Reactions of hexane isomers on H-mordenite at moderate temperatures in liquid and gas phases: the effect of cyclic hydrocarbons

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Abstract

H-mordenite, a more active acid catalyst than HZSM-5, showed features of a carbocationic/cationoidic isomerization in the reaction of liquid 3-methylpentane, but not of liquid hexane. The carbocationic isomerization features were not seen in the gas phase, for either reactant. Thus, there are mechanistic differences between the reactions of alkanes in the liquid phase and in the vapor phase on the zeolite. The liquid-phase reaction of hexane in the presence of methylcyclopentane, cyclopentane, and deuteromethylcyclopentane showed the absence of hydride transfer catalysis. The label redistribution between deuterated and nondeuterated reactants showed that the products were formed from olefinic reaction intermediates, although none were found in the products desorbed. Each olefin exchanged repeatedly hydrogen with the catalyst before being hydrogenated and desorbed. The possibility that alkenyl cations retained on the catalyst play a role, as in trifluoromethanesulfonic acid, is discussed. As the space requirement of hydride transfer is smaller than that of β-cracking, the results speak against protonated alkanes ("carbonium" ions) in the catalysis on zeolites. The type of activation observed in superacid catalysts, where the standard carbocationic mechanism operates, does not occur in zeolites. The chemisorbed alkenes may be formed by one-electron oxidation or by dehydrogenation on tetracoordinated aluminum atoms, either in the lattice or in cages (extralattice aluminum).
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1. Introduction

The reversible isomerization of hexane [1] has long been considered a standard for the study of cationic reactions of alkanes [2]. Careful studies of its equilibrium [3] and kinetics have been published [4,5]. We chose, therefore, hexane and 3-methylpentane, together with the cyclic hydrocarbon methylcyclopentane, as model substrates for a comparison of solid and liquid acids. The goal was to investigate the activity of various solid acid catalysts at lower temperatures than normally used, for better comparison with the strong liquid acid catalysts. Because the reactions with liquid acids normally use liquid hydrocarbons, whereas on solid acids the reactants are usually in the vapor phase, we undertook a study of the reactions on the solid acids at moderate temperatures with both liquid and gaseous reactants. The reactions of the same compounds catalyzed by trifluoromethanesulfonic acid (TFMSA), a weak superacid, served as terms of comparison. We found that the reactions of hexane and 3-methylpentane catalyzed by TFMSA can be either isomerization or cracking by a chain mechanism and that the reaction pathway is determined by the concentration of alkenyl (substituted allyl) cations, formed by an oxidation reaction in the acid layer near the interface with the organic layer [6,7].

For the zeolite HZSM-5, we found that small but consistent conversions can be achieved at 120–175 °C, in both the liquid- and the gas-phase reactions [8,9]. Mordenite (HMOR), an acid zeolite with larger pores, gave a much higher conversion than HZSM-5 in the reaction of hexane in the liquid phase [10]. Here, we report a comparative study of the reactivities and products in the conversion of hexane and 3-methylpentane on HMOR in the liquid and vapor phases.

2. Experimental

2.1. Reactants

Commercial, reagent-grade, hexane contained up to 0.45% methylcyclopentane (by GLC). The reagent-grade methylcyclopentane contained about 2% hexane. Cyclopentane, 99.5%, contained ⩽ 0.5% 2,2-dimethylbutane and < 0.05% methylcyclopentane. Hexane of 99.95% purity,

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containing no methylcyclopentane and no olefins, was pre-
pared from 1-bromohexane via the Grignard reagent and
was purified by repeated washing with chilled concentrated
sulfuric acid [11,12]. Uniformly labeled hexane, containing
an average of 4.3 deuterium atoms per molecule (hexane-
u-$d_{4.3}$) was obtained by the catalytic addition of deuterium
to 1,5-hexadiene and purified in the same manner [12]. It
was a mixture of all isotopomers, with the distribution: 5.3,
9.8, 13.1, 14.8, 14.3, 12.8, 10.0, 7.4, 5.0, 3.2, 2.0, 1.2, 0.7,
0.3, and 0.2%, for the isotopomers from d_0 to d_{14}, respec-
tively (GC-MS). ^{2}H NMR analysis indicated that the isotope
was statistically distributed among all methyl and methylene
groups. The synthesis of methylcyclopentane deuterated at
the tertiary position has also been published [13].

2.2. Catalyst

Ammonium mordenite CBV-30A, $SiO_2/Al_2O_3 = 35$,
0.02% (wt) Na_2O, of 541 m^2/g, was obtained from Conteka.
For each experiment, the catalyst was activated by gradual
heating in air to 480 °C over a period of 8 h and maintained
at this temperature for 13 h [10].

2.3. Reactant and product analyses

The GLC and GC-MS (70 eV) analyses were conducted
as described before [6,7]. Three of the compounds of inter-
est, cyclopentane, 2-methylpentane, and 2,3-dimethylbutane,
were not separated by GLC at the lowest temperature acces-
sible (25 °C), but were separated in the GC-MS instrument
at a column temperature of 13 °C. Thus, the sum of these
compounds was obtained from the GC analysis and their ra-
tios from the total ion current in GC-MS.

2.4. Catalytic reactions

For a reaction with liquid reactant, the catalyst (0.04–
0.05 g) was activated directly in a 12 cm × 6 mm i.d.
glass tube, before the reaction. As soon as the tube was
cool enough to be handled, a Teflon-coated stirring bar was
added and the tube was capped with a rubber septum. When
the tube with catalyst reached room temperature, the reac-
tant (0.25 g) was injected from a syringe. The tube was then
cooled in liquid nitrogen, sealed under vacuum [10], swirled
for mixing, immersed vertically in an oil bath thermostated
at the desired temperature, and then placed over a magnetic
stirring plate [14]. The mixture was allowed to react with
stirring for a determined length of time. It was checked that
the catalyst was fully covered with liquid throughout the
experiment. The sample was then frozen in liquid nitrogen
and the tube was cut open and capped with a rubber sep-
tum. Upon heating to room temperature, samples were taken
through the septum from both the gas phase and the liquid
phase and analyzed by GLC and GC-MS.

For a gas-phase reaction, a mixture of hydrocarbon and
He (9.6 mL/min total flow) was passed through 0.3 g of

catalyst which had been activated in the tubular glass re-
actor. Samples of the effluent were withdrawn with a gas
syringe and analyzed. Two concentrations of reactant were
examined. The first, 7%, was achieved by keeping the va-
por saturator at 0 °C; at that temperature the vapor pres-
sures of hexane and 3-methylpentane differ by very little.
For the second, 17%, the saturator temperature was 15.5 °C
for 3-methylpentane and 20 °C for hexane.

3. Results and discussion: reactivity patterns of alkanes and cycloalkanes

3.1. Reactions of 3-methylpentane

The liquid-phase reaction of 3-methylpentane was clean
isomerization. The reaction was much cleaner than the reac-
tion on HZSM-5 at a temperature lower by 20 °C and cleaner
than the reaction in TFMSA in the isomerization mode at
room temperature [6,7]. On HZSM-5, disproportionation
and cracking accounted for over 25% of the products after
4 h and hexane was formed as an early product in a ratio
hexane:2-methylpentane = 0.7–0.8 [8]. On HMOR, crack-
ing and disproportionation were negligible. The conversion
exhibited the characteristic pattern of stepwise isomeriza-
tion, described by Eqs. (1)–(4) [4–6], as shown in Fig. 1 and,
even more clearly, in Fig. 2. Thus, whatever the nature of the
activation of the reactant, the product and rate patterns fit a
carbocationic (or cationoidic [15]) mechanism, which can-
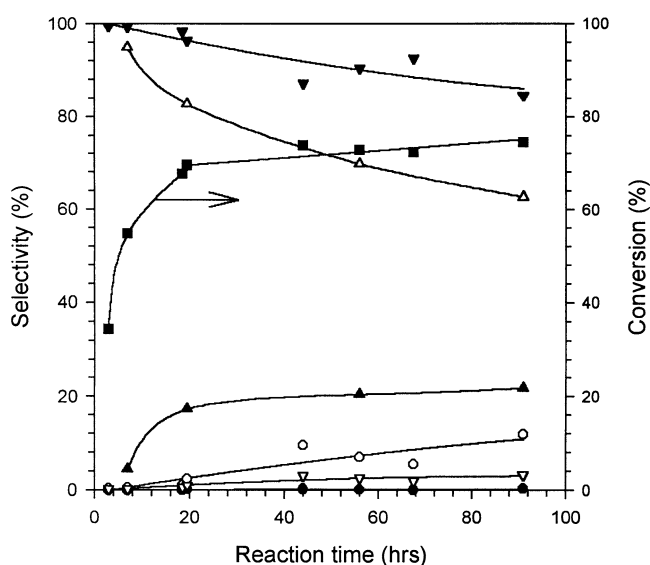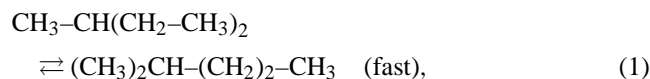not be said about the reaction on HZSM-5 [8].

$$CH_3-CH(CH_2-CH_3)_2$$
$$\rightleftarrows (CH_3)_2CH-(CH_2)_2-CH_3 \quad (fast), \qquad (1)$$

Fig. 1. Conversion of 3-methylpentane on HMOR at 160 °C, in the liquid
phase: (●) C$_{\leqslant 5}$; (○) 2,2-dimethylbutane; (▼) 2-methylpentane + 2,3-di-
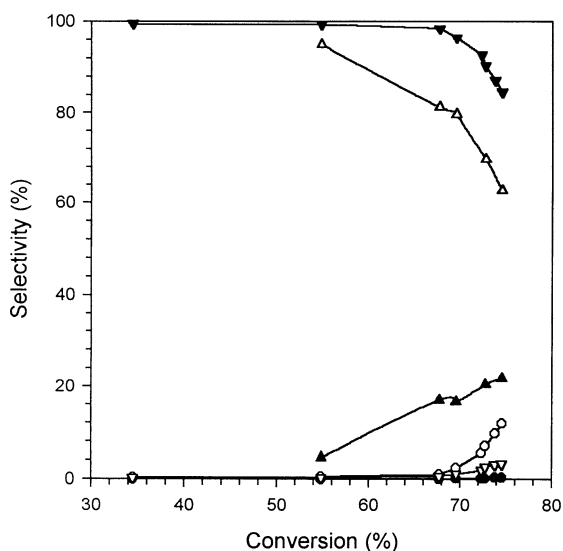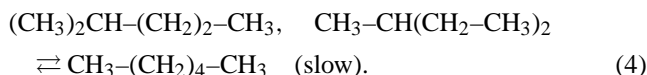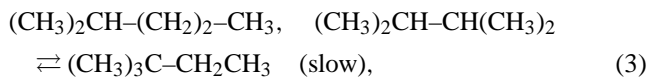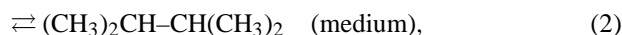methylbutane; (△) 2-methylpentane; (▲) 2,3-dimethylbutane; (▽) hexane;
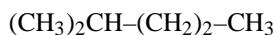(■) conversion.

Fig. 2. Product selectivity from 3-methylpentane on HMOR at 160 °C, in the liquid phase: (●) $C_{\leqslant 5}$; (○) 2,2-dimethylbutane; (▼) 2-methylpentane + 2,3-dimethylbutane; (△) 2-methylpentane; (▲) 2,3-dimethylbutane; (▽) hexane.
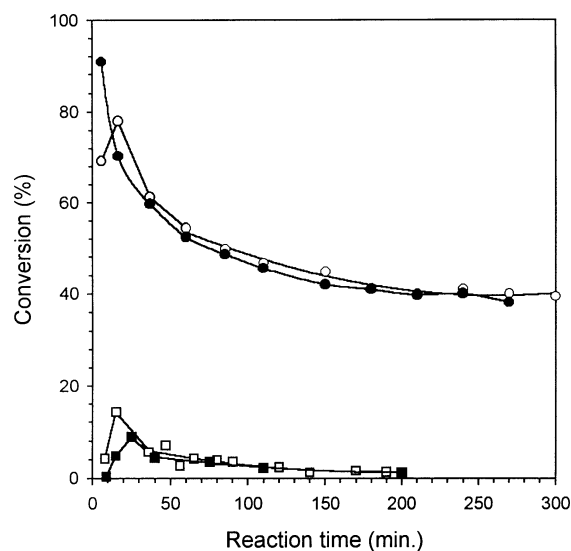

Fig. 3. Conversion of 3-methylpentane on HMOR and HZSM-5 at 142 °C, in the gas phase: (□) HZSM-5, 7% 3-methylpentane in the feed; (■) HZSM-5, 17% 3-methylpentane in the feed; (○) HMOR, 7% 3-methylpentane in the feed; (●) HMOR, 17% 3-methylpentane in the feed.

$$(CH_3)_2CH–(CH_2)_2–CH_3$$
$$\rightleftharpoons (CH_3)_2CH–CH(CH_3)_2 \quad \text{(medium)}, \tag{2}$$

$$(CH_3)_2CH–(CH_2)_2–CH_3, \quad (CH_3)_2CH–CH(CH_3)_2$$
$$\rightleftharpoons (CH_3)_3C–CH_2CH_3 \quad \text{(slow)}, \tag{3}$$

$$(CH_3)_2CH–(CH_2)_2–CH_3, \quad CH_3–CH(CH_2–CH_3)_2$$
$$\rightleftharpoons CH_3–(CH_2)_4–CH_3 \quad \text{(slow)}. \tag{4}$$

The catalyst exhibited reasonable stability. It was still active after 91 h of reaction at 160 °C (Fig. 2). Also, the activity of HMOR was much higher than that of HZSM-5. The 3-methylpentane conversion for the former was 34% after 3 h and for the latter it was 5.9% after 4 h. The number of aluminum sites per gram was about the same for the two zeolites. At the level of conversion observed on HMOR, the reverse reaction was important enough to be included in a calculation of the rate constant. The pseudo-first-order rate constants can then be estimated as $\sim 4 \times 10^{-5}$ s^{-1} for HMOR and $\sim 4 \times 10^{-6}$ s^{-1} for HZSM-5 [8], a 10-fold higher reaction rate for HMOR at 160 °C.

Differences in the activity of HMOR and HZSM-5 were also observed for the reaction of 3-methylpentane in the gas phase (Fig. 3 and Ref. [8]). The reaction was conducted at two different concentrations of reactant in He, 7 and 17%. An induction period had been evidenced in the reaction on HZSM-5 [8] and it was also observed in the reaction on HMOR at the lower concentration of reactant in the feed, 7%, but not at 17% reactant in the feed. It is possible, however, that in the latter case the induction period was shorter than 6 min, when the first sample was taken. At the point of highest activity, the conversion on HMOR was higher for 17% reactant in the feed than for 7% reactant in the feed, opposite from that observed for HZSM-5 [8]. The conversion

then decreased to about 40% at 2.5 h on stream and it remained constant and the same for the two concentrations of reactant, for the next 2.5 h (Fig. 3).

Two different patterns of reactivity were observed in the gas-phase reaction as a function of catalyst aging. During the induction period and at the peak of catalyst activity, the reaction consisted mostly of cracking, as shown in Fig. 4 for the dilute reactant. (The cracking was even higher for the concentrated reactant.) At 6 min reaction time, the conversion was 69.6% and lighter products ($C_{\leqslant 5}$) represented 60.0% of the product (effluent minus 3-methylpentane). The
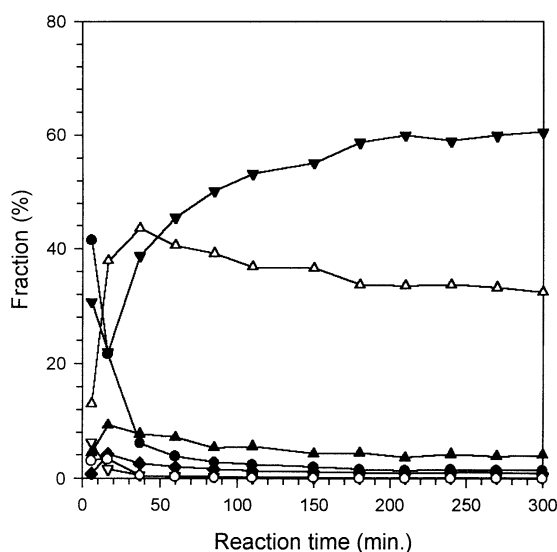

Fig. 4. Effluent composition in the reaction of 3-methylpentane (7%) on HMOR at 142 °C, in the gas phase: (●) $C_{\leqslant 5}$; (○) 2,2-dimethylbutane; (▼) 3-methylpentane; (△) 2-methylpentane; (▲) 2,3-dimethylbutane; (▽) hexane; (◆) $C_{\geqslant 7}$.

amount of heavy alkanes ($C_{\geqslant 7}$) passed through a maximum during that period. They represented 1.3% of the product at 6 min and 5.4% of the product at 16.5 min. The excess of light over heavy alkanes in the effluent means that unsaturated species accumulate on the catalyst during the induction period. Thus, in the early stages, HMOR exhibited a similar reaction pattern as HZSM-5 [8,9] (cracking mode reaction [6,7]), but the reactivity is higher for HMOR than for HZSM-5 in that mode as well.

After it reached the peak of activity, HMOR switched from a cracking catalyst to (mostly) an isomerization catalyst. At 37 min time-on-stream (TOS) the conversion was 61.5%, but the lighter alkanes represented only 10.0% of the products (effluent minus 3-methylpentane) and the heavy alkanes, 4.2%. The change in the light/heavy ratios indicates a tapering off in the buildup of unsaturated species on the catalyst. Thus, as the catalyst ages, the process becomes superficially closer to the reaction of liquid 3-methylpentane on HMOR. It appears that the reactivity of the catalytic sites changed as a certain concentration of organic species favoring isomerization was formed on them. The alternative explanation that there are two different types of sites seems less satisfactory. In any case, it is seen that the reactivity patterns for liquid reactant and gas-phase reactant are different.

The time-selectivity pattern for HMOR is different from that for HZSM-5, where the cracking products remain strongly predominant throughout a run and the amount of hexane is similar to, or greater than, the amount of 2-methylpentane, throughout [8].

The variation of isomeric product selectivity with time (Fig. 5) is mechanistically relevant. Of the isomerization products, 2,3-dimethylbutane behaved as a consecutive reaction product, peaking when the conversion to 2-methylpentane was the highest [cf. Eq. (2)]. Hexane and 2,2-dimethylbutane, however, peaked when the reaction was

mostly cracking and the 2-methylpentane:3-methylpentane ratio in effluent was low, in contradiction with the reaction sequence and reactivity order of Eqs. (1)–(4). More specifically, hexane is formed by the carbocationic mechanism directly from either 2-methylpentane or 3-methylpentane; it is an initial product from 3-methylpentane as feed [Eq. (4)]. 2,3-Dimethylbutane is a consecutive product, accessible only in a two-step process [Eqs. (1) and (2)]. It is formed in the carbocationic isomerization only after the methylpentanes had reached equilibrium, but is formed faster than hexane because of the relative specific rates of Eq. (2) and Eqs. (4) [5]. The isomer ratio at 6 min (3-methylpentane:2-methylpentane:2,3-dimethylbutane:hexane = 52.9:23.0:7.9:10.9) would require that the relative rates of Eqs. (1), (2), and (4) be drastically altered on HMOR as catalyst. Such an alteration cannot explain, however, the drop in the selectivity to hexane (3-methylpentane:2-methylpentane:2,3-dimethylbutane:hexane = 29.2: 51.5:12.6:2.2) at 16.5 min, when the conversion was higher (78.4%, meaning that the catalyst had high activity) and the decrease in the cracking/disproportionation products (from 61.3 to 33.1%) ensured a much higher concentration of the precursors of hexane [2-methylpentane and 3-methylpentane, Eq. (4)] than at 6 min. A simple change in relative rates of isomerization steps cannot explain the change in the selectivity to 2,2-dimethylbutane, either. The total concentration of its precursors [2-methylpentane and 2,3-dimethylbutane, Eq. (3)] in the mixture was much higher at 16.5 and 37 min than at 6 min, yet the total and relative (percentage of the mixture of isomers) concentration of 2,2-dimethylbutane decreased drastically during that time. The data led to the same conclusion as reached for the cracking mode reaction in TFMSA [6], that the isomeric products are largely formed by a mechanism other than the standard carbocationic isomerization mechanism. This mechanistic feature was even stronger for HZSM-5 as catalyst [8].

The C_4 and C_5 fraction consisted almost entirely of the branched isomers. At the shortest time isobutane was the most important product, but isopentane predominated at 16.5 min and thereafter. A predominance of the branched isomers in the cracking products had also been observed on HZSM-5 [8].

3.2. Reactions of hexane

High-purity (synthetic) hexane in the liquid phase at 160 °C reacted much slower than 3-methylpentane under the same conditions. At low conversions, the rate ratio 3-methylpentane/hexane can be estimated at about 100, which is less than the ratio for the carbocationic isomerization mechanism (ca. 1000 [5,7]), but larger than the ratio with TFMSA in the cracking mode (ca. 10 [7]). The reaction of hexane on HMOR was also faster than its reaction on HZSM-5 [8]. The catalyst underwent deactivation, however, and the reaction virtually stopped at about 15% conversion.
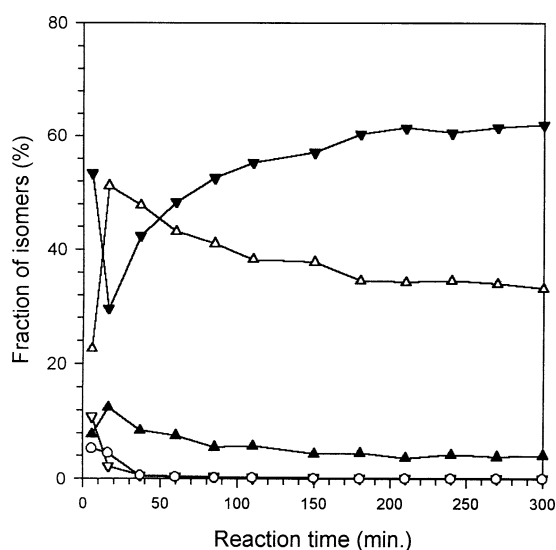

Fig. 5. C_6H_{14} composition in the effluent from 3-methylpentane (7%) on HMOR at 142 °C, in the gas phase: (○) 2,2-dimethylbutane; (▼) 3-methylpentane; (△) 2-methylpentane; (▲) 2,3-dimethylbutane; (▽) hexane.

There was very little disproportionation and cracking (up to 1.6% isobutane and isopentane and up to 1.5% $C_{\geqslant 7}$ alkanes in the product). Remarkably, the doubly branched isomers, 2,2-dimethylbutane and 2,3-dimethylbutane, were present in significant quantities at the lowest conversion (0.6%) and stayed the same at longer reaction times. The ratio of isomeric products was 3-methylpentane:2-methylpentane:2,3-dimethylbutane:2,2-dimethylbutane = 22.4:41.8:13.3:22.4 at 3.2% conversion [10]. Commercial hexane, containing 0.3% methylcyclopentane, gave the same isomer ratio. This distribution and its invariance with conversion show again that the isomer formation did not occur by the carbocationic isomerization of Eqs. (1)–(4). The isomer distribution is strikingly similar to that found in the oxidatively promoted chain reaction mode of hexane with TFMSA, which we named the cracking mode [7,10,12].

The gas-phase reaction of hexane (at 142 °C) in the flow reactor exhibited the same pattern as the reaction on HZSM-5. An induction period, during which the conversion increased, was followed by a steady decrease in conversion, presumably because of catalyst deactivation (Fig. 6). At the peak of activity, the conversion level of 7% hexane in He was somewhat higher on HMOR than on HZSM-5, but the change in concentration of reactant had a more pronounced effect upon the reaction on HMOR than upon the reaction on HZSM-5. At the 17% hexane in He, the relative activity of the two catalysts was reversed (Fig. 6).

The variation of products with time in the reaction with low concentration of hexane in the feed stream, shown in Fig. 7, was similar to that observed for the reaction of 3-methylpentane. At first, the catalyst induced mostly cracking, then it switched to isomerization. Among the lighter products ($C_{\leqslant 5}$), the iso/normal ratio was very large at first and decreased later (Fig. 8). The behavior of HMOR was in

Fig. 7. Product composition in the reaction of hexane (7%) on HMOR at 142 °C, in the gas phase: (●) $C_{\leqslant 5}$; (○) 2,2-dimethylbutane; (▼) 3-methylpentane; (△) 2-methylpentane; (▲) 2,3-dimethylbutane; (◆) $C_{\geqslant 7}$.

a sense similar to that of HZSM-5, for which apparent cracking predominated even more heavily (96%), yet it was different, because on HZSM-5 the lighter alkanes remained the main products from hexane (> 60%) throughout the run [8]. Notably, the amount of light products at short TOS was much smaller for the reaction with higher concentration of 17% hexane in the feed stream (Fig. 9). It is as if the reaction pattern moves toward the one observed for the liquid reactant (above) with the increase in the partial pressure of reactant.

On the other hand, when the amount of unsaturated adsorbed species was small and fast growing (short TOS) 2-methylpentane and 3-methylpentane were produced in a ratio close to the equilibrium value. At longer TOS,
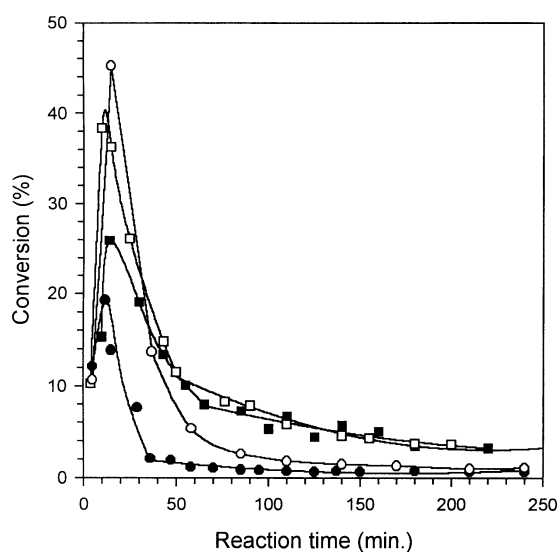

Fig. 6. Conversion of hexane on HMOR and HZSM-5 at 142 °C, in the gas phase: (□) HZSM-5, 7% hexane in the feed; (■) HZSM-5, 17% hexane in the feed; (○) HMOR, 7% hexane in the feed; (●) HMOR, 17% hexane in the feed.
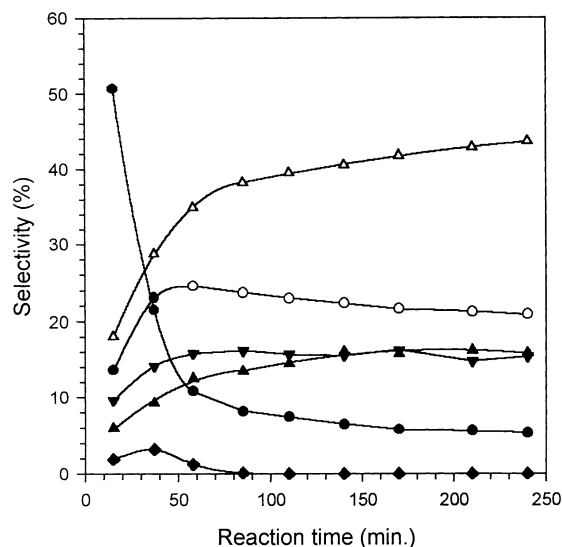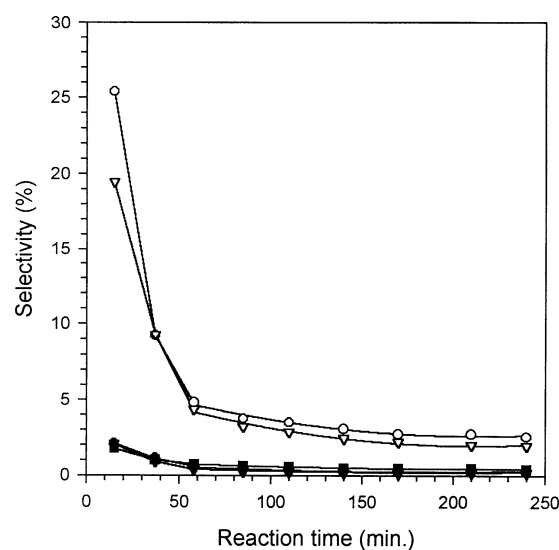

Fig. 8. Cracking product composition in the reaction of hexane (7%) on HMOR at 142 °C, in the gas phase: (●) C_3; (○) i-C_4; (▼) n-C_4; (▽) i-C_5; (◆) $C_{\geqslant 7}$; (■) n-C_5.
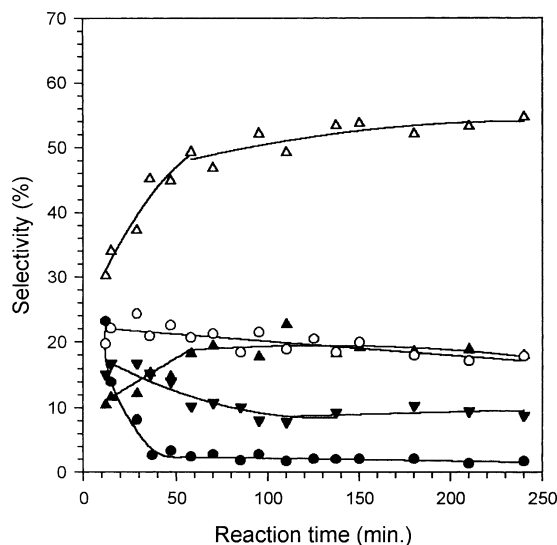
Fig. 9. Product composition in the reaction of hexane (17%) on HMOR at 142 °C, in the gas phase: (●) $C_{\leqslant 5}$; (○) 2,2-dimethylbutane; (▼) 3-methylpentane; (△) 2-methylpentane; (▲) 2,3-dimethylbutane.

the 2-methylpentane:3-methylpentane equilibrium was not reached (2-methylpentane was in excess), yet the concentration of 2,2-dimethylbutane in the product was higher than that of 3-methylpentane. These features were observed at both concentrations of hexane in the feed investigated (cf. Figs. 9 and 7). Thus, the distribution of products shows a deviation from the carbocationic isomerization pathway in the formation of isomers from hexane on HMOR in the gas phase as well.

3.3. Reactions of cyclopentane, methylcyclopentane, and their mixtures with hexane

These hydrocarbons were studied only in the liquid phase. The reaction of cyclopentane was examined as a blank for the studies of hydrogen transfer with deuterated hexane; it was found unreactive. No products of ring cleavage (cracking) were observed at 160 °C. Because the possible products with higher hydrogen content were not formed, the formation of heavier unsaturated or polymeric products, which would be retained by the catalyst, is unlikely.

The only product observed in the reaction of methylcyclopentane was cylohexane. Because the starting material contained almost 2% hexane, it was not possible to determine whether very small amounts of the ring-opened hydrocarbons might have been formed. The quantities of hexane and its isomers observed throughout the run, however, were accounted for by the initial hexane in the feed. Therefore, any ring opening of methylcyclopentane was less than the uncertainty of integration. The reactivity of methylcyclopentane was similar to that of hexane (except that the conversion increased up to 120 h). In this respect, HMOR was similar to HZSM-5, but different from TFMSA in the isomerization mode and sulfated zirconia, for which methylcyclopentane reacted about 10 times faster than hexane (unpublished re-
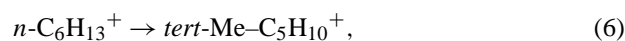
sults by P. Lukinskas and A. Vinslava, respectively, in our laboratory).

Examination of mixtures of hexane and methylcyclopentane was of interest in connection with the possibility of hydride transfer catalysis [16]. The hydride transfer catalysis had been established for certain reactions in superacidic or strongly acidic solutions [17]. For the isomerization of hexane, its intervention rests on the carbocationic mechanism described in Eqs. (5)–(7) and on the Brouwer–Oelderik kinetic model, by which the hydride transfer, Eq. (7), is the rate-determining step [5,18]. Note that the carbocationic isomerization does not have a termination step as long as the catalyst is active. Termination occurs by poisoning or quenching (mechanistically, the same thing). For hydride transfer catalysis by methylcyclopentane, Eqs. (8) and (9) must be added to the mechanistic scheme. (In the equations, methylcyclopentane, cyclohexane, and their corresponding cations are labeled MCP, CH, MCP$^+$, and CH$^+$, respectively.) The low conversions allow us to neglect the reversibility, except for Eq. (8). The tertiary–tertiary hydride shift of Eq. (8) is fast [19,20] and may occur back and forth several times before the ions react by Eqs. (7) or (9). The catalysis occurs if Eq. (9) is faster than Eq. (7) (Curtin–Hammett principle) [21]. The methylcyclopentyl cations also undergo ring expansion to cyclohexyl cations, bringing about the concurrent isomerization of methylcyclopentane to cyclohexane [Eqs. (10) and (11)]:
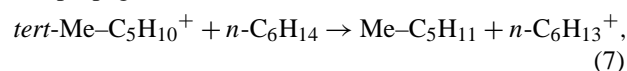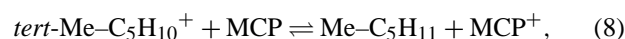
Initiation:

$$n\text{-}C_6H_{14} \rightarrow n\text{-}C_6H_{13}{}^+, \tag{5}$$

Chain propagation:

$$n\text{-}C_6H_{13}{}^+ \rightarrow tert\text{-}Me\text{–}C_5H_{10}{}^+, \tag{6}$$

Chain propagation:

$$tert\text{-}Me\text{–}C_5H_{10}{}^+ + n\text{-}C_6H_{14} \rightarrow Me\text{–}C_5H_{11} + n\text{-}C_6H_{13}{}^+, \tag{7}$$

Chain transfer:

$$tert\text{-}Me\text{–}C_5H_{10}{}^+ + MCP \rightleftharpoons Me\text{–}C_5H_{11} + MCP^+, \tag{8}$$

Chain transfer:

$$MCP^+ + n\text{-}C_6H_{14} \rightarrow MCP + n\text{-}C_6H_{13}{}^+, \tag{9}$$

$$MCP^+ \rightarrow CH^+, \tag{10}$$

$$CH^+ + MCP \rightarrow CH + MCP^+, \tag{11}$$

Chain transfer:

$$CH^+ + n\text{-}C_6H_{14} \rightarrow CH + n\text{-}C_6H_{13}{}^+. \tag{12}$$
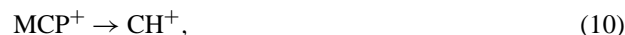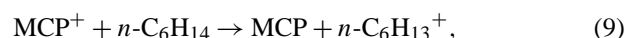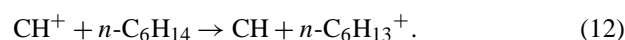
Mixing hexane and methylcyclopentane affected the reactivity of both. As seen in Fig. 10, the conversion of hexane was reduced from about 5.3% in 30 h to about 3% in more than 40 h by mixing hexane with methylcyclopentane (1:1). The product distribution could not be determined very accurately because of the low amounts of products in the mixture, but there was more 3-methylpentane and less 2,2-dimethylbutane than in the reaction of pure hexane (Table 1). The ratio 2-methylpentane:3-methylpentane changed

Fig. 10. Conversion of hexane, methylcyclopentane, 1:1 hexane + methylcyclopentane, and 1:1 hexane + cyclopentane on HMOR at 142 °C, in the liquid phase: (●) hexane; (○) methylcyclopentane; (▲) hexane in (hexane + methylcyclopentane); (□) methylcyclopentane in (hexane + methylcyclopentane); (■) hexane in (hexane + cyclopentane).

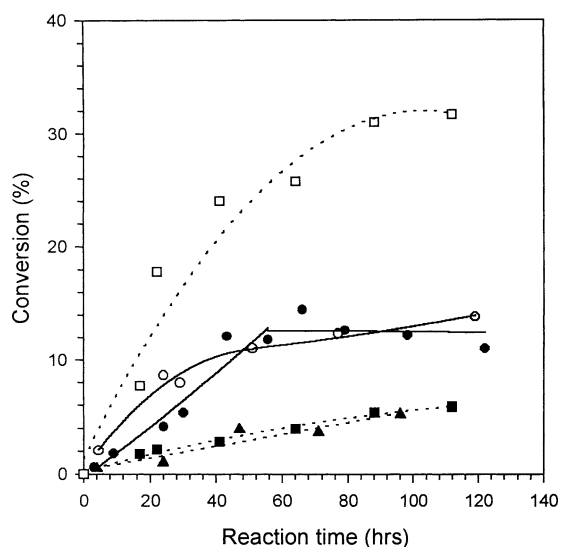between 2 and 5% conversion, indicating that the catalyst had some "true" isomerizing ability. The catalyst did not lose its reactivity to convert hexane in the mixture for at least 112 h, whereas the conversion of pure hexane stopped after about 50 h. On the other hand, the conversion of methylcyclopentane was higher in the mixture with hexane than for the pure hydrocarbon (or rather the 98:2 methylcyclopentane:hexane mixture). These findings would be compatible with the isomerization of the methylcyclopentyl cation of Eq. (10) being much faster than the hydride transfer of Eq. (9) and the hydride transfer of Eq. (11) being much faster than the hydride transfer of Eq. (12). The intermediates of the hexane isomerization reaction would then be blocked out of the catalytic sites, with the consequence that methylcyclopentane would react with a higher (at the limit, double) quantity of catalyst on a molar basis. The required relation-

ship of rates of Eqs. (11) and (12) is not likely, however, because both thermoneutral and exothermic hydride shifts are intrinsically fast [19,20].

Any explanation based entirely on rate differences of carbocationic steps is undermined, however, by the observation that mixing with cyclopentane had the same effect on the reaction of hexane as mixing with methylcyclopentane (Fig. 10). As stated above, cyclopentane was not converted at all by HMOR under our, relatively mild, conditions. Arguments based on relative rates of hydride transfer steps are inapplicable to cyclopentane, because the cyclopentyl cation and the two hexyl (2-hexyl and 3-hexyl) cations are all secondary carbocations and, therefore, cannot differ too much in stability. The product distribution was more similar to the one observed for pure hexane than to the one found in the presence of methylcyclopentane (Table 1). The effect of cycloalkanes on hexane reaction on HMOR brings to mind the TFMSA-catalyzed reaction of hexane, where cycloalkanes inhibited the initiation of the fast cracking-mode reaction [12].

The cyclic hydrocarbons, methylcyclopentane and cyclopentane, did not seem to have the same kind of effect on the hexane conversion on HZSM-5 [9] and on HMOR.

4. Results and discussion: dehydrogenation and rehydrogenation by the zeolite

4.1. Hydrogen transfer between reactants, studied by deuteration

The difference between the reactions on HZSM-5 and on HMOR was also apparent in the reaction of hexane in the presence of 5.5% methylcyclopentane-1-d [12]. The deuterium content and distribution were determined from the GC-MS analyses, in the molecular ion for most compounds. For 2,3-dimethylbutane, both the molecular ion, $m/z = 86$, and the (M–CH$_3$)$^+$ ion, $m/z = 71$, were measured. To correct for the isotope fractionation on the GLC column [22],

Table 1

Product selectivity in the reaction of hexane alone or mixed with cycloalkanes, on HMOR[a]

Product	Reactant			
	Hexane[b]	Hexane + methylcyclopentane[c]	Hexane + methylcyclopentane[d]	Hexane + cyclopentane[e]
2-Methylpentane	41.0	43.2	48.9	38.2
3-Methylpentane	21.9	36.8	32.1	22.8
2,3-Dimethylbutane	12.6	9.5	8.0	12.5
2,2-Dimethylbutane	21.8	9.3	10.7	25.8
C$_{\leqslant 5}$	1.6[f]	1.3	0.3	0.8

[a] Reactants in liquid phase, at 160 °C. The mixtures (hexane + methylcyclopentane) and (hexane + cyclopentane) were made in 1:1 ratios. Selectivities are given as percentage.

[b] Reaction time, 23 h; conversion, 3.2%. The product distribution did not change between 2 and 15% conversion [10].

[c] Reaction time, 22 h; hexane conversion 2.2%.

[d] Reaction time, 88 h; hexane conversion, 5.1%.

[e] Reaction time, 96 h; hexane conversion, 5.2%.

[f] Heavier alkanes (1.5%) were also formed.

Table 2
Deuterium distribution in the reaction products from hexane and methyl-cyclopentane-1-d, on HMOR[a]

Product	Deuterium distribution (content of isotopomer, %)[b]			
	d_0	d_1	d_2	d_3
Hexane	> 99.7	< 0.3[c]	0.0	0.0
2-Methylpentane	32.2 ± 1.1	56.5 ± 1.7	8.8 ± 0.6	2.5 ± 2.1
3-Methylpentane	39.4 ± 6.9	51.4 ± 3.0	9.2 ± 3.9	0.0
2,3-Dimethylbutane[d]	43.4 ± 1.0	46.6 ± 0.4	8.2 ± 0.7	1.7 ± 1.2
	42.5 ± 2.0	47.6 ± 3.3	6.3 ± 2.2	3.6 ± 0.9
2,2-Dimethylbutane[e]	87.2 ± 0.6	12.3 ± 0.8	0.5 ± 0.2	0.0
i-C$_4$	27.0 ± 1.8	69.8 ± 1.5	3.2 ± 3.2	0.0
Methylcyclopentane	26.6 ± 0.9	62.9 ± 0.2	9.9 ± 0.6	0.5 ± 0.1
Cyclohexane	64.2 ± 1.4	31.9 ± 0.6	3.6 ± 1.6	0.4 ± 0.1

[a] Reactants in liquid phase, at 160 °C; methylcyclopentane-1-d content 5.5%.
[b] Average of two catalytic conversions, at 16 h (conversion 2.6%). GC-MS separation achieved at an oven temperature of 11 °C. The relative intensity of each isotopomeric ion was integrated over the entire GC peak. The accuracy of the determination decreases as the quantity of material decreases, that is, in the order: hexane, methylcyclopentane > 2-methyl-pentane > 2,2-dimethylbutane, 3-methylpentane > 2,3-dimethylbutane > cyclohexane > i-C$_4$.
[c] Less than the uncertainty of the measurement.
[d] The first number from the (M–Me) fragment, the second number, from the molecular ion.
[e] From the (M–CH$_3$) fragment.

the isotope content was always determined by integration over the entire GLC peak. Because 2,2-dimethylbutane does not have a molecular ion peak in the spectrum, only the (M–CH$_3$)$^+$ ion was examined for it. The results are shown in Table 2.

In the reaction on HZSM-5, the isomers formed (2-methylpentane, 3-methylpentane) contained 0.1–0.2 deuterium atoms per molecule and the loss of label from deuteromethylcyclopentane was within the uncertainty of the measurements. At a similar conversion (2.6%) on HMOR, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane contained 0.7–0.8 deuterium atoms, whereas methylcyclopentane had lost about 15% of its label. *Thus, the more active catalyst also produces more H/D exchange*. A comparison of the molecular ion and the (M–CH$_3$)$^+$ fragment of 2,3-dimethylbutane suggested that more deuterium may be present in the tertiary positions than in the methyl groups. Isobutane was formed in the highest amount among the cracking products and could be analyzed with higher accuracy. It contained a number of deuterium atoms in the molecule similar to 2-methylpentane, which would mean that the deuterium concentration in isobutane (10 hydrogen atoms) was greater than in isohexane (14 hydrogen atoms). As the signals measured were small, we are reluctant to assign much to the differences.

There are two possible mechanisms for transferring deuterium from methylcyclopentane-1-d to the products of hexane. The first, direct, pathway is deuteride transfer to a carbocation. (A transfer to an incompletely formed, weakly coordinated carbocation [23], or cationoidic species [15], not considered before, cannot be precluded.) In the second

pathway, the hydrogen transfers occur also by eliminations and readditions, with the catalyst as a deuterium relay.

The first pathway is unlikely because cyclohexane formed in the mixture contains only 64% nondeuterated molecules. The cyclohexyl cation is formed from deuteromethylcyclopentane by deuteride loss to a tertiary isohexyl cation [Eq. (8)] followed by ring enlargement, so it contains no label. It leads to labeled cyclohexane by Eq. (11) and unlabeled cyclohexane by Eq. (12). Energetically, the cyclohexyl cation should not discriminate significantly between the exothermic Eq. (11) and the thermoneutral Eq. (12), because hydride transfers have small intrinsic energy barriers [19,20]. Reaction by Eq. (12) is favored by the concentration ratio of hexane to methylcyclopentane-1-d in the mixture (18:1) multiplied by the primary isotope effect manifested in the reaction of Eq. (11). Contrastingly, for the tertiary isohexyl cations, competition between a thermoneutral channel [Eq. (8)] and an endothermic channel [Eq. (7)] should result in a high level of discrimination favoring the former.

In the alternative pathway, cationoidic intermediates are in equilibrium with the corresponding olefins adsorbed on the catalyst, which acquires the isotope in the process. The labeled cyclohexane results form the deuteration of cyclohexene by the catalyst. The case for the second pathway is strengthened by the existence of doubly labeled molecules in the reaction products. By the deuteride transfer pathway, the branched isomers, which are formed in the largest quantity, should incorporate deuterium at the reactive tertiary position; therefore, they cannot acquire more than one deuterium atom per molecule. Whereas the numbers in Table 2 are not highly accurate, because of the small concentrations of the species analyzed, the existence of molecules containing at least two deuterium atoms is unquestionable. Most interestingly, methylcyclopentane-1-d not only loses deuterium to give the unlabeled species (ca. 27%), but also acquires a second label (10%) and possibly even a third (to a marginal extent). This label randomization and formation of multiply labeled molecules show that all the products came from olefinic intermediates, in the same way as in the reaction catalyzed by TFMSA [12] and HZSM-5 [9]. At the low level of conversion investigated, the probability of return of a neutral product molecule to the catalytic site is negligible. Therefore, the intermediate olefins (or a kinetic equivalent thereof) should undergo multiple exchanges with the catalyst before being saturated and desorbed. Remarkably, no olefin is desorbed and found in the product with any of these catalysts. Any hydrogen-deficient species formed remained on the catalyst. In TFMSA, they were identified as allyl cations, which participate in the reaction of alkanes [6,7,12]. It is likely that similar species are formed and play a role in the reactions on the solid catalysts as well.

No deuterium incorporation above the uncertainty limit was seen in the unreacted hexane (Table 2). Because of the low concentration of label in the total hydrogen pool, this was not a conclusive observation. The isotope fractionation

on the GLC column [22] would concentrate, however, any labeled molecules at the beginning of the GLC peak. A careful search of the initial part of that peak failed to reveal a significant increase in the (M + 1) signal over the normal value, indicating that there was no deuterium enrichment in hexane.

To validate these findings, we conducted another series of experiments, in which a small amount of regular methylcyclopentane was added to deuterated hexane. We preferred partially but uniformly labeled hexane to the fully deuterated material, because differences in the label content of products could give information about the relative importance of the isotope effect-sensitive hydride transfer step in their formation. Catalytic deuteration of 1,4-hexadiene without solvent at ambient temperature and pressure gave hexane containing on the average 4.3 deuterium atoms per molecule (30.7% isotope enrichment), statistically distributed among the two methyl groups and four methylene groups [12]. Mixtures of this material with 5.5% methylcyclopentane were reacted for 24 and 31 h, to conversions smaller than the amount of methylcyclopentane added (0.9 and 1.1%, respectively).

The results in this series of experiments are quantitatively less accurate than in the runs with hexane and methylcyclopentane-1-d, because it is easier to determine small incorporations of label in unlabeled molecules, than small losses of it from labeled molecules. Nonetheless, it was definitely established that there was a significant loss of label from the isomerization products of hexane. Methylcyclopentane and its isomerization product, cyclohexane, acquired deuterium during the reaction. Again, no measurable loss of deuterium from the unreacted hexane was detected. This is not surprising, because there were 1.2–1.5 meq of aluminum in the catalyst per 100 mmol of hexane. If all the aluminum atoms were in active sites and had exchanged hydrogen to deuterium to statistical distribution with hexane, the label loss from the latter would be hardly perceptible.

Considering the conversions of hexane (ca. 1%) and methylcyclopentane (ca. 4%) and the deuterium content of products, given in Table 3, we conclude that the majority of label lost from hexane that reacted remained in the catalyst.

4.2. Mechanistic considerations

Our results reveal a contrasting behavior of 3-methylpentane and hexane when reacted as liquids on HMOR. The former exhibits a clean (very little cracking) isomerization, with products formed in the sequence and with relative rates characteristic for the carbocationic mechanism [Eqs. (1)–(4)] [4,5]. Contrastingly, the product composition from hexane in the liquid phase cannot be rationalized by the carbocationic isomerization mechanism involving secondary and tertiary $C_6H_{13}^+$ cations (whether free, ion-paired, or partially coordinated), established with superacid catalysts in the liquid phase (e.g., HF–SbF$_5$) [4,5].

Hydrogen exchange of hexane with a typical hydride donor is important, but it occurs mostly through the cata-

Table 3
Deuterium content (atoms per molecule) in the reaction products from hexane-u-d$_{4.3}$ with methylcyclopentane, on HMOR[a]

Product	Deuterium content[b]
Hexane	4.3 ± 0.1
2-Methylpentane	0.6 ± 0.2
3-Methylpentane	(Small peak)
2,3-Dimethylbutane	(Small peak)
2,2-Dimethylbutane	0.5 ± 0.2
i-C$_5$[c]	0.7 ± 0.1
i-C$_4$[c]	0.6 ± 0.02
Methylcyclopentane[d]	0.27 ± 0.06
Cyclohexane[e]	0.60 ± 0.04

[a] Reactants in liquid phase, at 160 °C, methylcyclopentane content 5.5%.
[b] Average of two catalytic conversions, at 24 h (conversion 0.95%) and 31 h (conversion 1.1%). The data are from GC-MS analyses, oven temperature 13–16 °C. The relative intensity of isotopomeric ions was integrated over the entire GC peak.
[c] The quantity of normal isomer was too small to afford a reliable number for its deuterium content.
[d] Distribution: 77.9% d_0, 17.4% d_1, 4.0% d_2, 0.7% d_3.
[e] Distribution: 63.8% d_0, 16.0% d_1, 16.5% d_2, 3.7% d_3.

lyst. No hydride transfer catalysis intervenes. Isotope exchange between deuterated solid acids and alkanes has long been known [24–27] and was confirmed recently by NMR investigations [28]. The process was interpreted as occurring in parallel or in competition with skeletal rearrangement [28]. We now find that the elimination and addition, which exchange hydrogen, constitute steps of the rearrangement mechanism. Alkenes are critical reaction intermediates, although no alkenes are found in the reaction products that desorb from the catalyst (except at much higher temperatures).

A comparison of the conversion of methylcyclopentane to cyclohexane (4%) and its hydrogen–deuterium exchange (over 25 atoms of deuterium incorporated in 100 molecules of methylcyclopentane, cf. Table 3) in the reaction conducted in the presence of hexane-u-d$_{4.3}$ shows that the exchange with the catalyst was faster than isomerization.

An analogy exists with the reaction of these alkanes in the weak superacid, TFMSA, where a duality of mechanisms was observed: an isomerization mode and a cracking-disproportionation mode. The latter exhibited features of a radicalic chain reaction, mixed with a carbocationic (cationoidic) process. The transition from the former to the latter was triggered by the accumulation of unsaturated, allylic-type carbocations in the acid and was promoted by electron acceptors [6,7]. Both hexane and 3-methylpentane reacted faster in the cracking mode than in the isomerization mode, but the acceleration was much greater for hexane. The reactivity ratio 3-methylpentane:hexane was ca. 1000 in the isomerization mode and ca. 10 in the cracking mode [7,12]. On HMOR, 3-methylpentane reacts in the isomerization mode. The transition to the cracking mode did not occur for the length of our experiments. Productwise, the reaction of hexane on HMOR fits the cracking mode,

but its relative acceleration was less than in TFMSA. The reactivity ratio 3-methylpentane:hexane was ca. 100. Even in TFMSA, however, the reaction was not initiated by the cleavage of C–H or C–C bonds by the superacid, but by an oxidative activation with the apparent participation of the allylic cations [6,7,12]. The solid acids are, inherently, weaker acids than the liquid analogs [29,30] and zeolites are nowhere near superacidic strength [15,30–32]. The inconsistencies of theoretical concepts thought to support zeolite superacidity, like pseudoliquid character and electronegativity equalization, have been discussed elsewhere [15]. One cannot presume that sigma bond acidolysis should occur on the zeolite catalyst.

It is noteworthy that intervention of superacid-like activation of alkanes was proposed for HZSM-5 as catalyst [33], a material of rather low acidity [34,35]. The reactions of hexane and 3-methylpentane on HZSM-5 at moderate temperatures were even farther from unimolecular carbocationic processes than the reactions on HMOR [8,9].

Allylic cations, particularly cycloalkenyl cations, have been observed by Haw et al., as products from alkenes in zeolites [36,37]. It is possible that more reactive alkenyl cations, formed early in the reaction, play a role in the conversion of alkanes in zeolites, as in TFMSA.

The chemisorbed alkenes may be formed by the one-electron oxidation of alkanes, as proposed earlier [38–41], or by metal ion catalysis by the tetracoordinated aluminum centers in the lattice or extraframework aluminum species, as shown more recently [42]. The intermediacy of alkenes makes the reactions possible at the acid strength available in zeolites. The product distribution does not substantiate a simple, monomolecular cationic or cationoidic mechanism. Alkene formation, alkylation/oligomerization, cracking, and rehydrogenation are part of the overall isomerization reaction. Some contribution of a superimposed radicalic process cannot be definitely precluded. The product composition might be controlled by the rates of cracking and rehydrogenation.

5. Conclusions

Features of a carbocationic/cationoidic mechanism were seen in the reaction of 3-methylpentane in the liquid phase on H-mordenite (a more active acid catalyst than HZSM-5), but not in the gas phase and not for hexane in either phase. Thus, there are mechanistic differences between the reactions of alkanes in the liquid phase and in the vapor phase on the zeolite.

The liquid-phase reaction of hexane in the presence of methylcyclopentane, cyclopentane, and deuteromethylcyclopentane showed the absence of hydride transfer catalysis.

No olefins were found in the products desorbed, but the products were formed from olefinic reaction intermediates. Each olefin exchanged repeatedly hydrogen with the catalyst before being hydrogenated and desorbed. The chemisorbed

alkenes may be formed by one-electron oxidation or by dehydrogenation on tetracoordinated aluminum atoms, either in the lattice or in extralattice aluminum species [42].

Disproportionation is important as a pathway for isomerization. Because small molecules predominate in the desorbed products, there must be unsaturated products retained by the catalyst. It is possible that alkenyl cations on the catalyst play a role in the reaction, as they do in trifluoromethanesulfonic acid.

The mechanism of alkane conversion on zeolites involving sigma bond protonolysis like in liquid superacids [43,44] and mechanistic control by the size and shape of the channels [33] because of steric requirements of cracking and hydride transfer [45] has been contradicted. Thus, the reactivity ratio of hexane to 3-methylpentane varies with factors other than the size of cavities, and the transverse space requirement of the transition structure for hydride transfer is smaller than for β-cracking [46]. Now, our results further impugn the "carbonium" ion (protonated alkane) mechanism of catalysis on zeolites.

The catalytic properties of zeolites have been correlated with their acidity (and the latter with the Si/Al ratio). We see now that other properties, such as hydrogenating–dehydrogenating ability and one-electron oxidizing properties are also of critical importance for reactivity.

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