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Skeletal Isomerization of Hexane over Pt/H-Beta Zeolites: Is the Classical Mechanism Correct?

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The isomerization of *n*-hexane occurs over Pt-loaded H-β zeolites in a highly selective manner. At 250°C, with 45 Torr *n*-hexane and 2.0×10^3 Torr H_2 over a 0.65% Pt/H-β zeolite, the isomerization activity was 3.7 μmol g^{-1} s^{-1}, and the isomerization selectivity was 99%. Both the activity and the selectivity were stable with respect to time on stream. Pure H-β zeolite was only about 10% as active as the Pt-loaded sample, and the isomerization selectivity was 66%, with the remaining 34% caused by cracking reactions. The addition of 1-hexene by several means decreased both the overall reaction rate and the isomerization selectivity. Moreover, the reaction of 1-hexene over H-β zeolite did not result in the formation of any observable hexene isomers. These results, together with the fact that the equilibrium hexene concentration is very small (4.9×10^{-4} Torr) under the reaction conditions, suggest that hexene produced by the dehydrogenation of hexane at the metal component is not directly involved in the isomerization reaction. An alternate mechanism is proposed in which an acid-catalyzed chain reaction involving methyl shifts and hydrogen transfer is responsible for the isomerization of hexane. The chain is terminated when an alkene reacts with a $C_6H_{13}^+$ species that is bonded to the zeolite. The principal role of the Pt is to hydrogenate alkenes so that their steady-state concentration remains negligibly small. The proximity of the Pt particles and the acid sites is important in order to prevent an increase in the local concentration of alkenes. © 1998 Academic Press

INTRODUCTION

More stringent limits on the amount of aromatics that may be included in gasoline have resulted in a renewed interest in the skeletal isomerization of *n*-alkanes with a view to using the branched isomers as octane-enhancing components. Multiply branched isomers are more desirable because of their higher octane numbers. At equilibrium, lower temperatures favor branched isomers; therefore, there has been an effort to develop catalysts that are effective at 250°C or less. Over the past several decades the progression has been from Pt/Al_2O_3, which is active for *n*-hexane isomerization in the 450–500°C range, to Pt/chlorided Al_2O_3, which is active in the 350–400°C range, and, more recently, to Pt/H–zeolite catalysts, which are active in the 200–250°C range. Additional research has been carried out on Pt/sulfated ZrO_2, Pt/WO_x–ZrO_2 and related materials (1–3).

Based on the earlier studies of Mills *et al.* (4) and Weisz and Swegler (5), a bifunctional mechanism (which we will refer to as the "classical mechanism") was proposed. According to this mechanism, (i) dehydrogenation of the alkane occurs at the metal center, (ii) the resulting alkene molecule is isomerized at an acid site, and (iii) the isomerized alkene intermediate is hydrogenated at the metal center to form the product. Molecular hydrogen at relatively high pressures is added to the system in order to enhance isomerization selectivity and to prevent deactivation of the catalyst. Although the problems with this mechanism will be discussed in detail later, it is important to note here that the equilibrium concentration of alkenes is strongly affected by temperature. Even though the equilibrium alkene concentration may be significant at 500°C, it would be very small at 200°C. Thus, the classical mechanism may not be applicable for the newer generation of catalysts that are able to achieve reasonable conversions at much lower temperatures.

Other research groups have recognized that there are problems with the classical mechanism and have suggested alternative pathways. Steijns and Froment (6) questioned the role of alkene intermediates at the lower temperatures and developed a mechanism that was based on rearrangement of carbenium ions, regardless of how they were formed. Iglesia *et al.* (2), working with Pt/sulfated ZrO_2, similarly pointed out that the equilibrium concentration of alkene intermediates would be extremely small at the low temperatures and high H_2 pressures currently employed in *n*-alkane isomerization. According to their mechanism, hydrogen adsorbed on Pt particles serves as a hydride donor and reacts with the isomerized carbenium ion to form the product molecule. The shorter residence time of the carbenium ion limits the extent of β-scission (i.e., cracking). Fujimoto and co-workers (7), who studied the isomerization of *n*-pentane over hybrid catalysts consisting of Pt/SiO_2 and H-ZSM-5, suggested that hydrogen

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spills over from the Pt to the zeolite as H^+ and H^- ions. The H^+, regenerates Brønsted acid sites and the H^- reacts with i-C_n^+ intermediates to form the isomerized product.

The purpose of the present study was twofold: (i) to further explore the behavior of Pt/H-β zeolites as catalysts for the isomerization of *n*-hexane and (ii) to use the results from this and related catalyst systems to establish a mechanism for the isomerization reaction. Smirniotis and Ruckenstein (8) compared the *n*-hexane isomerization activity of a Pt/H-β zeolite with that of Pt/Al_2O_3 and concluded that the former had a much higher activity. Yashima *et al.* (9) similarly compared the activity of a Pt/H-β with Pt/H-mordenite and Pt/H-ZSM-5 for the same reaction and found that the conversion was significantly larger over the Pt/H-β catalyst. Both groups interpreted their kinetic results in terms of the classical mechanism. As part of a larger study on hexane reforming, Tatsumi and co-workers (10) also determined the conversion and selectivity obtained during the reaction of hexane over Pt/H-β, Pt/H-L, and Pt/H-FSM-16 (Toyota). Among these three catalysts, the Pt/H-β zeolite had the largest conversion and most favorable isomerization selectivity under comparable conditions.

EXPERIMENTAL

Catalysts. Impregnated Pt/H-β catalysts were prepared by mixing 10.0 g of H-β zeolite (PQ Corp., Si/Al = 12.8) with 200 ml of deionized water that contained the appropriate amount of hexachloroplatinic acid ($H_2PtCl_6 \cdot nH_2O$, Alfa). The slurry was stirred vigorously and heated to dryness in an oil bath. The catalyst was then reduced in flowing H_2 at 500°C for 8 h, ground and sieved to 150 μm particle size. The Pt loadings were 0.026, 0.13, 0.65, 2.6, and 6.4 wt%, calculated on the dry basis for the zeolite. A similar method was used to prepare an impregnated 0.52% Pt/SiO_2 (SiO_2, Mallinckrodt, Grade 62 special) catalyst. A commercial alkane isomerization catalyst consisting of 20 wt% of 0.3% Pt/mordenite in an alumina matrix was employed for several comparison experiments.

An ion-exchanged sample, containing 0.41 wt% Pt/H-β zeolite was prepared by adding a $Pt(NH_3)_4Cl_2$ (Strem Chemicals) solution dropwise to a slurry of the zeolite and deionized water (1 g) zeolite/100 ml H_2O), with continuous stirring. The slurry was stirred vigorously and maintained in a temperature range of 60–80°C under reflux for 24 h. The catalyst was filtered, washed several times with deionized water, dried in air at 25°C for one day, and ground into a powder. It was heated in flowing O_2 at 500°C for 6 h and then reduced in H_2 at 500°C for 8 h. After reduction, the catalyst was again ground and sieved into 150 μm particle size.

Metal dispersions for the Pt-loaded catalysts were determined by the temperature-programmed desorption (TPD) method. Hydrogen and argon (both Matheson, 99.99%) were further purified by oxygen removal (Chromatography Research Supplies) and water adsorption in an activated 4A molecular sieve. A catalyst sample (0.10 g) was reduced *in situ* in flowing H_2 for 3 h at 300°C, flushed with argon, and cooled in H_2 from 100 to 25°C. Subsequently, argon at a flow rate of 28 ml min^{-1} was passed through the catalyst bed for 1 h at 25°C to remove physisorbed hydrogen, and the catalyst was rapidly heated to 280°C at a ramp rate of ca. 200°C min^{-1}. The amount of hydrogen that desorbed was determined using a thermal conductivity detector.

Catalytic reaction. A zeolite sample (1.20 g, apparent density = 2.5 g cm^{-3}) was placed in a plug-flow reactor constructed of fused quartz (1 cm I.D.). The catalyst was located between two layers of quartz wool, and quartz chips were placed above the quartz wool to serve as a preheating zone. A thermocouple was placed on the outside wall of the reactor, midway along the length of the catalyst bed. A stream of H_2 (Airco, 99.995%) was passed at a flow rate of 22 ml/min through a saturator containing *n*-hexane (Janssen Chemica, 99+%) that was cooled in an ice-water bath. The vapor pressure of *n*-hexane at 0°C is 45 Torr. The H_2/*n*-hexane gas mixture was passed through an activated 4A molecular sieve to remove moisture. In some cases, the H_2 was replaced by N_2 (Airco, 99.995%). The reactor with the catalyst was flushed with H_2 or N_2, depending on which was used as the vector gas, for 0.5 h before introduction of the reactant gases. Unless stated otherwise, the reaction temperature was 250°C and the contact time was ca. 6.0 s. In one experiment, methylcyclopentane (TCI, 99+%) was used as the reactant instead of *n*-hexane.

Activation energies and orders of reaction with respect to *n*-hexane and hydrogen were determined under differential conditions. Smaller amounts of catalyst and/or larger flow rates were used to decrease the conversion level. For the H-β zeolite, a fresh catalyst was used to determine each datum point because this catalyst deactivates slowly with time on stream.

Product analysis and data treatment. The gas phase products were analyzed using an on-line gas chromatograph (Hewlett Packard Model 5890II) equipped with an integrator. The gases were separated by a 50 m × 0.32 mm Al_2O_3/KCl-coated, fused-silica capillary column and detected by a flame ionization detector. The system was calibrated using standard gases (Scott Specialty Gases).

The conversion was determined from the relationship

$$\text{Total Conversion } (X\%) = \frac{[\text{original reactant}] - [\text{reactant remaining}]}{[\text{original reactant}]} \times 100. \quad [1]$$

Product selectivities were obtained from

$$S_n(\%) = \frac{nN_n}{rN_rX} \times 100, \quad [2]$$

where N_n is the total number of moles of product molecules that contain n carbon atoms per molecule, N_r is the number of moles of reactant molecules that contains r carbon atoms per molecule, and X is the fractional conversion of reactant. The rate of reaction was calculated from the expression

$$\text{Rate (mole g}^{-1}\text{s}^{-1}) = \frac{P_r X}{RTFm}, \qquad [3]$$

where P_r is the pressure (Torr) of the reactant, X is the fractional conversion, R is the appropriate gas constant, T is 298 K, F is the flow rate (ml s^{-1}) of the feed gas at NTP, and m is the mass of the catalyst.

RESULTS

Reaction of n-hexane over H-β zeolite. Conversion and selectivity results are first reported for the reaction of *n*-hexane over an H-β zeolite without platinum. With 45 Torr of *n*-hexane in 2.0×10^3 Torr (2.7 atm) of H_2, the conversion level slowly declined over a period of 18 h on stream as shown in Fig. 1. It is most significant that even in the absence of an active metal for hydrogenation/dehydrogenation, the selectivity for skeletal isomerization was greater than that for cracking and increased with time on stream. This implies that the acid centers themselves have isomerization activity, although one could also argue that the zeolite has hydrogenation/dehydrogenation activity.

More details on the hydrocarbon product selectivity after 2 h on stream are given in Table 1, from which it is evident that the principal isomerization products were 2-methylpentane and 3-methylpentane, whereas the main cracking product was isobutane. No alkenes were detected, and no coke (determined from material balance and, qualitatively, from the color of the catalyst) was formed. The ratios $\Sigma C_4/\Sigma C_2$ and $\Sigma C_5/C_1$ are reported as an indication of the extent of unimolecular versus bimolecular and secondary reactions. For strictly unimolecular cracking reactions, these ratios will be unity (vide infra). From the large ratios reported in Table 1, it is evident that more complex cracking reactions occur.

According to the classical mechanism, if a higher concentration of C_6 alkenes were present, one might expect that the isomerization selectivity would increase. To explore this possibility, H_2 was replaced by N_2 in the feed gas, with all other reaction conditions remaining the same. The results reported in the third column of Table 1 show that after 2 h on stream, the *n*-hexane conversion was nearly the same as in the presence of H_2, but the isomerization selectivity was lower and the cracking selectivity correspondingly higher. Indeed, a small concentration of C_6 alkene isomers was detected among the products, and coke was also produced. When 1-hexene was added to the reagents

TABLE 1

Distribution of Products for the Reaction of *n*-Hexane over H-β Zeolite[a]

	Selectivity (%)			
Makeup gas (2.0×10^3 Torr)	H_2	N_2	N_2	H_2
Pressure of 1-hexene (Torr)	0	0	0.047	0.1
Time on stream (h)	2	2	2.8	2
Methane	0.02	0.01	0.01	0.03
Ethane	0.11	0.10	0.01	0.11
Ethylene	0	0	0	0
Propane	6.70	8.00	5.29	7.3
Propylene	0	0.06	0	0.04
Isobutane	18.9	26.3	18.6	26.5
n-Butane	3.19	4.60	3.03	4.10
C_4 alkenes	0	0.06	0	0
Neopentane	0.38	0.23	0.21	0.33
Isopentane	9.94	14.8	8.4	15.7
n-Pentane	2.57	3.6	2.95	4.0
C_5 alkenes	0	0.04	0	0
Methylcyclopentane	0	0	0	0
2,2-Dimethylbutane	2.51	0.59	1.05	1.1
Cyclohexane	0.39	0	0	0.5
2,3-Dimethylbutane	6.49	0.16	2.95	5.2
2-Methylpentane	31.5	21.0	13.5	22.5
3-Methylpentane	17.4	8.50	6.68	12.7
n-Hexane	—	—	—	—
C_6 alkenes	0	1.3	1.4	0
Coke	0	11.7	35.3	0
Cracking	41.7	57.8	38.5	58.1
Isomerization	58.3	30.2	24.2	42.0
Conversion (%)	31.2	31.4	27.8	32.7
$\Sigma C_4/\Sigma C_2$	100	160	1100	140
$\Sigma C_5/C_1$	130	370	230	130

[a] 45 Torr *n*-hexane reacted over 1.20 g H-β zeolite at 250°C; contact time = 6 s.

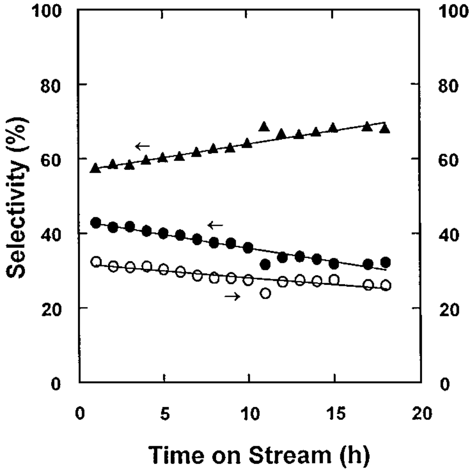


FIG. 1. Selectivities and conversion obtained during the reaction of *n*-hexane over a H-β zeolite: ▲, selectivity for isomerization; ●, selectivity for cracking; ○, total *n*-hexane conversion. The reaction of 45 Torr *n*-hexane was carried out in 2.0×10^3 Torr H_2 at 250°C over 1.20 g catalyst at a contact time of 6.0 s.

with N_2 as the vector gas (column 4), coke formation increased further, at the expense of both the cracking and isomerization selectivities. Finally, in this series of experiments, the N_2 was replaced by H_2, and a small amount of 1-hexene was again added to the reagent stream. The results show (column 5) that the coke formation decreased to zero; no alkene products were detected, and the cracking selectivity remained greater than the isomerization selectivity. These results suggest that the zeolite does have hydrogenation/dehydrogenation activity, but the effect of C_6 alkenes that might be formed is detrimental to the isomerization reactions. The hydrogenation/dehydrogenation activity is believed to be an intrinsic property of the acidic zeolite, as discussed by Longstaff and Hanson (11), and not a result of impurities (e.g., Fe).

In order to study the reaction of pure 1-hexene over an aged H-β zeolite, the reaction of 45 Torr of *n*-hexane in 2.0×10^3 Torr H_2 was first carried out for 8 h at 250°C. The *n*-hexane reactant was then replaced by 0.08 Torr of 1-hexene in 2.0×10^3 Torr N_2. The value of 0.08 Torr of 1-hexene is considerably greater (see following discussion) than the concentration of 1-hexene that would exist in equilibrium with 45 Torr of *n*-hexane and 2.0×10^3 Torr H_2 at 250°C. After 5 min on stream with the 1-hexene/N_2 mixture, the major products were coke and those derived from the cracking reaction; *no C_6 skeletal isomerization products were detected*.

Reactions of n-hexane over Pt/H-β zeolites. The results of Fig. 2 confirm that 0.65% Pt/H-β zeolite is an active, stable, and highly selective catalyst for the isomerization of *n*-hexane at 250°C. At a contact time of 6.0 s, the total (nearly equilibrated) conversion was 84%, and the isomerization selectivity was 97%. The conversion increased to 87% (the thermodynamic equilibrium value for *n*-hexane) when the contact time was 16 s.

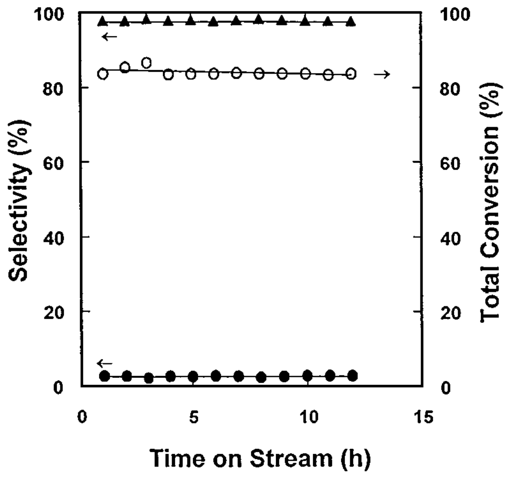


FIG. 2. Selectivities and conversion obtained during the reaction of *n*-hexane over 0.65% Pt/H-β zeolite: ▲, selectivity for isomerization; ●, selectivity for cracking; ○, total *n*-hexane conversion. The reaction of 45 Torr *n*-hexane was carried out in 2.0×10^3 Torr H_2 at 250°C over 1.20 g catalyst at a contact time of 6.0 s.

TABLE 2

Distribution of Products for the Reactions of *n*-Hexane over Pt/H-β Zeolites with Different Metal Loadings at High Conversions[a]

	Selectivity (%)					
Pt content (wt%)	0.026	0.12	0.41[b]	0.65	2.6	6.4
Methane	0.01	0.05	0.64	0.11	0.82	1.31
Ethane	0.04	0.08	1.83	0.19	1.38	1.59
Ethylene	0	0	0	0	0	0
Propane	0.38	0.6	7.57	0.94	5.44	5.54
Propylene	0	0	0	0	0	0
Isobutane	0.28	0.42	1.45	0.41	1.03	1.40
n-Butane	0.10	0.18	2.47	0.29	1.84	2.16
C_4 alkenes	0	0	0	0	0	0
Neopentane	0	0	0	0	0	
Isopentane	0.13	0.33	2.19	0.54	2.43	4.42
n-Pentane	0.06	0.14	1.15	0.30	1.55	2.28
C_5 alkenes	0	0	0	0	0	0
Methylcyclopentane	0	0	0	0	0	0
2,2-Dimethylbutane	4.23	23.0	22.3	24.0	20.1	20.2
Cyclohexane	0.08	0	0	0	0	0
2,3-Dimethylbutane	11.2	10.0	8.24	9.5	7.56	7.92
2-Methylpentane	50.8	39.6	31.9	38.5	35.2	32.1
3-Methylpentane	32.7	25.6	20.2	25.2	22.6	21.1
n-Hexane	—	—	—	—	—	—
C_6 alkenes	0	0	0	0	0	0
Coke	0	0	0	0	0	0
Cracking	1.0	1.8	17.3	2.8	14.5	18.7
Isomerization	99.0	98.2	82.7	97.2	85.5	81.3
Conversion (%)	75.4	83.5	86.3	83.6	82.7	85.5
$\Sigma C_4/\Sigma C_2$	4.8	3.8	1.1	1.8	1.0	1.1
$\Sigma C_5/C_1$	3.8	1.9	1.0	1.5	0.97	1.0

[a] 45 Torr *n*-hexane reacted over 1.20 g Pt/H-β zeolite at 250°C in 2.0×10^3 Torr H_2; contact time = 6 s.

[b] Catalyst prepared by the ion-exchanged method.

Product selectivities for this and other Pt loadings are given in Table 2. The major isomerization products were 2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane, in that order. The total extent of *n*-hexane isomerization for all the catalysts with Pt loadings ≥0.12 wt% was near equilibrium, but the C_6 isomers themselves were not in equilibrium with each other [thermodynamic equilibrium concentrations at 250°C: 2,2-dimethylbutane = 38.8%; 2,3-dimethylbutane = 10.0%; 2-methylpentane = 25.0%; 3-methylpentane = 12.9%; *n*-hexane = 13.3%. (12)]. In particular, the 2-methylpentane and the 3-methylpentane selectivities were greater than the equilibrium values and the 2,2-dimethylbutane selectivity was less than the equilibrium value. This results, in part, from the fact that 2,2-dimethylbutane is a secondary isomerization product, whereas the remaining isomers are primary products (vide infra).

The results obtained at lower (nonequilibrium) *n*-hexane conversion levels are compared in Table 3 for the H-β

TABLE 3

Distribution of Products for the Reactions of *n*-Hexane over Pt/H-β Zeolites with Different Metal Loadings at Low Conversions[a]

	Selectivity (%)				
Pt content (%)	0	0.12	0.41[b]	0.65	6.4
Time on stream (h)	13	5	1	6	4
Methane	0.02	0.04	0.02	0.03	0.05
Ethane	0.11	0.03	0.21	0.05	0.10
Ethylene	0	0	0	0	0
Propane	5.9	0.08	1.0	0.28	0.49
Propylene	0	0	0	0	0
Isobutane	15	0.09	0.09	0.03	0.06
n-Butane	2.6	0.05	0.04	0.09	0.19
C_4 alkenes	0	0	0	0	0
Neopentane	0.28	0	0	0	0
Isopentane	7.5	0	0.11	0.08	0.10
n-Pentane	2.80	0.05	0.22	0.60	0.27
C_5 alkenes	0	0	0	0	0
Methylcyclopentane	0	0	0	0	0
2,2-Dimethylbutane	2.60	1.0	3	3.3	4.42
Cyclohexane	0.40	0	0.13	0	0.22
2,3-Dimethylbutane	7.32	6.5	4.1	6.06	3.49
2-Methylpentane	36.4	56.7	56.3	54.0	55.5
3-Methylpentane	19.5	35.5	34.6	35.5	35.2
n-Hexane	—	—	—	—	—
C_6 alkenes	0	0	0	0	0
Coke	0	0	0	0	0
Cracking	34	0.34	1.9	1.1	1.2
Isomerization	66	99.7	98	99	99
Conversion (%)	27.5	20.8	27.7	29.3	26.3
$\Sigma C_4/\Sigma C_2$	78	2.33	0.31	1.2	1.3
$\Sigma C_5/C_1$	106	0.25	3.3	4.5	1.5

[a] 45 Torr *n*-hexane reacted over H-β or Pt/H-β zeolites at 250°C in 2.0×10^3 Torr H_2.

[b] Catalyst prepared by the ion-exchanged method.

zeolite and for Pt/H-β catalysts with $\geq$0.12 wt% Pt. Comparable *n*-hexane conversions (20–30%) were achieved by appropriately adjusting the contact time for each catalyst. The three catalysts with the largest Pt loadings gave similar C_6 isomer selectivities, whereas the 0.12% Pt/H-β catalyst produced significantly less 2,2-dimethylbutane. The total isomerization selectivity was $\geq$98% over all of the Pt-loaded catalysts. By contrast, the H-β zeolite induced more cracking. It is interesting to note, however, that the 2,3-dimethylbutane selectivity over the H-β, 0.12% Pt/H-β, and 0.65% Pt/H-β zeolites was similar, which further suggests a comparable isomerization mechanism over the catalysts with and without platinum. The 2,3-dimethylbutane selectivity over the 0.41% and 6.4% Pt/H-β zeolites was somewhat less, possibly because of secondary reactions.

At higher conversion levels (Table 2), the cracking selectivity over the 0.41% Pt/H-β zeolite prepared by the ion exchange method was significantly greater than that observed over the impregnated catalyst containing a comparable Pt loading (0.65 wt%). The major cracking product over the ion-exchanged catalyst was propane. The $\Sigma C_4/\Sigma C_2$ and $\Sigma C_5/C_1$ ratios were close to unity for the Pt-loaded catalysts with $\geq$0.41 wt% Pt, which suggests that the cracking in these cases is dominated by unimolecular reactions, even at 250°C. The significantly higher $\Sigma C_4/\Sigma C_2$ and $\Sigma C_5/C_1$ ratios observed for the 0.026 and 0.12% Pt/H-β catalysts, however, indicate that bimolecular cracking and secondary reactions clearly begin to play a role at these lower Pt loadings.

The initial products of *n*-hexane isomerization were determined by carrying out the reaction at progressively smaller conversion levels and extrapolating the results to zero conversion, as shown in Fig. 3. It is evident that 2-methylpentane and 3-methylpentane were the major primary products, but that 2,3-dimethylbenzene also was a primary product. 2,2-Dimethylbutane was not a primary

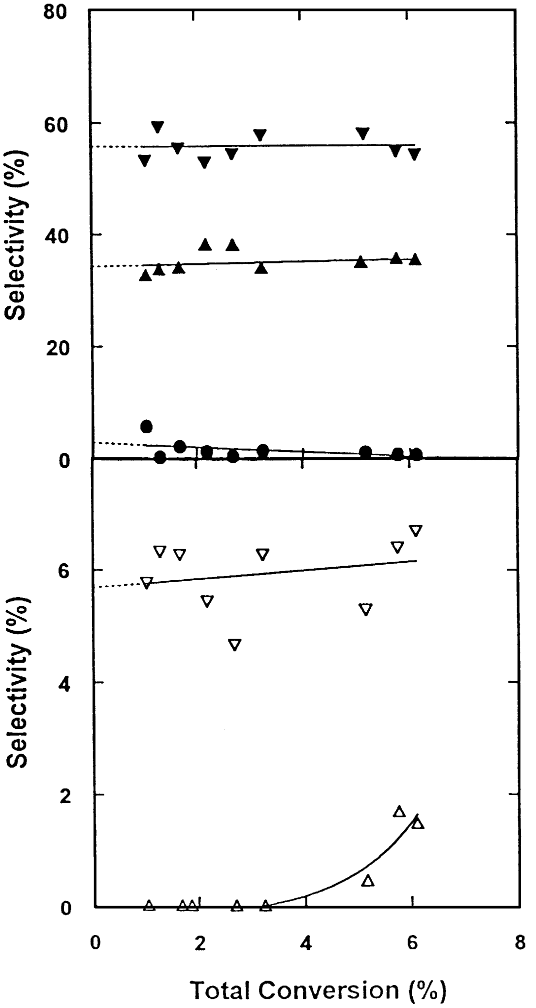


FIG. 3. Variation of selectivities as a function of total *n*-hexane conversion over 0.65% Pt/H-β zeolite: ▼, 2-methylpentane; ▲, 3-methylpentane; ●, cracking; ▽, 2,3-dimethylbutane; △, 2,2-dimethylbutane. The reaction of 45 Torr *n*-hexane was carried out in 2.0×10^3 Torr H_2 at 250°C.

product, as indicated by the fact that it had zero selectivity (extrapolated) at zero conversion. Cracking products are probably also formed initially, but there is a rather large error associated with the small conversion and selectivity.

Group VIII metals themselves are capable of catalyzing the isomerization of alkanes, independent of any acidic support (1, 13, 14). One type of metal-catalyzed mechanism involves a cyclic intermediate, which for *n*-hexane would be methylcyclopentane (MCP). Over the H-β and Pt/H-β zeolites, the amount of MCP formed during *n*-hexane isomerization was either small or nondetectable. Nevertheless, in order to address the possible role of MCP in the isomerization of *n*-hexane, the reaction of 39 Torr of this hydrocarbon in 2.0×10^3 Torr H_2 was carried out over the 0.65% Pt/H-β zeolite at 250°C. The results of Fig. 4 demonstrate that the principal product (ca. 90% selectivity) was cyclohexane, which was not observed during *n*-hexane isomerization over any of the Pt-loaded zeolites except for a trace amount over the 0.026 wt% of catalyst. Minor products from the isomerization of MCP were 2-methylpentane, 3-methylpentane, and *n*-hexane. The aggregate selectivity for all these products was less than 3%. From the product distribution in Fig. 4, it is evident that MCP is not an intermediate in the isomerization of *n*-hexane; therefore, the isomerization reaction under these conditions is not extensively catalyzed by the metal acting independently of the acid sites, at least via a cyclic intermediate. This was further confirmed by studying the reaction of *n*-hexane over a 0.41% Pt/K-β zeolite, that is, a zeolite in which the protons had been exchanged by K^+ ions. This catalyst was inactive for *n*-hexane conversion at 250°C.

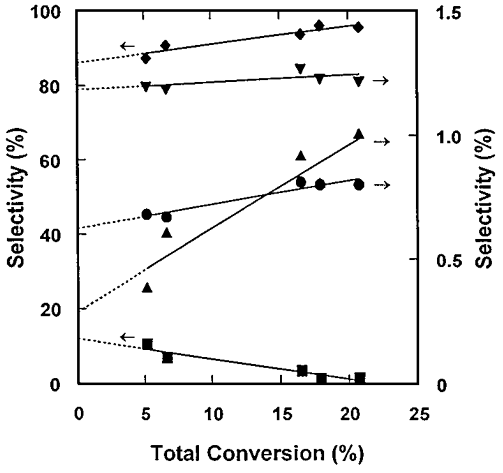


FIG. 4. Selectivities obtained during the reaction of methylcyclopentane over 0.65% Pt/H-β zeolite: ◆, cyclohexane; ▼, 2-methylpentane; ▲, 3-methylpentane; ■, *n*-hexane; ●, cracking products. The reaction of 39 Torr of methylcyclopropane was carried out in 2.0×10^3 Torr H_2 at 250°C.

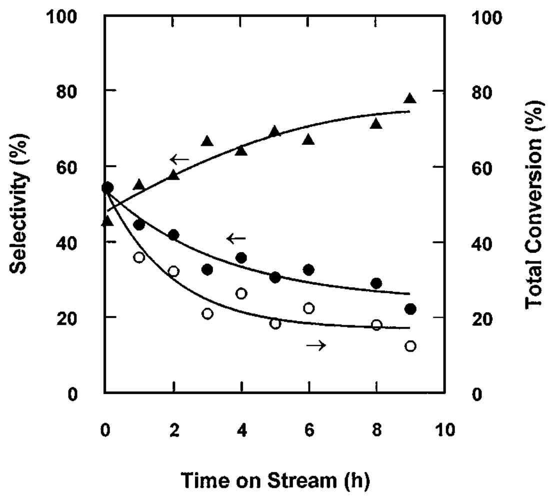


FIG. 5. Selectivities and conversion obtained during the reaction of *n*-hexane over a physical mixture of 0.52% Pt/SiO_2 and H-β zeolite: ▲, selectivity for isomerization; ●, selectivity for cracking; ○, total *n*-hexane conversion. The reaction of 45 Torr *n*-hexane was carried out in 2.0×10^3 Torr H_2 at 250°C over 0.60 g Pt/SiO_2 and 0.60 g H-β zeolite at a contact time of 6.0 s.

Effect of separating the Pt and the acid site. In order to assess the importance of the proximity of the Pt particles to the zeolitic acid centers, experiments were carried out similar to those reported by Fujimoto and co-workers (7). Equal amounts of 0.52 wt% Pt/SiO_2 (0.60 g) and H-β zeolite (0.60 g) of the same nominal particle size (150 μm) were physically mixed together under different conditions. In one case, the mixture was not compressed; in a second case, the mixture was manually compressed using a mortar and pestle; and in a third case, the mixture was compressed at a pressure of 700 kg/cm^2. The compressed material was then broken into smaller particles and sieved. Although the state of the resulting materials is not precisely defined, it is obvious that the average distance between the metal particles and the acid sites is different for the three samples.

As shown in Fig. 5, the uncompressed catalyst mixture behaved in a manner similar to that of the pure H-β zeolite (Fig. 1). The major products resulted from the isomerization of *n*-hexane, and their selectivity increased with time on stream, whereas the overall conversion decreased. For the manually compressed catalyst, the conversion, which was only about 20%, decreased very slowly with time on stream, as shown in Fig. 6. The isomerization selectivity in this case was $>$90%, whereas the cracking selectivity was $<$10%. Finally, the catalyst that had been compressed at 700 kg/cm^2 was completely stable with respect to time on stream, as shown in Fig. 7. The total conversion increased to 50%, and the isomerization selectivity was ca. 99%. The $\Sigma C_4/\Sigma C_2$ ratios decreased from 31 for the uncompressed sample to 5 for the sample compressed at 700 kg/cm^2, indicating that the extent of bimolecular cracking and secondary reactions decreased as the sample was compressed.

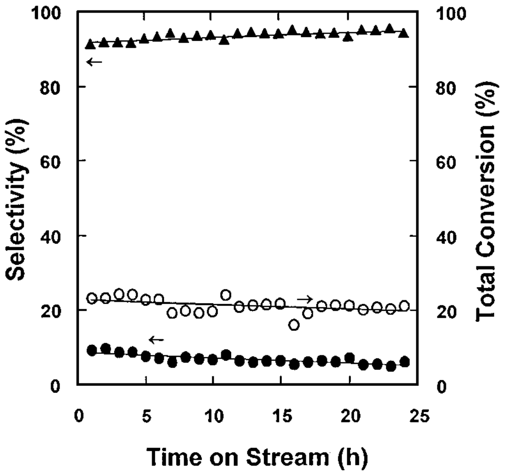


FIG. 6. Selectivities and conversions obtained during the reaction of *n*-hexane over a manually compressed mixture of 0.52% Pt/SiO_2 and H-β zeolite: ▲, selectivity for isomerization; ●, selectivity for cracking; ○, total *n*-hexane conversion. The reaction conditions were the same as those in Fig. 5.

TABLE 4

The Order of Reaction with Respect to Hydrogen and *n*-Hexane

Catalyst	Order of reaction	
	$P_{hydrogen}$[a]	$P_{n\text{-hexane}}$[b]
0.65% Pt/H-β zeolite	−0.71 (200°C)[c] −0.68 (250°C)	0.72 (200°C) 0.70 (250°C)
Commercial catalyst	−0.68 (180°C)	0.70 (200°C)
0.52% Pt/SiO_2 + H-β zeolite compressed manually	−0.88 (250°C)	
0.52% Pt/SiO_2 + H-β zeolite compressed at 700 kg/cm^2	−0.93 (250°C)	

[a] Hydrogen pressure range: 720 Torr to 3×10^3 Torr.

[b] *n*-Hexane pressure range: 45 Torr to 150 Torr.

[c] The numbers in the parentheses are the temperatures at which the reaction order was determined.

Kinetic parameters. The orders of *n*-hexane reaction with respect to hydrogen and *n*-hexane for three catalysts are given in Table 4. For the impregnated 0.65% Pt/H-β zeolite, the orders of reaction at both 200 and 250°C were −0.7 with respect to H_2 and 0.7 with respect to *n*-hexane, giving an overall reaction order of zero. For the two compressed mixtures, the negative order with respect to H_2 was somewhat larger.

The apparent activation energies for the overall reaction and for the isomerization and cracking reactions separately are given in Table 5. The metal dispersions, reaction rates and turnover frequencies for these catalysts are given in Table 6. The activation energies of the overall reaction and for the isomerization reaction increased with the metal loading. Consistent with this trend, the activation energies for the overall reaction and for the isomerization reaction were smaller for the H-β zeolite than for the Pt-loaded zeolites. The compressed mixtures had intermediate activation energies.

The rates of reaction for the overall *n*-hexane transformation and for isomerization, as well as the turnover frequencies for these reactions, were the largest for the 0.41% Pt/H-β zeolite prepared by the ion-exchange method. The rates obtained over this catalyst, however, were less than those measured over a commercial Pt/mordenite catalyst, particularly when one considers the fact that 80% of the

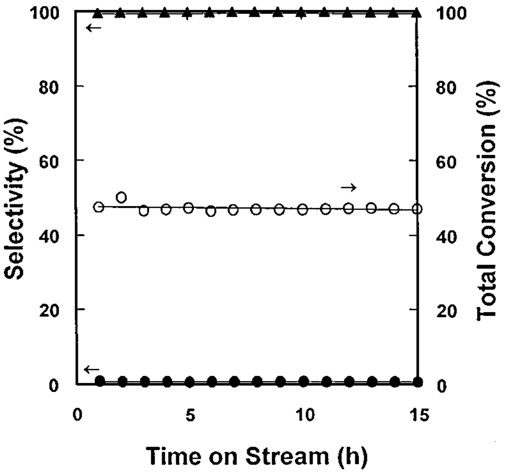


FIG. 7. Selectivities and conversions obtained during the reaction of *n*-hexane over a mixture of 0.52% Pt/SiO_2 and H-β zeolite that had been compressed at 700 kg/cm^2: ▲, selectivity for isomerization; ●, selectivity for cracking; ○, total *n*-hexane conversion. The reaction conditions were the same as those in Fig. 5.

TABLE 5

Activation Energies of the Overall Reaction, Isomerization Reaction, and Cracking Reaction for Various Catalysts[a]

Catalyst	Activation energy (kcal/mole)		
	Overall	Isomerization	Cracking
6.4% Pt/H-β zeolite	33.4	33.4	33.0
0.65% Pt/H-β zeolite	31.2	31.1	34.6
0.41% Pt/H-β zeolite (ion-exchanged)	27.1	27.3	19.6
0.12% Pt/H-β zeolite	26.8	26.8	
0.026% Pt/H-β zeolite	19.1	18.7	32.4
Commercial cat.[b]	26.3	26.4	30.7
H-β zeolite	12.6	4.8	22.2
0.52% Pt/SiO_2	30.2	30.5	25.8
0.52% Pt/SiO_2 + H-β zeolite (compressed manually)	15.2	14.1	
0.52% Pt/SiO_2 + H-β zeolite (compressed at 700 kg/cm^2)	19.2	19.0	

[a] 45 Torr *n*-hexane reacted in 2.0×10^3 Torr H_2.

[b] Commercial catalyst: 20% wt of 0.3% Pt/mordenite in alumina matrix.

TABLE 6

Rates and Turnover Frequencies for the Catalytic Reactions of *n*-Hexane[a]

Catalyst (D)[b]	Rate of reaction (10^{-7}mol g^{-1} s^{-1}) Overall	Isomerization	Cracking	TOF[c](s^{-1}) Overall	Isomerization
6.4% Pt/H-β zeolite (17)	43.3	42.8	0.5	0.104	0.103
0.65% Pt/H-β zeolite (27)	37.3	37.1	0.2	0.56	0.55
0.41% Pt/H-β zeolite (31) (ion-exchanged)	50.2	49.3	0.9	1.30	1.20
0.12% Pt/H-β zeolite	36.8	36.7	0.1		
0.12% Pt/H-β zeolite[d]	23.1	22.7	0.4		
0.026% Pt/H-β zeolite	6.2	6.1	0.1		
0.57% Pt/γ-Al_2O_3 (54)	1.4	1.4	0.03	0.010	
Commercial cat.[e]	62.7	62.1	0.6		
H-β zeolite	3.0	1.6	1.4		
0.52% Pt/SiO_2 (19) + H-β zeolite (Compressed manually)	1.6	1.5	0.1	0.067	0.062
0.52% Pt/SiO_2 (19) + H-β zeolite (compressed at 700 kg/cm^2)	3.5	3.5	0.03	0.15	0.15

[a] 45 Torr *n*-hexane reacted at 250°C in 2.0×10^3 Torr H_2.
[b] Dispersion values in percent are given in parentheses.
[c] Turnover frequency with respect to the metal surface atoms.
[d] 45 Torr *n*-hexane + 0.1 Torr 1-hexene as reactants.
[e] Commercial catalyst: 20% wt of 0.3% Pt/mordenite in alumina matrix.

mass of the commercial catalyst resulted from an alumina binder. Among the Pt-loaded H-β zeolites, the ion-exchanged sample also exhibited the largest cracking activity. The isomerization activity of the Pt-loaded H-β zeolites remained large down to a loading of 0.12% Pt. For the three catalysts with the most Pt, the TOF for isomerization decreased with loading level.

It is important to note that the mixtures of Pt/SiO_2 and H-β zeolite had much lower rates of reaction than did the impregnated or ion-exchanged zeolite catalysts. This distinction is not apparent from the conversion levels. The difference in rates is partly due to the fact that the mixture contains ∼50% SiO_2. Nevertheless, the rate of isomerization over the highly compressed 0.52% Pt/SiO_2 + H-β zeolite sample was only about one fifth that of the 0.65% Pt/H-β catalyst, on the basis of the same amount of zeolite.

DISCUSSION

Proposed isomerization mechanism. Clearly, Pt/H-β zeolite is an active, selective, and stable catalyst for the isomerization of *n*-hexane. Its activity is less than that of a commercial catalyst, although no attempt was made in this study to optimize the performance because mechanistic questions were of primary interest.

As pointed out in the introduction, the classical mechanism may not be relevant under the conditions of these experiments because of the very small equilibrium concentration of hexene intermediates. At 250°C, and at the pressures of reagents used in these experiments, the total equilibrium pressure of all *n*-hexene isomers is only 4.9×10^{-4} Torr. Moreover, three experiments with H-β zeolite, described in the previous section, indicate that skeletal isomers are not derived from hexene intermediates. First, the replacement of H_2 vector gas by N_2 would result in more steady-state *n*-hexene, but the result was a decrease in isomerization selectivity. Second, when 1-hexene was added to the reagents with N_2 as the vector gas, the isomerization selectivity again decreased. Third, small amounts of 1-hexene reacted over a partially aged H-β zeolite to form primarily coke and cracked products, and no C_6 skeletal isomers were detected. This behavior is in contrast to that observed during the reaction of 1-hexene over an amorphous silica–alumina catalyst, which is effective in the formation of skeletal isomers at 300°C (15). The difference in results for the two types of catalysts presumably is related to the much greater acid strength of the zeolite.

To be consistent with the results of this and other studies, an alternative mechanism must account for (i) the negative effects of alkenes, (ii) the negative order with respect to H_2, (iii) the fact that H-β itself is a reasonably selective isomerization catalyst, (iv) the positive role of Pt, and (v) the negative effect of separating the Pt from the acid sites. We therefore propose a mechanism in which the acid sites are mainly responsible for isomerization via a cyclic reaction. The cycle is interrupted primarily by alkenes, and the role of the Pt is to keep the local alkene concentration small by hydrogenation. If the Pt is located too far from the acid sites, the *local* concentration of alkenes becomes large, and isomerization is quenched. These concepts are developed in the following discussion.

The acid-catalyzed part of the isomerization reaction is described by the following chain mechanism, which is generalized for $n > 3$:

Initiation

$$n\text{-}\mathrm{C}_n\mathrm{H}_{2n+2} + \mathrm{H}^+\text{-}\mathrm{B}^- \rightarrow n\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+3}\text{-}\mathrm{B}^-, \tag*{[4]}$$

$$n\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+3}\text{-}\mathrm{B}^- \rightarrow n\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+1} + \mathrm{H}_2, \tag*{[5]}$$

$$\mathrm{C}_n\mathrm{H}_{2n} + \mathrm{H}^+\text{-}\mathrm{B}^- \rightarrow \mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^-, \tag*{[6]}$$

$$n\text{-}\mathrm{C}_n\mathrm{H}_{2n+2} + \mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^- \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^-. \tag*{[7]}$$

Propagation

$$n\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^- \rightarrow i\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^-, \tag*{[8]}$$

$$n\text{-}\mathrm{C}_n\mathrm{H}_{2n+2} + i\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^- \rightarrow i\text{-}\mathrm{C}_n\mathrm{H}_{2n+2} + n\text{-}\mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^-. \tag*{[9]}$$

Termination

$$\mathrm{H}_2 + \mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^- \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + \mathrm{H}^+\text{-}\mathrm{B}^-, \tag*{[10]}$$

$$\mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^- \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{H}^+\text{-}\mathrm{B}^-. \tag*{[11]}$$

$$\begin{array}{l} \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{C}_n\mathrm{H}^+_{2n+1}\text{-}\mathrm{B}^- \\ \rightarrow \mathrm{C}_{2n}\mathrm{H}^+_{4n+1}\text{-}\mathrm{B}^- \begin{array}{ll} \nearrow \text{Cracking products,} & [12a] \\ \searrow \mathrm{H}_2 + \mathrm{C}_{2n}\mathrm{H}^+_{4n-1}\text{-}\mathrm{B}^-. & [12b] \end{array} \end{array}$$

Here it is assumed that the hydrogen transfer and methyl shift, which results in isomerization, is rapid compared to C−C bond cleavage, which results in cracking. For isomerization selectivity to be high, the chain length must be large ($\sim 10^2$), and the rate of side reactions that result in cracking must be slow. The chain length refers to the number of times Reactions [8] and [9] occur relative to a termination step. In addition to influencing selectivity, chain termination also affects the overall reaction rate because the relatively slow initiation steps are needed to begin a new chain reaction. Termination by hydrogenation of the carbenium ion (Reaction [10]) has a negative effect on reaction rate, which is consistent with the observed −0.7 order with respect to H_2, but the selectivity would remain unaffected, at least within this set of reactions. The dissociation of the carbenium ion (Reaction [11]), however, produces an alkene, which can react with other carbenium ions (Reaction [12]). The higher carbon number intermediates more easily crack (Reaction [12a]), or they may further dehydrogenate (Reaction [12b]) to form coke precursors. Isomerization selectivity is diminished, of course, as cracking occurs.

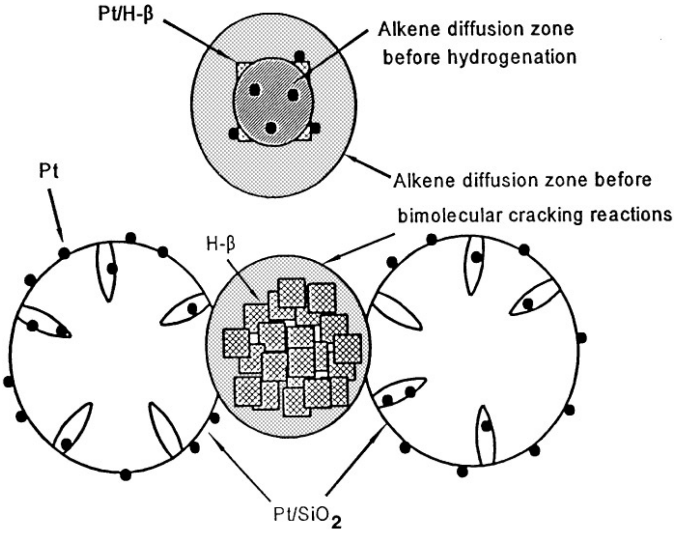
The principal role of Pt is to catalyze the hydrogenation of the alkene, and, thus, to prevent the alkene from interrupting the isomerization chain reaction. For this reaction to occur, H_2 is necessary, and at pressures greater than 760 Torr and with impregnated or ion-exchanged catalysts containing ≥0.4 wt% Pt, the rate of hydrogenation is rapid relative to the other steps. Hence, the steady-state alkene concentration is maintained at a sufficiently low level so that the contribution of Reaction [12] is small. At a sufficiently low Pt loading, the rate of hydrogenation becomes too small to minimize the concentration of alkenes adequately. With the 0.12% Pt/H-β catalyst, for example, the addition of 0.1 Torr of 1-hexene caused a decrease in *n*-hexane conversion (Table 6).

Provided Pt is adjacent to an acid center, it may have a secondary role in that the metal facilitates hydrogen transfer, but in a different sense than that proposed by Iglesia *et al.* (2). In particular, Pt may be involved in the protonation of hexane (Reaction [4]) and in the dehydrogenation of the resulting bound cation (Reaction [5]). The cation may undergo such cracking as

$$\mathrm{C}_n\mathrm{H}^+_{2n+3}\text{-}\mathrm{B}^- \rightarrow \mathrm{C}_m\mathrm{H}_{2m+2} + \mathrm{C}_{n-m}\mathrm{H}_{2n-2m} + \mathrm{H}^+\text{-}\mathrm{B}^-, \tag*{[13]}$$

with the rate for the *iso*-cation cracking being greater than that of the *n*-cation. The products are those expected from unimolecular cracking. As a consequence of this effect of Pt, unimolecular cracking occurs, albeit slowly, at 250°C instead of 350°C, which is the temperature that the reaction occurs over a pure H-β zeolite (16). Moreover, this role of Pt would give rise to the greater cracking selectivity that was observed at high conversions over the 0.41, 2.6, and 6.4% catalysts (Table 2). The 0.41% Pt/H-β catalyst was particularly effective in promoting cracking, even though the loading was small, because the method of preparation (exchange of a $[\mathrm{Pt(NH_3)_4}]^{2+}$ complex, followed by treatment in O_2) favors the incorporation of the metal within the zeolite cavities where most of the acidic protons reside.

Finally, it is important that the mechanism be consistent with the results obtained for the $\mathrm{Pt/SiO_2} + \mathrm{H}\text{-}\beta$ mixtures. In contrast to the interpretation given by Fujimoto and coworkers (7) based on hydrogen spillover, we propose that the *local* concentration of alkenes is the critical factor. As depicted in Scheme 1, the alkenes formed at the acid sites will diffuse a certain distance before they are hydrogenated. On average, this distance will define a diffusion zone. Within this zone, the alkenes will experience multiple collisions with other species, and a fraction of these collisions will result in the deleterious Reaction [12]. When Pt is on the external surface or inside the zeolite particle, the diffusion zone will be small because of rapid hydrogenation and the probability of Reaction [12] occurring will be small. But if the Pt is in a separate silica particle, the diffusion zone will be much larger, and Reaction [12] will have a greater effect on the acid-catalyzed isomerization within the zeolite particles. The diffusion zone will likewise increase as the $\mathrm{Pt/SiO_2}$ and the H-β zeolite are less tightly packed. For



SCHEME 1. Depiction of diffusion zones before hydrogenation and cracking reactions involving alkenes: (top) for a Pt-loaded zeolite, (bottom) for a physical mixture of Pt/SiO$_2$ and H-β zeolite. Note that the scale is different for the two cases.

this model to be correct, the following must be true: rate of alkene hydrogenation $>$ rate of Reaction [12] $>$ rate of alkene diffusion.

It will be noted from the results of Figs. 6 and 7 and Table 6 that the compressed mixtures were much less active than the Pt/H-β catalysts, but the isomerization selectivities were uniformly high. By contrast, the isomerization activity of the manually compressed catalyst was about the same as that of the H-β zeolite. These effects can likewise be understood by considering differences in the chain length. For example, if the chain length were decreased from 500 to 50 in going from an impregnated Pt/H-β catalyst to a compressed two-component catalyst, the activity would decrease by a factor of 10, whereas the isomerization selectivity would decrease only from 99+ to 98%. But if the chain length decreased to 5, the selectivity would decrease to 80%. The latter case is similar to the situation observed for the mixed, but uncompressed two-component catalyst. This simple analysis should be modified by a small background of cracking reactions that becomes more significant as the alkene concentration increases.

Relationship to other mechanisms. The experiments carried out on the Pt/SiO$_2$ + H-β zeolite mixture are reminiscent of the earlier work of Weisz and Swegler (17), who studied mixtures of Pt/SiO$_2$ + silica–alumina catalysts. The observation that the mixture was much more active for *n*-hexane isomerization than each of the individual components supported the concept of a bifunctional catalyst, and the results were interpreted according to the classical mechanism (vide supra). As a result of diffusional limitations, the extent of the conversion could be modified by varying the size of the silica–alumina particles. This is clearly not a factor in the present experiments because the size of the zeolite particles was constant, and the diffusion in the void volume between particles is rapid. Although hexenes may be important isomerization intermediates at higher temperatures (e.g., 300°C) and over less acidic catalysts, they almost certainly do not play a positive role in the isomerization reaction over Pt/zeolite catalysts.

The metal must be in the vicinity of the acid center for effective hydrogenation of alkenes; however, the two do not, in general, need to be adjacent to one another as required by the model of Iglesia *et al.* (2). The platinum particles prepared by impregnation of the H-β zeolite with chloroplatinic acid would be mainly located on the external surface of the zeolite crystallites where only a small fraction of the acidic protons reside. As noted earlier, the platinum in the ion-exchanged sample (0.41% Pt/H-β) would reside mainly within the channels of the zeolite, and the moderate enhancement in rates ($\sim$30% overall for 0.41% Pt/H-β compared with 0.65% Pt/H-β) may indeed result from the metal-assisted formation of carbenium ions, as suggested by Iglesia *et al.* (2). But in contrast to the proposal of Iglesia *et al.*, this metal-assisted hydrogen transfer appears to favor cracking, as well as isomerization of hexane.

Many of the results described here could be explained by hydrogen spillover, as proposed by Fujimoto and coworkers (7); however, the mechanism by which hydrogen atoms or ions move from one catalyst particle to another is not obvious. Hydrogen spillover in this sense is controversial, and until the phenomenon is better understood, it seems best to seek alternative explanations for catalytic phenomena related to the proximity of a metal and an acid site.

Details of methyl transfer. Following the proposal of Sie (18), it is reasonable to expect that a single methyl shift involves a nonclassical cyclopropyl carbenium species. The presence of 2,3-dimethylbutane as an *initial* product (Fig. 3) is more difficult to explain and suggests that a cyclobutyl cation also may be an intermediate. Because protonated cyclobutane is 31 kcal/mol less stable than protonated methyl cyclopropane (19), it is not surprising that the primary selectivity for 2,3-dimethylbutane was much less than those of the methylbutane isomers. In fact, considering this large difference in energy, the cyclobutyl cation, or the analogous alkoxy species, must be stabilized by the zeolite in order for this species to be an intermediate. By contrast, 2,2-dimethylbutane cannot be formed by a single methyl transfer, which explains why it appears as a secondary, rather than a primary, reaction product (Fig. 3).

CONCLUSIONS

Pt-loaded H-β zeolite is an active and selective bifunctional catalyst for the isomerization of *n*-hexane. In order to achieve maximum activity, the Pt metal must be on the zeolite particles or within the pore structure. The isomerization reaction is believed to occur at the acid sites via a chain mechanism. Alkenes that are formed by side reactions may terminate the chain reaction, and, thus, decrease the isomerization rate. Moreover, the alkenes promote oligomerization, cracking, and coke-forming reactions. Alkenes may be involved in the initiation of the reaction chain through the formation of bound carbenium ions, but because of alternate routes for the formation of carbenium ions, the positive effect on chain initiation is much less than the negative effect that they have on chain termination. In contrast to the classical mechanism, which involves alkenes as direct intermediates, it appears that over strongly acidic zeolites alkenes have a negative effect on both the activity and selectivity for isomerization. The principal role of the Pt is to catalyze the hydrogenation of the alkenes and maintain their steady-state concentration at a sufficiently low level to allow the isomerization pathway to predominate. The proximity of the Pt and the acid site is important because the local concentration of alkenes must be kept at a very low level. The presence of H_2 obviously is required for the removal of alkenes, but at the levels used in these experiments it also has a negative effect on activity because it provides another pathway for the termination of the chain reaction through hydrogenation of carbenium ions.

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