Normal Butane–HZSM-5 at 450°C)

Conversion mol%	.64	1.1	5.8	16.0	33.5	44.8
Hydrogen	10.3	9.7	4.7	5.2	3.5	2.8
Methane	30.0	22.6	9.8	7.6	5.4	2.6
Ethane	37.5	30.6	13.2	10.5	8.1	5.2
Ethylene	43.8	37.8	21.8	17.8	11.1	4.8
Propane	16.2	29.3	59.8	68.6	81.7	88.8
Propene	18.1	15.5	14.0	12.9	9.2	5.3
Isobutane	—	6.5	10.2	11.3	11.0	11.3
trans-Butene	5.3	5.0	2.3	1.6	1.0	0.7
1-Butene	3.8	2.8	1.1	0.7	0.5	0.3
Isobutene	11.8	9.1	4.1	2.8	1.8	1.2
cis-Butene	5.3	3.0	1.3	0.5	0.7	0.4
Σ Butenes	26.2	19.9	8.8	5.6	4.0	2.6
Branched pentanes	—	—	1.0	0.7	1.2	1.7
n-Pentane	—	—	1.1	1.4	1.2	1.4
Pentenes	—	—	—	0.9	0.6	0.5
Hexane/hexene	—	—	—	0.2	0.2	0.5
Aromatics	—	—	—	0.6	0.9	1.4
$H_2 + C_1 + C_2$	77.8	62.9	27.7	23.3	17.0	10.6
C_2/C_2^{2-}	.86	.81	.61	.59	.73	1.1
C_3/C_3^{2-}	.90	1.9	4.3	5.3	8.9	17
C_4/C_4^{2-}	—	.33	1.2	2.0	2.8	4.3
Total mass	5800	5782	5788	5760	5750	5742

TABLE 11

Mol Product per 100 Mol Butane Converted (Normal Butane–HZSM-5 at 500°C)

Conversion mol%	4.5	11.1	13.1	25.3
Hydrogen	15.3	8.4	9.8	7.4
Methane	28.9	15.6	14.5	12.4
Ethane	34.8	20.5	19.1	16.8
Ethylene	42.0	30.3	27.9	24.0
Propane	17.7	49.7	54.9	62.7
Propene	25.4	20.2	19.5	18.4
Isobutane	0.6	3.9	3.4	1.7
trans-Butene	5.3	2.7	2.5	2.0
1-Butene	3.3	1.5	1.4	1.1
Isobutene	8.9	4.6	4.6	3.5
cis-Butene	3.8	1.9	1.6	1.4
Σ Butenes	21.3	10.7	10.1	8.0
Branched pentanes	—	0.5	0.4	0.8
n-Pentane	0.1	0.9	0.7	0.9
Pentenes	0.3	1.3	1.2	1.3
Hexane/hexene	—	—	0.1	0.1
Aromatics	—	0.2	0.3	0.8
$H_2 + C_1 + C_2$	79.0	44.5	43.4	36.6
C_2/C_2^{2-}	.83	.68	.68	.7
C_3/C_3^{2-}	.70	2.4	2.8	3.4
C_4/C_4^{2-}	.03	.36	.34	.21
Total mass	5816	5806	5811	5785

TABLE 12

Mol Product per 100 Mol Butane Converted (Normal Butane–HZSM-5 at 550°C)

Conversion mol%	4.4	8.7	12.1	19.5	36.0	46.4
Hydrogen	24.4	26.2	22.2	23.1	21.7	20.5
Methane	31.5	31.9	31.8	31.5	30.3	29.9
Ethane	35.9	32.6	32.0	32.6	31.9	30.8
Ethylene	42.3	38.4	39.6	42.4	46.3	47.6
Propane	5.4	6.5	7.3	9.9	12.5	18.4
Propene	31.5	35.3	35.9	37.4	37.5	35.0
Isobutane	—	1.0	1.6	1.1	0.2	—
trans-Butene	6.6	6.0	5.4	4.8	3.4	2.6
1-Butene	4.8	4.8	4.4	4.0	2.7	2.1
Isobutene	10.0	9.4	8.9	7.3	5.5	4.2
cis-Butene	5.0	4.7	4.3	3.1	2.6	2.0
Σ Butenes	26.4	24.9	23.0	19.2	14.2	10.9
Branched pentanes	—	—	—	—	0.2	0.1
n-Pentane	—	—	—	—	—	0.1
Pentenes	—	—	—	—	—	0.3
Hexane/hexene	—	—	—	—	—	—
Aromatics	—	—	—	—	1.1	1.5
$H_2 + C_1 + C_2$	91.6	90.7	86.0	87.2	83.9	80.4
C_2/C_2^{2-}	.85	.85	.80	.77	.69	.65
C_3/C_3^{2-}	.17	.18	.20	.26	.33	.53
C_4/C_4^{2-}	—	.04	.07	.06	.01	—
Total mass	5846	5839	5831	5824	5810	5816

Thus at the highest temperature where the mechanism is least complicated protolytic/radical cleavage occurs most readily at the branched C–C bond and not at the branched C–H bond. A similar result is found by Lombardo and Hall (*5*) for isobutane on HZSM-5 at 500°C, where both the methane and propene selectivities far exceed that for butenes. This is opposite to the order found by Olah *et al.* (*29*) for paraffin reactions done in superacid solutions. Their results obtained at much lower temperatures showed that the order of protolytic attack was

$$(\text{tert C–H}) > (\text{C–C}) > (\text{sec C–H}) \gg (\text{primary C–H}).$$

On the other hand, Mindo/3 calculations (*39*) suggest that protonation of the C–C bond is favored over the C–H bond for butane and heavier molecules. Our results also indicate, however, that as the temperature is decreased the order reverses and at 400°C the amount of hydrogen and butenes is greater than that of the methane–propene pair.

In the case of *n*-butane the interior C–C bond is cleaved in preference to the end C–C bond. This is generally true in linear paraffin cracking (*26*).

At the lowest temperature, 300°C, it is clear, as in the case of isobutane, that only secondary reactions are of importance. None of the products expected from primary reactions are found in any significant amount. The only products are propane, isobutane, and the pentanes.

The initial selectivities in Table 7(b) show that the initial products are similar to the case for isobutane except for the expected addition of the ethane–ethylene pair and the fact that at 300°C the products from *n*-butane are more classical. This is expected since *n*-butane can accommodate the bulky transition state for hydride transfer more readily than isobutane (*1*). Therefore, the initial reactions will be similar to those outlined for isobutane with the addition of the formation of C_2 products.

While the product distribution tables do not include the contact times required to effect a particular conversion it was found that *n*-butane conversion was only slightly more difficult than isobutane. Fuentes and Gates had similar results (*36*). At first glance this might be unexpected especially at high temperatures when primary reactions are dominant. In the case of isobutane the cleavage would result in a *t*-butyl or an *s*-propyl cation but for *n*-butane the carbenium ions associated with the products methane and ethane are the energetically unfavorable primary ethyl and propyl cations. At high temperatures where barriers are more easily overcome this may not matter but at low temperatures if the stability of the product cation were the only determinant factor in the protolytic/radical attack the amount of methane and ethane produced from *n*-butane should be very small. That this is not the case indicates that the energy barrier for pentacoordinated carbonium ions undergoing cleavage to primary carbenium ions may be lower than that for a carbenium ion undergoing cracking to produce smaller carbenium ions. Similarly the isomerization of butanes might result from a rearrangement step of the carbonium ion rather than that of the *t*-butyl or *n*-butyl carbenium ion (*26*). Such a path avoids the difficulty of primary carbenium ion formation and may explain why the production of isomerized butenes is relatively independent of temperature. Theoretical calculations for this situation similar to those carried out by Corma *et al.*(*3*) would be of great interest.

REFERENCES

1. Haag, W. O., and Dessau, R. M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 305. Dechema, Frankfurt-am-Main, Berlin, 1984.
2. McVicker, G. B., Kramer, G. M., and Ziemiak, J. J., *J. Catal.* **92,** 355 (1985).
3. Corma, A., Planelles, J., Sanchez-Marin, J., and Tomas, F., *J. Catal.* **93,** 30 (1985).
4. Lombardo, E. A., Pierantozzi, R., and Hall, W. K., *J. Catal.* **110,** 171 (1988).
5. Lombardo, E. A., and Hall, W. K., *J. Catal.* **112,** 565 (1988).
6. Kramer, G. M., and McVicker, G. B., *J. Catal.* **115,** 608 (1989).
7. Hall, W. K., Lombardo, E. A., and Engelhardt, J., *J. Catal.* **115,** 611 (1989).
8. Choukroun, H., Brunel, D., and Germaine, A., *J. Chem. Soc. Chem. Commun.,* 6 (1986).
9. Rimmelin, P., Brenner, A., Fisher, K., and Sommer, J., *J. Chem. Soc. Chem. Commun.,* 1497 (1986).
10. Hunter, R., Hutchings, G. J., and Pickl, W., *J. Chem. Soc. Chem. Commun.,* 843 (1987).
11. Centi, G., and Golinelli, G., *J. Catal.* **115,** 452 (1989).
12. Greensfelder, B. S., Voge, H. H., and Good, G. M., *Ind. Eng. Chem.* **41,** 2573 (1979).
13. Dooley, K. M., and Gates, B. C., *J. Catal.* **90,** 347 (1985).
14. Bolton, A. P., Ladd, I. R., and Weeks, T. J., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 316. The Chemical Society, London, 1976.
15. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw–Hill, New York, 1979.
16. Emmett, P., *J. Am. Chem. Soc.* **84,** 4410 (1962).
17. Daage, M., and Fajula, F., *J. Catal.* **81,** 394 (1983).
18. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966).
19. Guisnet, M., *in* "Catalysis by Acids and Bases" (B. Imelik, C. Naccache, Y. Ben Taarit, and J. C. Vedrine, Eds.), p. 283. Elsevier, Amsterdam, 1985.
20. Benesi, H. A., *J. Catal.* **8,** 368 (1967).
21. Manness, J. A., and Dooley, K. M., *J. Catal.* **117,** 322 (1989).
22. Rastelli, H., Lok, B. M., Dussman, J. A., Earls, D. E., and Mullhaupt, J. T., *Can. J. Chem. Eng.* **60,** 44 (1982).
23. Bizreh, Y. W., and Gates, B. C., *J. Catal.* **88,** 240 (1984).
24. Kitagawa, H., Sendoda, Y., and Ono, Y., *J. Catal.* **101,** 12 (1986).
25. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **113,** 353 (1983).
26. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **115,** 1 (1989).
27. Shih, S., *J. Catal.* **79,** 390 (1983).
28. Olah, G. A., *J. Am. Chem. Soc.* **94,** 808 (1972).

29. Olah, G. A., DeMember, J. R., and Shen, J., *J. Am. Chem. Soc.* **95,** 4952 (1973).

30. Olah, G. A., Surya Prakash, G. K., and Sommer, J., "Superacids." Wiley, New York, 1985.

31. Dass, D. V., and Odell, A. L., *J. Catal.* **113,** 259 (1988).

32. Ko, A.-N., and Wojciechowski, B. W., *Prog. React. Kinet.* **12**(4), 201 (1983).

33. Hilaire, P., Bearez, C., Chevalier, F., Perot, G., and Guisnet, M., *Zeolites* **2,** 69 (1982).

34. Brunel, D., Choukroun, H., Germain, A., and Commeyras C., *in* "Catalysis by Acids and Bases" (B. Imelik, C. Naccache, Y., Ben Taarit, and J. C. Vedrine, Eds.), p. 371. Elsevier, Amsterdam, 1985.

35. Frilette, V. J., and Rubin, M. K., *J. Catal.* **4,** 311 (1965).

36. Fuentes, G. A., and Gates, B. C., *J. Catal.* **76,** 440 (1982).

37. Nenitzescu, N., *in* "Carbonium Ions" (G. A. Olah and P. R. Schleyer, Eds.), Vol. II, p. 499. Wiley-Interscience, New York, 1984.

38. Bearez, C., Chevalier, F., and Guisnet, M., *React. Kinet. Catal. Lett.* **22,** 405 (1983).

39. Planelles, J., Sanches-Marin, S., and Tomas, F., *Theochem.* **17,** 15 (1984).

40. Hall, W. K., Engelhardt, J., and Sill, G. A., *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), p. 1253. Elsevier, Amsterdam, 1989.

41. Lombardo, E. A., Sill, G. A., and Hall, W. K., *J. Catal.* **119,** 426 (1989).

42. Ball, W. J., and Stewart, D. G., *USP* **4,** 452, 907 (1984).

43. Harris, I. M., PhD. thesis, University of Manchester Institute of Science and Technology 1987.