

## Reactions of 3-Methylpentane and 2,3-Dimethylbutane on Aluminosilicate Catalysts

J. ABBOT

*Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia*

Received September 29, 1989; revised May 30, 1990

Catalytic reactions of 3-methylpentane and 2,3-dimethylbutane on HY, amorphous silica–alumina, and HZSM-5 have been studied at 500°C. Both kinetic phenomena and product selectivities have been reported. Cracking reactions on HZSM-5 can be attributed to initiation through protonation occurring at Brønsted sites. Bimolecular processes leading to chain reactions via hydride transfer are restricted within the narrow pore pentasil zeolite. On HY and amorphous silica–alumina, initiation of cracking also occurs at Brønsted sites. No direct evidence was found for participation of Lewis acid sites on the catalyst framework itself. Following initiation, reactions on these catalysts are accelerated through a chain process occurring at Lewis sites generated by adsorption of product olefins at Brønsted sites. The resulting change in the dominant cracking mechanism is reflected in the product selectivity, illustrated here by a falling off in formation of molecular hydrogen as conversion increases. © 1990 Academic Press, Inc.

### INTRODUCTION

There has been renewed interest in understanding the mechanism of cracking reactions of saturated hydrocarbons on solid acid catalysts (1–5). This has been motivated in part by the synthesis of new classes of zeolite (6–9) and also by the concept of initiation through carbonium ion intermediates (10–12), thereby paralleling reactions of hydrocarbons in liquid superacid media (13). Most studies on the reactions of pure hydrocarbons have concentrated on the behavior of linear paraffins under cracking conditions. Studies on the branched isomers, an important component of high octane gasoline, have been reported to a lesser extent (10, 11, 14–17). Molecular dimensions of the feed paraffin are important in consideration of shape selectivity (14, 16), while intrinsic reactivity can be significantly influenced by the presence of a hydrogen atom bonded to a tertiary carbon atom (11, 17).

Previous studies appear to show that for reaction of branched C<sub>6</sub> paraffins on HY zeolite, initiation of cracking is followed by

an acceleration in rate as product olefins are adsorbed at Brønsted sites (5, 11). It might be expected that this kinetic phenomenon would be reflected in concurrent changes in product selectivity, with an increase in the proportion of the total reaction proceeding via interaction with Lewis sites (i.e., adsorbed carbenium ions) if cracking occurs through different pathways on the two types of active site. The present study reports on the behavior of 3-methylpentane and 2,3-dimethylbutane on aluminosilicates under cracking conditions. Both kinetics and selectivity have been examined to establish whether such effects can be identified.

This study also attempts to detect evidence for the participation of Lewis sites on the catalyst framework itself. This process should be favored for feedstocks where hydride ion abstraction is facilitated by the molecular structure of the paraffin, as in the case of these branched C<sub>6</sub> paraffins, where a hydrogen atom is bonded to a tertiary carbon. The relative importance of Brønsted and Lewis acid sites on solid acid catalysts during cracking processes has been debated for many years (4, 18–20) and the present

study provides evidence to help resolve this issue for reaction of paraffins on zeolites.

#### EXPERIMENTAL

The feedstocks were obtained from Aldrich and used without further purification. The purity of the feedstocks was as follows: 3-methylpentane, 99.16%, 2,3-dimethylbutane, 99.80%. Impurities present were other  $C_6$  isomers, and their presence was taken into consideration when calculating initial selectivities.

HZSM-5 was provided by Snamprogetti, Milan, Italy. The sample ( $Si/Al = 105$ ) was prepared according to methods in the patent literature and was exchanged with aqueous ammonium nitrate. HY zeolite (97.3% exchanged) was prepared from NaY (Linde Co., Lot No. 45912, SK40;  $Si/Al = 2.4$ ) by repeated exchange with 0.5 *N* ammonium nitrate solution. Amorphous silica-alumina (25%  $Al_2O_3$ ) was obtained from Davison Chemical.

Catalysts were calcined at 500°C before use. All experiments were carried out using catalysts with mesh size 80/100. Reduction of the catalyst particle size had no influence on the cracking reaction, showing that the reaction was not diffusion controlled.

All experiments were performed by using an integral, fixed-bed gas-phase plug flow reactor with an independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described in previous studies (21). All reactions were carried out at 500°C and 1 atm pressure.

Liquid products were analyzed by a Varian 6000 gas chromatograph with a 60-m SE-54 capillary column and flame ionization detection. Products up to  $C_7$  were eluted at 35°C followed by a temperature program of 5°/min up to 300°C. Gaseous products were analyzed by a Carle SX1156 gas chromatograph. This enabled determination of all hydrocarbons in the range  $C_1$ – $C_5$  and the direct determination of hydrogen, if present. The identification of products was facilitated by use of a Finnigan 1020 automated GC/MS.

Heat pretreatment experiments at 600°C were carried out by heating the catalyst for 4 h at 600°C with dry nitrogen flowing through the reactor. Rehydration experiments were carried out by adding distilled water to the reactor at 100°C. The reactor temperature was increased to the reaction temperature (500°C) with a stream of dry nitrogen flowing over the catalyst.

#### RESULTS AND DISCUSSION

##### *Initiation of Cracking Reactions*

Initial selectivities of products formed from reaction of 3-methylpentane and 2,3-dimethylbutane on HZSM-5, HY, and amorphous silica-alumina at 500°C were determined by plotting yield against conversion for each product (11, 21). Blank runs using inert sand in place of the catalyst showed small thermal cracking effects. Catalytic conversions and yields were therefore determined by subtraction of the corresponding thermal conversions and yields of each product for each experimental condition (22). Thermal cracking effects for the branched  $C_6$  paraffins were found to be lower than for those of *n*-hexane at 500°C (22). Figure 1a shows the variation in total thermal conversion of 3-methylpentane with time on stream at 500°C. Figure 1b shows the corresponding amount of methane produced thermally under these conditions. Figures 2–6 show examples of selectivity curves constructed in this way for the catalytic reaction of each paraffin.

Tables 1 and 2 show the initial catalytic weight selectivities and identify types (23) for all products from reaction of 3-methylpentane and 2,3-dimethylbutane, respectively. It is apparent that all the initial products were acyclic paraffins or olefins in the range  $C_1$ – $C_6$ , and molecular hydrogen. Products above  $C_6$  such as aromatics were formed only through secondary reactions. Tables 3 and 4 show the corresponding initial catalytic molar selectivities for molecular hydrogen, paraffins (P), and olefins (O). From the molar selectivities, it is possible to postulate reaction schemes to account for

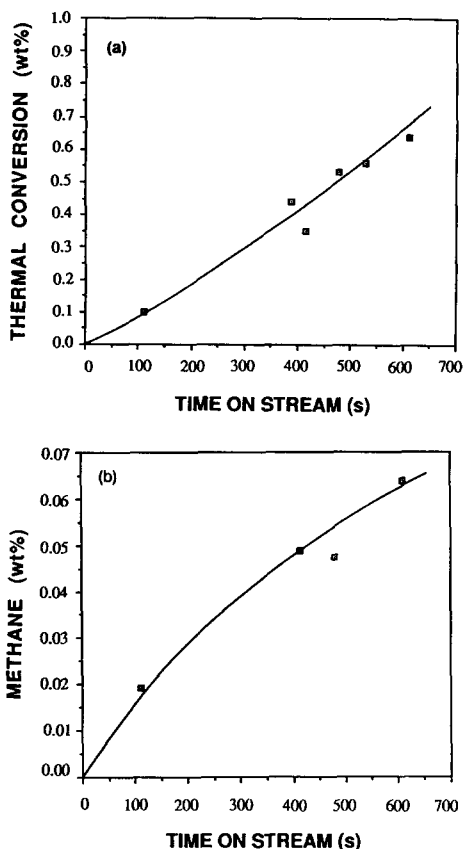
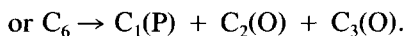
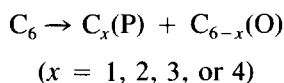


FIG. 1. (a) Plot of total thermal conversion of 3-methylpentane at 500°C. (b) Thermal production of methane from 3-methylpentane at 500°C.

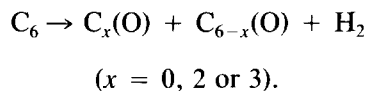
the initial modes of fragmentation of the  $C_6$  feed molecules (24).

For reactions of  $C_6$  paraffins on HZSM-5, good agreement with initial experimental selectivities was obtained (24) by considering a series of monomolecular processes of the following types:

1. Cracking to give one paraffin (P) and either one or two olefin (O) species:



2. Cracking to produce olefins and molecular hydrogen:



3. Skeletal isomerization:

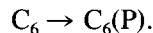


Table 5 shows the ratios of experimental molar selectivities (from Tables 3 and 4) to that calculated for each product species using this type of reaction scheme for initial reactions of 3-methylpentane and 2,3-dimethylbutane on HZSM-5. The individual steps for obtaining the "calculated" values have been previously described in detail (24). As each ratio is close to unity, the proposed sets of monomolecular reaction processes (24) can be considered plausible on this catalyst. However, it should be emphasized that the schemes proposed may not yield a unique solution. The degree of fitting for any particular set of postulated processes will also depend on the accuracy of the experimental selectivity values and may also be influenced by the order in which various postulated steps are considered.

Table 5 shows that when a similar reaction scheme is applied to reactions of 3-methylpentane or amorphous silica-alumina at 500°C, again assuming that only monomolecular processes occur, the fitting is less satisfactory than that reported for reaction on HZSM-5. In particular, there appear to be excess amounts of  $C_4(P)$  and  $C_5(P)$ , so that the overall carbon balance in the proposed scheme accounts for only ~91% of the total observed. Table 5 also indicates that consideration of only monomolecular fragmentation processes for reactions of 3-methylpentane and 2,3-dimethylbutane on HY also gives a poorer fitting than for the corresponding reaction networks on HZSM-5, again with an apparent excess experimental formation of  $C_4(P)$  and  $C_5(P)$  on the faujasite.

It can be postulated that these residual amounts of  $C_4$  and  $C_5$  paraffins initially observed are formed in association with processes leading to coke species. Alternatively, the inclusion of dimer-

TABLE 1

Products Formed from Reaction of 3-Methylpentane on HZSM-5, HY, and Silica-Alumina at 500°C

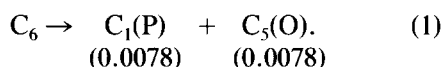
Product	Type <sup>a</sup>			Initial weight selectivity <sup>b</sup>		
	HZSM-5	HY	Silica-alumina	HZSM-5	HY	Silica-alumina
Hydrogen	1S	1U	1U	0.0053	0.0025	0.0058
Methane	1U	1S	1U	0.058	0.0033	0.0154
Ethylene	1U	1S	1U	0.130	0.025	0.040
Ethane	1U	1S	1S	0.090	0.013	0.0200
Propylene	1U	1U	1S	0.294	0.294	0.310
Propane	(1 + 2)S	(1 + 2)S	(1 + 2)S	0.017	0.192	0.031
Isobutane	1S	(1 + 2)S	(1 + 2)S	0.0339	0.0556	0.050
<i>n</i> -Butane	(1 + 2)S	(1 + 2)S	(1 + 2)S	0.0127	0.0265	0.0102
<i>trans</i> -2-Butene	1U	1S	(1 + 2)S	0.057	0.00886	0.0151
<i>cis</i> -2-Butene	1U	1S	(1 + 2)S	0.0418	0.00359	0.0115
Isobutene	1S	1S	(1 + 2)S	0.107	0.0144	0.014
Isopentane	2S	(1 + 2)S	(1 + 2)S	0	0.0610	0.050
<i>n</i> -Pentane	2S	2S	2S	0	0	0
C <sub>5</sub> -Olefins	(1 + 2)S	2S	(1 + 2)S	0.069	0	0.00632
2,3-Dimethylbutane	1U	1S	1U	0.0029	0.0446	0.100
2-Methylpentane	1S	1S	1U	0.0629	0.233	0.257
3-Methylpentane	Feed	Feed	Feed	Feed	Feed	Feed
<i>n</i> -Hexane	2U	1S	1S	0	0.0329	0.0092
C <sub>6</sub> -Olefins	1U	2S	1U	0.0069	0	0.0267
Aromatics	2S	2S	2S	0	0	0
Coke	(1 + 2)S	(1 + 2)S	(1 + 2)S	0.0050	0.0050	0.0220
Total				0.9934	1.014	0.994

<sup>a</sup> 1, primary; 2, secondary; S, stable; U, unstable.

<sup>b</sup> The initial weight selectivity is determined by the initial slope of the corresponding yield-conversion plot (see Figs. 2-4).

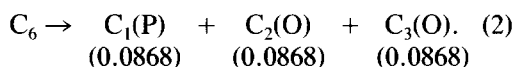
ization-cracking processes (25) as well as the simple monomolecular processes already considered can improve the overall fitting procedure as outlined below for reaction of 3-methylpentane on amorphous silica-alumina.

Simple cleavage of the 3-methylpentane molecule into two fragments [i.e., one olefin (O) and one paraffin (P)] can occur through the process

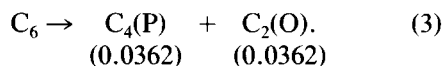


The numbers in parentheses below each product refer to the initial molar selectivity for that product from that process. These are taken from the experimental initial molar selectivities (Table 3) for the product formed in lesser amount [i.e., C<sub>5</sub>(O) for process (1)].

The remaining initial selectivity for C<sub>1</sub>(P) can be assigned to the process



The molar selectivity for C<sub>1</sub>(P) assigned to process (2) is the total molar selectivity for C<sub>1</sub>(P) (Table 3) minus that assigned to C<sub>1</sub>(P) in process (1). The selectivities for C<sub>2</sub>(O) and C<sub>3</sub>(O) in process (2) follow from stoichiometry. The remaining C<sub>2</sub>(O) can be accounted for by the process



Process (4) can account for the observed initial selectivity for C<sub>2</sub>(P):

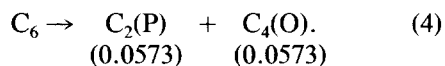


TABLE 2

Products Formed from Reaction of 2,3-Dimethylbutane on HZSM-5 and HY at 500°C

Product	Type <sup>a</sup>		Initial weight selectivity <sup>b</sup>	
	HZSM-5	HY		
			HZSM-5	HY
Hydrogen	(1 + 2)S	1U	0.0050	0.0036
Methane	1U	1U	0.125	0.0379
Ethylene	1S	1U	0.160	0.0683
Ethane	—	—	0	0
Propylene	1U	1S	0.480	0.279
Propane	(1 + 2)S	(1 + 2)S	0.0151	0.0888
Isobutane	2S	(1 + 2)S	0	0.0259
<i>n</i> -Butane	2S	(1 + 2)S	0	0.0060
<i>trans</i> -2-Butene	2S	(1 + 2)S	0	0.00345
<i>cis</i> -2-Butene	2S	(1 + 2)S	0	0.00216
Isobutene	2S	(1 + 2)S	0	0.0055
Isopentane	2S	(1 + 2)S	0	0.0862
<i>n</i> -Pentane	2S	2S	0	0
C <sub>5</sub> -Olefins	1U	1U	0.220	0.0129
2,3-Dimethylbutane	Feed	Feed	Feed	Feed
2-Methylpentane	—	(1 + 2)S	0	0.137
3-Methylpentane	—	(1 + 2)S	0	0.149
<i>n</i> -Hexane	—	1S	0	0.0371
C <sub>6</sub> -Olefins	2S	1U	0	0.055
Aromatics	2S	2S	0	0
Coke	(1 + 2)S	(1 + 2)S	0.0018	0.0040
Total			1.007	1.0018

<sup>a</sup> 1, primary; 2, secondary; S, stable; U, unstable.

<sup>b</sup> The initial weight selectivity is determined by the initial slope of the corresponding yield-conversion plot (see Figs. 5 and 6).

TABLE 3

Initial Molar Selectivities for Products from Reaction of 3-Methylpentane on HZSM-5, HY, and Amorphous Silica-Alumina at 500°C

Product	Initial molar selectivity <sup>a</sup>		
	HZSM-5	HY	Silica-alumina
Hydrogen	0.228	0.108	0.249
C <sub>1</sub> (P)	0.356	0.0203	0.0946
C <sub>2</sub> (P)	0.258	0.0373	0.0573
C <sub>2</sub> (O)	0.399	0.0768	0.123
C <sub>3</sub> (P)	0.033	0.375	0.0606
C <sub>3</sub> (O)	0.602	0.602	0.635
C <sub>4</sub> (P)	0.0691	0.122	0.0893
C <sub>4</sub> (O)	0.316	0.0412	0.0624
C <sub>5</sub> (P)	0	0.0729	0.0597
C <sub>5</sub> (O)	0.0848	0	0.00776
C <sub>6</sub> (P)	0.0658	0.311	0.366
C <sub>6</sub> (O)	0.0071	0	0.0273

<sup>a</sup> Initial molar selectivities were calculated from initial weight selectivities in Table 1 using the relationship

$$\text{Molar Selectivity} = \text{Weight Selectivity} \times \frac{\text{MW of Feed}}{\text{MW of Product}}$$

TABLE 4

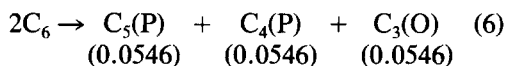
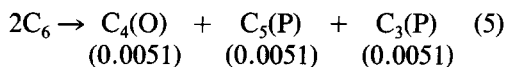
Initial Molar Selectivities for Products from Reaction of 2,3-Dimethylbutane on HZSM-5 and HY at 500°C

Product	Initial molar selectivity <sup>a</sup>	
	HZSM-5	HY
Hydrogen	0.215	0.155
C <sub>1</sub> (P)	0.768	0.233
C <sub>2</sub> (P)	0	0
C <sub>2</sub> (O)	0.491	0.210
C <sub>3</sub> (P)	0.0295	0.174
C <sub>3</sub> (O)	0.983	0.579
C <sub>4</sub> (P)	0	0.0473
C <sub>4</sub> (O)	0	0.0171
C <sub>5</sub> (P)	0	0.100
C <sub>5</sub> (O)	0.270	0.0158
C <sub>6</sub> (P)	0	0.323
C <sub>6</sub> (O)	0	0.056

<sup>a</sup> Initial molar selectivities were calculated from initial weight selectivities in Table 2 using the relationship

$$\text{Molar Selectivity} = \text{Weight Selectivity} \times \frac{\text{MW of Feed}}{\text{MW of Product}}$$

The remaining C<sub>4</sub>(O) and C<sub>5</sub>(P) cannot easily be accounted for by simple monomolecular processes. Dimerization-cracking processes (25) have previously been suggested to account for the observed cracking modes during reaction of *n*-hexane. Although the inclusion of these processes may not be entirely satisfactory, they account for only ~10% of total initial selectivity and allow completion of the overall reaction scheme with a better overall agreement between ratios of experimental/calculated selectivities as shown in Table 6. The proposed processes would be



Selectivities for C<sub>5</sub>(P) and C<sub>3</sub>(P) in reaction (5), and for C<sub>4</sub>(P) and C<sub>3</sub>(O) in reaction (6), follow from stoichiometry.

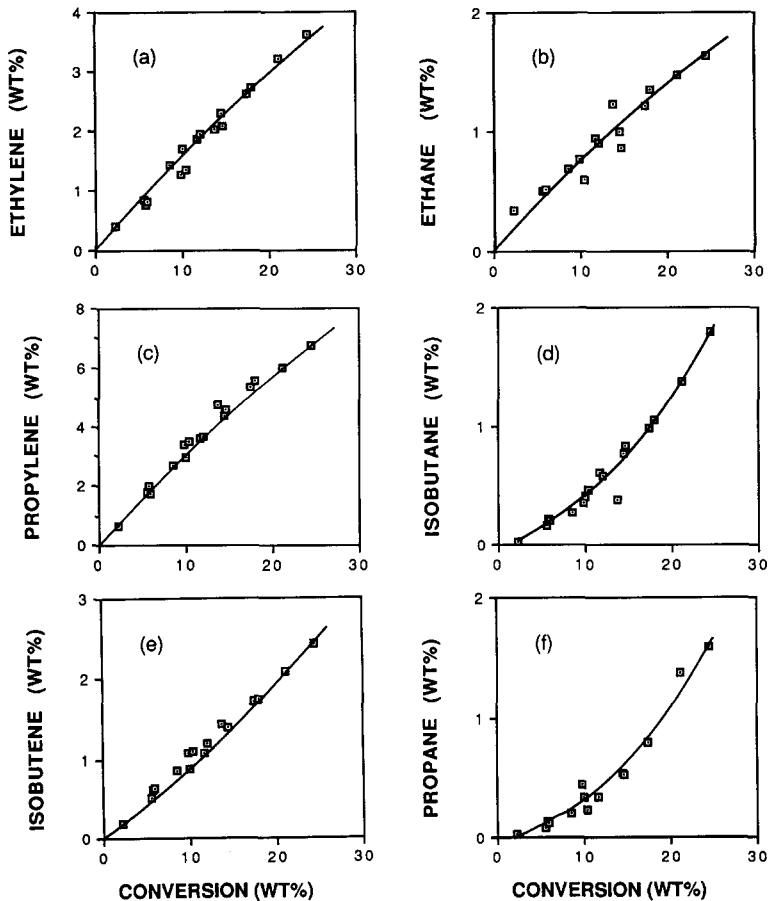


FIG. 2. Yield-conversion plots for products from reaction of 3-methylpentane on HZSM-5 at 500°C (a) Ethylene, (b) ethane, (c) propylene, (d) isobutane, (e) isobutene, (f) propane.

TABLE 5

Ratios of Experimental/Calculated Initial Molar Selectivities with only Monomolecular Processes Assumed

Product	3-Methylpentane			2,3-Dimethylbutane	
	HZSM-5	HY	Silica-alumina	HZSM-5	HY
Hydrogen	1.07	1.04	0.92	0.94	1.00
C <sub>1</sub> (P)	1.00	1.00	1.00	1.00	1.00
C <sub>2</sub> (P)	1.00	1.00	1.00	(n.o.)	(n.o.)
C <sub>2</sub> (O)	1.00	1.00	1.00	0.99	0.97
C <sub>3</sub> (P)	1.00	1.00	1.00	1.00	1.00
C <sub>3</sub> (O)	1.00	1.00	1.00	1.00	1.00
C <sub>4</sub> (P)	1.00	2.16	2.47	(n.o.)	(0.0473/0) <sup>a</sup>
C <sub>4</sub> (O)	1.00	1.10	1.09	1.00	(0.171/0) <sup>a</sup>
C <sub>5</sub> (P)	(n.o.)	(0.0729/0) <sup>a</sup>	(0.0597/0) <sup>a</sup>	(n.o.)	(0.100/0) <sup>a</sup>
C <sub>5</sub> (O)	1.00	(n.o.)	1.00	1.00	1.00
C <sub>6</sub> (P)	1.00	1.00	1.00	(n.o.)	1.00
C <sub>6</sub> (O)	1.00	(n.o.)	1.00	(n.o.)	1.00

Note. The (n.o.) indicates that the product was not observed initially under experimental conditions.

<sup>a</sup> These ratios ( $\infty$ ) arise because the product is observed experimentally but not accounted for in the proposed reaction scheme.

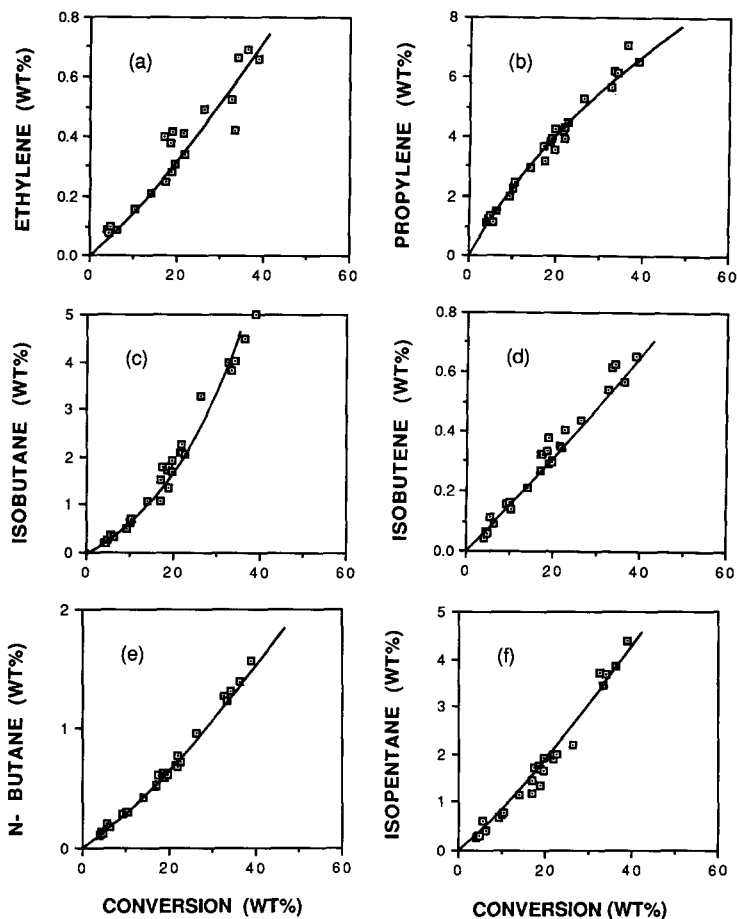


FIG. 3. Yield-conversion plots for products for reaction of 3-methylpentane on HY at 500°C. (a) Ethylene, (b) propylene, (c) isobutane, (d) isobutene, (e) *n*-butane, (f) isopentane.

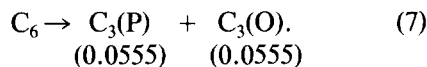
TABLE 6

Ratios of Experimental/Calculated Initial Molar Selectivities with Monomolecular and Bimolecular Processes Assumed

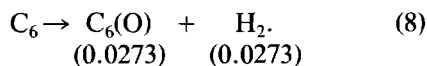
Product	3-Methylpentane		2,3-Dimethylbutane
	Silica-alumina	HY	HY
Hydrogen	1.00	1.00	1.00
C <sub>1</sub> (P)	1.00	1.00	1.00
C <sub>2</sub> (P)	1.00	1.00	(n.o.)
C <sub>2</sub> (O)	1.00	1.00	0.97
C <sub>3</sub> (P)	1.00	1.00	1.06
C <sub>3</sub> (O)	0.99	1.00	1.00
C <sub>4</sub> (P)	0.98	0.93	1.00
C <sub>4</sub> (O)	1.00	1.10	1.00
C <sub>5</sub> (P)	1.00	1.00	1.55
C <sub>5</sub> (O)	1.00	(n.o.)	1.00
C <sub>6</sub> (P)	1.00	1.00	1.00
C <sub>6</sub> (O)	1.00	(n.o.)	1.00

Note. The (n.o.) indicates that the product was not observed initially under experimental conditions.

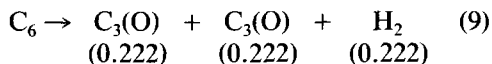
From the total selectivity for C<sub>3</sub>(P) in Table 3, and that accounted for by process (5), the selectivity for process (7) can be calculated:



The initial molar selectivity for C<sub>6</sub>(O) can be assigned to the process



The remaining C<sub>3</sub>(O) produced can be accounted for by process (9), using the total observed initial selectivity for hydrogen in Table 3:



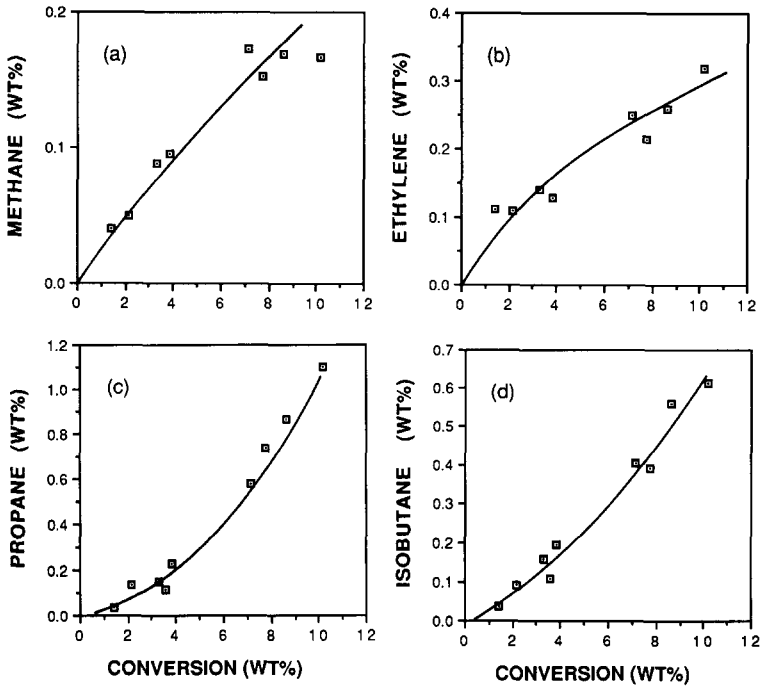


FIG. 4. Yield-conversion plots for products from reaction of 3-methylpentane on amorphous silica-alumina at 500°C. (a) Methane, (b) ethylene, (c) propane, (d) isobutane.

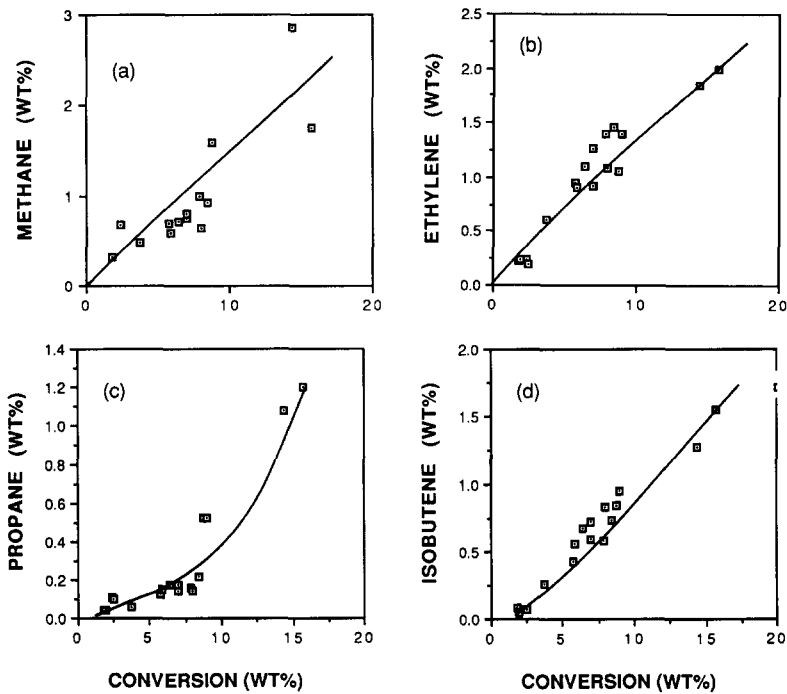


FIG. 5. Yield-conversion plots for products from reaction of 2,3-dimethylbutane on HZSM-5 at 500°C. (a) Methane, (b) ethylene, (c) propane, (d) isobutane.



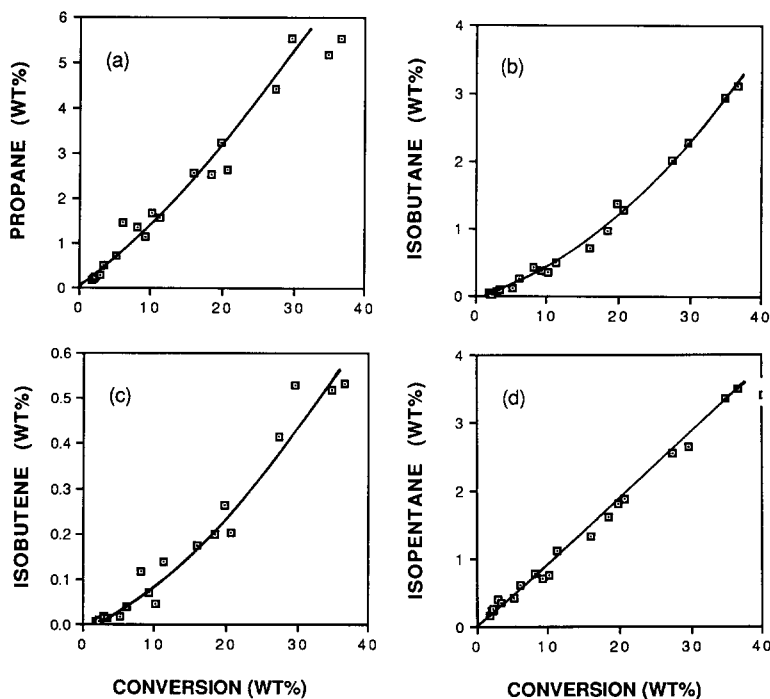
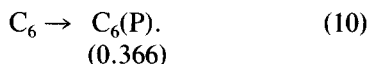


FIG. 6. Yield-conversion plots for products from reaction of 2,3-dimethylbutane on HY at 500°C. (a) Propane, (b) isobutane, (c) isobutene, (d) isopentane.

The total initial selectivity for  $C_3(O)$  from processes (2), (6), (7), and (9) is 0.641, close to the observed value (0.635) in Table 3.

Skeletal isomerization accounts for the remaining reaction process:



Summaries of initial reaction processes for 3-methylpentane and 2,3-dimethylbutane, including dimerization-cracking processes, are given in Tables 7 and 8, respectively. The selectivity values given are based on the reactant, so that the values given for the proposed dimerization-cracking processes (j) and (k) are double the numerical values of the calculated selectivities for individual products formed through these reactions. In this way, addition of the total selectivities in Tables 7 and 8 is close to unity in each case. Having examined the principle modes of reaction taking place for the branched paraffins on these aluminosili-

cates, the nature of the active sites on the catalysts can be considered.

#### Active Sites

There is now significant evidence to support the proposal that cracking of paraffins on HZSM-5 is initiated at Brønsted sites through formation of a carbonium ion (6, 10, 26-28). Several studies have shown a direct correlation between cracking activity and the number of strong Brønsted sites (6, 27, 28). Initiation of cracking of a saturated molecule at a Brønsted site can occur through two pathways (10). Protonation of the hydrocarbon can be followed by C-H bond cleavage, with liberation of molecular hydrogen, or through C-C cleavage, producing a shorter paraffin and a residual carbonium ion. Similar reactions have been established for paraffins in liquid superacid media at low temperatures (13).

Initiation of cracking for 3-methylpentane and 2,3-dimethylbutane on HZSM-5 by pro-

TABLE 7

Initial Reaction Processes Occurring on HZSM-5, HY, and Silica-alumina for Reaction of 3-Methylpentane at 500°C

Process	Initial molar selectivity <sup>a</sup>		
	HZSM-5	HY	Silica-alumina
(a) C <sub>6</sub> → C <sub>1</sub> (P) + C <sub>5</sub> (O)	0.0848	0	0.0078
(b) C <sub>6</sub> → C <sub>2</sub> (P) + C <sub>4</sub> (O)	0.258	0.0373	0.0573
(c) C <sub>6</sub> → C <sub>3</sub> (P) + C <sub>3</sub> (O)	0.033	0.375	0.0555
(d) C <sub>6</sub> → C <sub>4</sub> (P) + C <sub>2</sub> (O)	0.0691	0.0565	0.0362
(e) C <sub>6</sub> → C <sub>1</sub> (P) + C <sub>2</sub> (O) + C <sub>3</sub> (O)	0.271	0.0203	0.0868
(f) C <sub>6</sub> → C <sub>3</sub> (O) + C <sub>3</sub> (O) + H <sub>2</sub>	0.149	0.108	0.222
(g) C <sub>6</sub> → C <sub>4</sub> (O) + C <sub>2</sub> (O) + H <sub>2</sub>	0.072	0	0
(h) C <sub>6</sub> → C <sub>6</sub> (O) + H <sub>2</sub>	0.0071	0	0.0273
(i) C <sub>6</sub> → C <sub>6</sub> (P)	0.0658	0.311	0.366
(j) 2C <sub>6</sub> → C <sub>5</sub> (P) + C <sub>3</sub> (O) + C <sub>4</sub> (P)	0	0.1458	0.1092
(k) 2C <sub>6</sub> → C <sub>4</sub> (P) + C <sub>3</sub> (P) + C <sub>4</sub> (O)	0	0	0.0102
Total	1.01	1.05	0.978

<sup>a</sup> The initial molar selectivities reported are based on reaction of 1 mole of reactant C<sub>6</sub> paraffin.

tonation followed by formation of molecular hydrogen accounts for ~23% of the total initial selectivity, corresponding to reaction modes (f), (g), and (h) in Tables 7 and 8. Cracking via direct C–C bond cleavage (i.e., without rearrangement) of the carbonium ion can account for the dominant reaction modes on HZSM-5 corresponding to pro-

TABLE 8

Initial Reaction Processes Occurring on HZSM-5 and HY for Reaction of 2,3-Dimethylbutane at 500°C

Process	Initial molar selectivity <sup>a</sup>	
	HZSM-5	HY
(a) C <sub>6</sub> → C <sub>1</sub> (P) + C <sub>5</sub> (O)	0.270	0.0156
(b) C <sub>6</sub> → C <sub>2</sub> (P) + C <sub>4</sub> (O)	0	0
(c) C <sub>6</sub> → C <sub>3</sub> (P) + C <sub>3</sub> (O)	0.0295	0.122
(d) C <sub>6</sub> → C <sub>4</sub> (P) + C <sub>2</sub> (O)	0	
(e) C <sub>6</sub> → C <sub>1</sub> (P) + C <sub>2</sub> (O) + C <sub>3</sub> (O)	0.498	0.217
(f) C <sub>6</sub> → C <sub>3</sub> (O) + C <sub>3</sub> (O) + H <sub>2</sub>	0.228	0.099
(g) C <sub>6</sub> → C <sub>4</sub> (O) + C <sub>2</sub> (O) + H <sub>2</sub>	0	0
(h) C <sub>6</sub> → C <sub>6</sub> (O) + H <sub>2</sub>	0	0.056
(i) C <sub>6</sub> → C <sub>6</sub> (P)	0	0.343
(j) 2C <sub>6</sub> → C <sub>5</sub> (P) + C <sub>4</sub> (P) + C <sub>3</sub> (O)	0	0.0946
(k) 2C <sub>6</sub> → C <sub>5</sub> (P) + C <sub>3</sub> (P) + C <sub>4</sub> (O)	0	0.105
Total	1.026	0.982

<sup>a</sup> The initial molar selectivities are based on reaction of 1 mole of reactant C<sub>6</sub> paraffin.

cesses (a), (b), (d), and (e). Tables 7 and 8 show that these would account for ~68% and ~77% of the total initial selectivities for 3-methylpentane and 2,3-dimethylbutane, respectively. Reaction (c) corresponding to cracking of 2,3-dimethylbutane to give propane and propylene can also be attributed to direct cleavage of a C–C bond, so that the total initial selectivities via both routes at Brønsted sites are 91 and 100% for 3-methylpentane and 2,3-dimethylbutane, respectively. The remaining processes for 3-methylpentane on HZSM-5 are cracking to produce propane and propylene (reaction (c)) and skeletal isomerization (reaction (i)). These processes cannot occur without rearrangement of the carbon skeleton, and may be attributed to either a rearrangement of a protonated structure (11) or through carbenium ion formation at a Lewis site (4).

Tables 7 and 8 show that these latter processes involving isomerization are more important for reactions of HY and amorphous silica-alumina at 500°C. Processes (c) and (i) account for 69 and 42% of the total initial selectivity for reaction of 3-methylpentane on HY and silica-alumina respectively (Table 7). Skeletal isomerization also accounts for 34% of the total initial selectivity for reaction of 2,3-dimethylbutane on HY (Table 8). There is clear evidence for the presence of Brønsted sites on both HY and amorphous silica-alumina from various physical measurements (29–33). The participation of these sites in cracking reactions has also been demonstrated by experiments where catalysts have been subjected to heat pretreatment at different temperatures (32–35).

For reaction of linear paraffins on HY, it has been found that subjecting the catalyst to a pretreatment temperature above 500°C causes loss in cracking activity (36). This effect has been demonstrated to be reversible up to 600°C, by "adding back" water to the catalyst. Dehydration is assumed to occur through loss of a water molecule from two Brønsted sites, resulting in formation of one Lewis site (36).

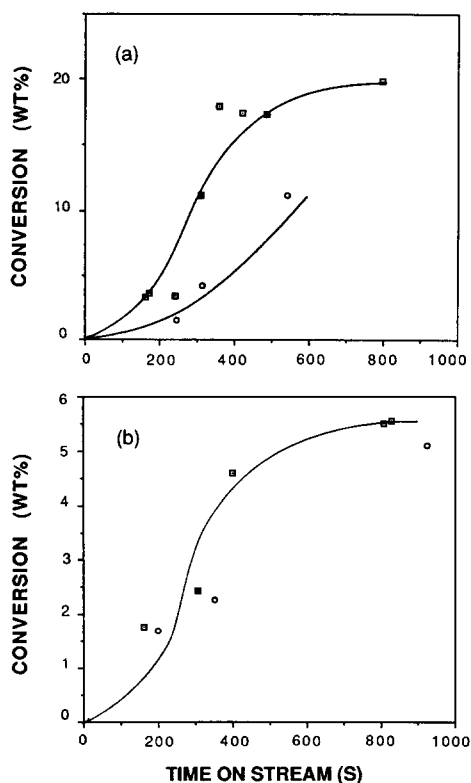


FIG. 7. Effects of heat treatment and rehydration on reactions of 3-methylpentane on (a) HY, catalyst to reactant ratio 0.0075; (b) amorphous silica-alumina, catalyst to reactant ratio 0.415. Pretreatment temperatures: (O) 600°C; (□) 500°C. Full symbol shows the influence of rehydration.

In spite of this evidence, recent reports by Corma and co-workers maintain the role of Lewis sites as the dominant active centers (4) during cracking reactions of *n*-heptane on HY. It is hoped to resolve this issue here by considering the influence of heat pretreatment on HY and the amorphous catalyst on selectivity and conversion of the branched C<sub>6</sub> paraffins. Figure 7a shows that for reaction of 3-methylpentane on HY at 500°C, there is a reversible loss of activity corresponding to a catalyst pretreatment at 600°C. Figure 7a clearly shows that the total activity is directly related to the presence of Brønsted sites on the catalyst.

Cracking processes (f), (g), and (h) in Table 7 involving formation of molecular hy-

drogen are considered very unlikely to occur at Lewis sites. Similarly processes (a) and (e) involving formation of methane are most easily attributed to cracking at Brønsted sites, as formation of a C<sub>1</sub> fragment via β-scission of a carbenium ion at a Lewis site appears improbable. Formation of fragments smaller than C<sub>3</sub> via a carbenium ion route at Lewis sites is also considered unlikely (processes (b) and (d)). Of all the processes in Table 7, (e) and (i) are the most likely to occur at Lewis centres, via abstraction of a hydride ion at a tertiary carbon atom leading to formation of the carbenium ion. If this does occur, some shift in total selectivity in favor of these processes might be expected, at the expense of those cracking processes attributed to Brønsted sites, as the catalyst is dehydrated. Figure 8 shows that there is no significant variation in selectivity for skeletal isomerization on the dehydrated catalyst. No direct evidence can be found from this study for involvement of Lewis acid sites on the catalyst framework itself, and this provides further support for the rearrangement of protonated intermediates (10, 11), as suggested for isomerization of cyclohexane on HY (37). Assessment of the type of active sites on these catalysts would appear to be more easily achieved by the methods used here than by interpretations based on ratios of paraffin/olefins,

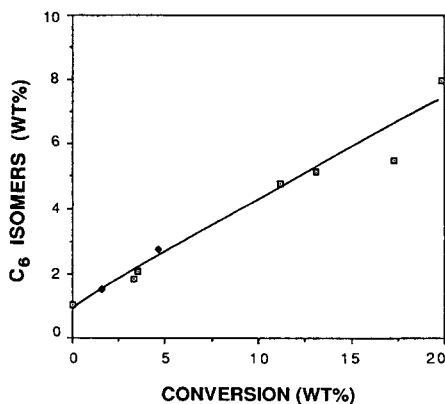


FIG. 8. Selectivity plots for isomerization of 3-methylpentane on HY corresponding to catalyst pretreatment temperatures of (□) 500°C; (◆) 600°C.

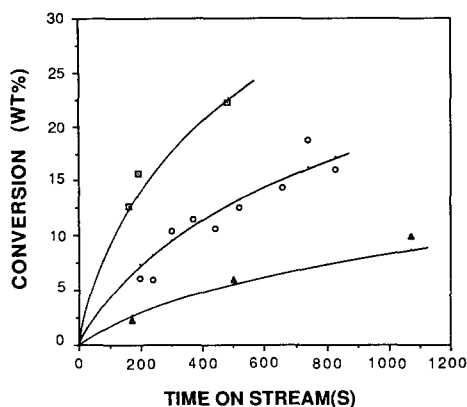


FIG. 9. Cumulative conversion curve for reaction of 3-methylpentane on HZSM-5 at 500°C. Catalyst to reactant ratios: 0.0154, 0.0384, 0.0755.

which also appear to be inconsistent with simple mass balance (21).

For reaction of 3-methylpentane on amorphous silica-alumina (Fig. 7b), no measurable effect was observed when the catalyst was subjected to a pretreatment temperature of 600°C. Neither was any influence detected when the catalyst was rehydrated. This observation can be explained in terms of a very sparse distribution of Brønsted sites on the amorphous aluminosilicate compared to that on HY (29, 30). For dehydration to occur, close proximity of pairs of surface hydroxyl groups may be required.

#### Kinetic Phenomena

Variation of conversion with time on stream for reaction of 3-methylpentane and 2,3-dimethylbutane on HZSM-5 at 500°C are shown in Fig. 9. The general characteristics of these curves are similar to those reported for reactions of linear paraffins on various aluminosilicate catalysts, and these results can be fitted by a kinetic model developed for reactions of *n*-alkanes on acid catalysts (38). In contrast, results for reactions of 3-methylpentane and 2,3-dimethylbutane on HY and amorphous silica-alumina show a different type of kinetic behavior (11). As shown in Fig. 10 these curves are S-shaped rather than lines of continuously declining

slope and cannot be fitted by the kinetic model applied to cracking of linear paraffins.

This kinetic phenomenon has been discussed previously (5, 11) in terms of differences in mechanisms for propagation of cracking reactions for linear and branched paraffins on HY zeolite. Curves of the type shown in Fig. 9 are produced where (Lewis) sites generated through adsorption of product olefins are less effective in causing of the feed than the original Brønsted sites. This is revealed as inhibition by applying the kinetic model. Under these conditions initiation of cracking through protonation occurs more easily than cracking via hydride abstraction from the feed molecule to produce a carbenium ion which can then undergo  $\beta$ -scission. This is generally found to be the case for linear paraffins, where abstraction

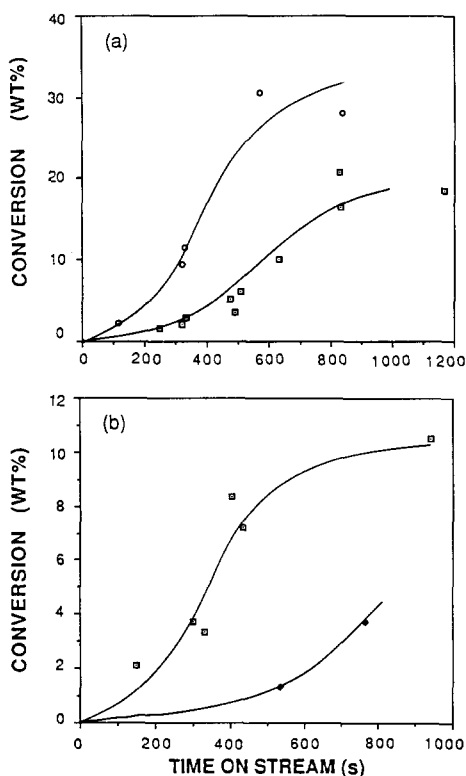


FIG. 10. Cumulative conversion curves for reactions of 2,3-dimethylbutane at 500°C on (a) HY, catalyst to reactant ratios: 0.0148, 0.0075; (b) amorphous silica-alumina, catalyst to reactant ratios: 1.21, 0.29.

of hydride ion from a secondary carbon is relatively difficult. Conversely, acceleration of cracking can be observed if the feed molecule contains a hydrogen atom bonded to a tertiary carbon atom, which gives rise to the S-shaped curves, shown for reaction of branched  $C_6$  paraffins on HY and silica-alumina. The absence of this kinetic effect for reaction on HZSM-5 can be attributed to the restrictions on bimolecular transition states in the narrow-pore zeolite (3). Evidence for this explanation has been provided by the influence of addition of small amounts of olefin to the feed. For reaction of 2,3-dimethylbutane on HY at 500°C addition of 1% 1-hexene produced a marked acceleration of the cracking reaction (5), whereas addition of an olefin to linear paraffin feeds has been found to retard the reaction.

#### Formation of Molecular Hydrogen

The kinetic phenomenon associated with the S-shaped curves illustrated in Fig. 10 has been attributed to an acceleration of the cracking reaction as product olefins are adsorbed on the original Brønsted sites to give carbenium ions. This process will effectively produce Lewis centers, and a change in product selectivity might be expected to accompany this transition in the dominant type of active site, as different mechanisms would apply. If this transition does indeed occur, it should be most apparent for a reaction process which can only occur on one type of site. For example, formation of molecular hydrogen (processes (f)–(h) in Tables 7 and 8) can be attributed to initiation at Brønsted sites, and is favoured when the feed hydrocarbon has a hydrogen atom bonded to a tertiary carbon atom. Formation of molecular hydrogen at Lewis centers would not be expected, so careful inspection of selectivity plots for molecular hydrogen might reveal a "falling off" for formation of this product as the Lewis sites are generated. This falling off does indeed occur for reactions of 3-methylpentane and 2,3-dimethylbutane on HY and silica-alumina at 500°C, and is illustrated in Fig. 11a. On the

other hand, for reactions of branched  $C_6$  paraffins on HZSM-5, the selectivity curves for molecular hydrogen show no falling off, as would be expected when bimolecular processes are inhibited (Fig. 11b). It is possible that the falling off in hydrogen formation could be compensated for by production of molecular hydrogen for other sources including coke formation (39, 40). However, this is considered to be very unlikely in the present example, as very small amounts of coke are produced during cracking on the pentasil at 500°C (41, 42).

The general shape of such selectivity plots have been explained in terms of the stability or instability of the product species (23). However, this interpretation in terms of product stability seems unlikely for molecular hydrogen under the reaction conditions

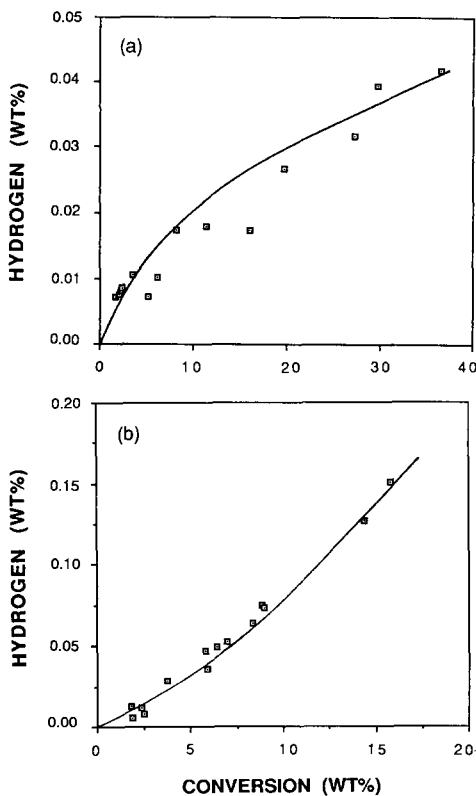


FIG. 11. Selectivity plots for formation of molecular hydrogen for reactions of 2,3-dimethylbutane at 500°C: (a) HY; (b) HZSM-5.

used here, particularly where we would need to assign hydrogen as unstable, as in Fig. 11a. These observations suggest that care must be taken in assigning product stability or in distinguishing between primary and secondary products, as the yield-conversion curves may in fact reflect changes in the active sites themselves, rather than the behaviours of the product species.

The present studies can also be related to investigations of the behavior of saturated hydrocarbons in liquid superacids (43-45). It appears that direct cracking of C-C bonds can occur easily in these systems, producing a shorter paraffin and a carbenium ion. Isomerization has also been observed in those systems, but this seems to have generally been attributed to loss of molecular hydrogen with subsequent rearrangement of the carbenium ion. Although alkylation of saturated paraffins by a carbenium ion has been described in liquid superacids, the possibility of isomerization of the intermediate carbonium ion (11) does not appear to have been considered to any great extent, and this possibility may account for the apparent "missing" hydrogen reported by some authors (43-45).

#### CONCLUSION

This study shows that Brønsted sites are the dominant active centers for catalytic reactions of branched paraffins on several aluminosilicate catalysts. No direct evidence could be found for participation of Lewis sites on the catalyst framework itself. Use of these feedstocks, where a hydrogen atom is bonded to a tertiary carbon atom, should provide conditions particularly favourable to such processes. These results give further cause to reexamine cracking mechanisms in which Lewis sites are presented as the dominant source of initial catalytic activity (4).

This study also shows that changes in product selectivity can occur if the reaction mechanisms which occur during initiation and subsequent propagation of reaction are different. This type of phenomenon, where

there is an effective change in the role of the active site can influence the apparent patterns of product stability as shown by plots of yield against conversion. Accordingly, assignments of product type (23) as stable or unstable may not be strictly valid.

#### ACKNOWLEDGMENTS

Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada under the URF programme. Facilities provided by the University of Tasmania are also acknowledged.

#### REFERENCES

1. Jacobs, P. A., Tielen, M., Martens, J., and Beyer, H. K., *J. Mol. Catal.* **27**(1-2), 11 (1984).
2. Lombardo, E. A., Pierantozzi, R., and Hall, W. K., *J. Catal.* **110**, 171 (1988).
3. Haag, W. O., Lago, R. M., and Weisz, P. B., *Faraday Discuss. Chem. Soc.* **72**, 317 (1982).
4. Corma, A., Planelles, J., Sanchez-Marin, J., and Tomas, F., *J. Catal.* **93**, 30 (1985).
5. Abbot, J., *Appl. Catal.* **47**, 33 (1989).
6. Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature (London)* **309**, 589 (1984).
7. Vaughan, D. E. W., *Chem. Eng. Prog.* **84**(2), 25 (1988).
8. Chen, N. Y., and Degnan, T. F., *Chem. Eng. Prog.* **84**(2), 32 (1988).
9. Kokotailo, G. T., Lawton, S. L., Olson, D. M., and Meier, W. M., *Nature (London)* **272**, 437 (1978).
10. Haag, W. O., and Dessau, R. M., in "Proceedings of the 9th Int. Cong. Catal.," Berlin, 1984.
11. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **115**, 1 (1989).
12. Planelles, J., Sanchez-Marin, J., Tomas, F., and Corma, A. *J. Chem. Soc. Perkin Trans. 2* **333** (1985).
13. Olah, G. A., Halpern, Y., Shen, J., and Mo, Y. K., *J. Amer. Chem. Soc.* **95**, 4960 (1973).
14. Chen, N. Y., and Garwood, W. E., *J. Catal.* **52**, 453 (1978).
15. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **113**, 353 (1988).
16. Choudhary, V. R., and Akolekar, D. B., *J. Catal.* **117**, 542 (1989).
17. Planelles, J., Sanchez-Marin, J., Tomas, F., and Corma, A., *J. Mol. Catal.* **32**, 365 (1985).
18. Corma, A., and Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **27**(1), 29 (1985).
19. Hattori, H., Takahashi, O., Takagi, M., and Tanabe, K., *J. Catal.* **68**, 132 (1981).
20. Corma, A., Fornes, V., Monton, J. B., and Orchilles, A. V., *J. Catal.* **107**, 288 (1987).
21. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **107**, 451 (1987).

22. Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **66**, 825 (1988).
23. Ko, A. N., and Wojciechowski, B. W., *Prog. React. Kinet.* **12**, 201 (1983).
24. Abbot, J., *Appl. Catal.* **57**, 105 (1990).
25. Bolton, A. P., and Bujalski, R. L., *J. Catal.* **18**, 1 (1970).
26. Sendoda, Y., and Ono, Y., *Zeolites* **8**, 101 (1988).
27. Borade, R. B., Hedge, S. G., Kulkasni, S. B., and Ratnasany, *Appl. Catal.* **13**, 27 (1984).
28. Klyachkoo, A. L., Kapustin, G. I., Brueva, T. R., and Rubinstein, A. M., *Zeolites* **7**, 119 (1987).
29. Borovkov, V. Y., Alexeev, A. A., and Kazansky, V. B., *J. Catal.* **80**, 462 (1983).
30. Liang, S. H. C., and Gay, I. D., *J. Catal.* **66**, 294 (1980).
31. Otouma, H., Yoshimasa, A., and Uhihashi, H., *Bull. Chem. Soc. Japan* **42**, 2449 (1969).
32. Hopkins, P. D., *J. Catal.* **12**, 325 (1968).
33. Benesi, H. A., *J. Catal.* **8**, 368 (1967).
34. Ward, J. W., *J. Catal.* **9**, 225 (1967).
35. Ward, J. W., *J. Catal.* **10**, 34 (1968).
36. Benesi, H. A., and Winquist, B. H. C., *Adv. Catal.* **27**, 97 (1978).
37. Abbot, J., *J. Catal.* **123**, 383 (1990).
38. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **104**, 80 (1987).
39. Abbot, J., and Wojciechowski, B. W., in "Proceedings of the 10th Int. Cong. Catal. Calgary, 1988."
40. Brouwer, D. M., *J. Catal.* **1**, 372 (1962).
41. Walsh, D. E., and Rollman, L. D., *J. Catal.* **56**, 195 (1979).
42. Dejaifre, P., Auroux, A., Gravelle, P. C., Vedrine, J. C., Gabelica, Z., and Deroune, E. G., *J. Catal.* **70**, 123 (1981).
43. Larsen, J. W., *J. Amer. Chem. Soc.* **99**, 4379 (1977).
44. Olah, G., and Lukas, J., *J. Amer. Chem. Soc.* **89**, 2227 (1967).
45. Olah, G., and Lukas, J., *J. Amer. Chem. Soc.* **89**, 4739 (1967).