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The Role of Platinum in Hexane Isomerization over $Pt/FeO_y/WO_x/ZrO_2$

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Hexane isomerization was investigated in Pt-free and Pt-containing highly acidic iron oxide/tungsten oxide zirconia ($FeO_y/WO_x/ZrO_2$) catalysts. It has been found that hexane isomerization on WO_x/ZrO_2–based catalysts takes place mainly on monofunctional acid sites via intermolecular hydride transfer reactions between neutral molecules and carbenium ions. The highly acidic character of WO_x/ZrO_2 is such that hexane isomerization does not proceed via the classical dual functional mechanism. These results are consistent with those obtained in strong acid systems, and contrast those of zeolite-based catalysts, where the presence of metal is required to achieve high conversions. The relative rate of hydrogen transfer and the thermodynamic limitation imposed on the hexane isomers dictate the product distribution. The presence of Pt is found to specifically facilitate the approach to equilibrium of the 2,2-dimethylbutane isomer. This isomer is shown to form from the most sterically-hindered carbenium ion intermediate. The results suggest that Pt-catalyzed hydrogen activation generates substantial amounts of surface atomic hydrogen which readily undergoes hydrogen transfer with this hindered intermediate, which would otherwise undergo very slow hydride transfer with neutral molecules. Our results also suggest that Pt-catalyzed hydrogen activation may play a more classical role in keeping the surface concentration of hexyl cations low, and consequently secondary reactions, oligomerization/cracking, that give rise to cracked products, are inhibited. The results of deuterium exchange measurements in D_2 at low conversion, are best explained by invoking both acid- and metal-facilitated deuteration pathways. The presence of Pt results in a moderately higher level of deuterium exchange in the isohexane products, but a large increase in the deuteration of the normal hexane starting material. At ∼20% conversion, nearly all of the *unreacted* normal hexane molecules contain at least one deuterium atom over $Pt/FeO_y/WO_x/ZrO_2$, while only 4–5% of the hexane is deuterated over Pt-free $FeO_y/WO_x/ZrO_2$. These results can be attributed to branched isomer exchange with deuterated Brønsted sites, supplemented by non-isomer-selective C–H bond activation by Pt.

I. INTRODUCTION

Light paraffin (C_5 and C_6) isomerization is an increasingly important process in the manufacture of high-octane clean fuels. This process and the alkylation of isobutane with olefins are the only refinery processes which produce significant quantities of the ideal component of reformulated gasoline: isoparaffins. Currently, there are two major commercial paraffin isomerization catalysts, Pt on highly chlorinated alumina, and Pt/mordenite. The high activity of the chlorinated alumina-based catalyst allows operation at low temperature (<125°C), which thermodynamically favors formation of the high-octane branched paraffins. These catalysts require the constant addition of a chloride-containing compound for chlorine maintenance and are very sensitive to moisture and sulfur. In addition, they are highly corrosive and are subject to stringent environmental control. Pt/mordenite does not have these drawbacks, but is considerably less active and consequently requires higher operating temperatures (∼260°C) where thermodynamic constraints give lower yields of the branched paraffins. Therefore, there is a need for a catalyst that combines the advantages of the above mentioned catalysts, i.e., high enough acidity to isomerize light paraffins at low temperature and operational and environmental friendliness.

Modified zirconia-based catalysts have been offered as an alternative. Highly acidic, sulfated zirconia is very active for *n*-butane isomerization at low temperatures (1). Arata and Hino (2, 3) reported a method for preparing a tungsten oxide/zirconia solid acid catalyst which involves the impregnation of $Zr(OH)_4$ with aqueous ammonium metatungstate followed by calcination in air at 800–850°C. When employed as a support for Pt, or Pt with a secondary metal (e.g., Fe, Mn), very effective dual functional catalysts were generated.

A more recent preparation method based on the coprecipitation of the tungsten salt with $Zr(OH)_4$ to form a WO_x/ZrO_2 catalyst with twice the strong acid site density of the materials prepared by impregnation, has been reported (4). These novel solid acids have paraffin isomerization activities approaching that of the chlorinated alumina-based catalyst, and much higher than that of Pt/mordenite. Coupled with their high thermal stability and excellent

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regenerability, the WO_x/ZrO_2-based catalysts show promise as an environmentally friendly replacement for the halogen-containing catalysts.

Two general mechanisms have been proposed for paraffin isomerization depending on the acid strength of the catalyst: bifunctional (metal–acid) and monofunctional (both metal-only and acid-only). The former takes place on metal catalysts supported on relatively low-acidity supports such as amorphous silica–alumina and zeolites and includes three consecutive steps (5); (i) paraffin dehydrogenation on the metal; (ii) skeletal rearrangement of the olefin on the acid site via a carbenium ion mechanism; and (iii) rehydrogenation of the isomerized olefin on the metal. Metals (6) and zeolites (4) are capable of isomerizing paraffins by themselves, but at very low rates. On catalysts exhibiting strong acidity, such as highly chlorinated alumina and BF_3/HF, paraffin isomerization can take place solely on acid sites via a monofunctional mechanism featuring a hydride-transfer chain reaction (7). In the case of the commercial chlorinated alumina, the noble metal was proposed to limit coke formation and acid site deactivation (8).

A monofunctional mechanism has also been proposed for the high acidity, modified zirconia catalysts (9–11). In this case, Pt has the important secondary function of hydrogen activation, which contributes to acid site creation and suppressed coking. Alternatively, a monofunctional mechanism has recently been proposed for the less acidic Pt/H-β catalyst involving acid-catalyzed methyl shift and hydrogen transfer reactions, with the principal role of Pt being to prevent the formation of large, local concentrations of olefins (12).

In this paper, we examine the role of Pt in the isomerization of *n*-hexane over novel, high-acidity $FeO_y/WO_x/ZrO_2$ catalysts. The results indicate that the acid sites in these catalysts are strong enough to perform the isomerization reaction via a monofunctional (i.e., hydride transfer) mechanism similar to that observed in other strong-acid catalysts. Hydride transfer reactions from neutral molecules to carbenium ions are fast, allowing hexane isomers, with the exception of 2,2-dimethylbutane, to reach equilibrium values at low temperatures ($\leq$150°C). The addition of Pt to the $FeO_y/WO_x/ZrO_2$ catalyst is required to increase the formation rate of 2,2-dimethylbutane. It is proposed that Pt opens a new reaction pathway that facilitates the formation of 2,2-dimethylbutane. This pathway eliminates the high kinetic barrier associated with intermolecular hydride transfer of the sterically hindered 3,3-dimethyl-2-butane cation precursor. A similar Pt role has been suggested for $Pt/SO_4/ZrO_2$ (10). The presence of Pt also maintains a low surface concentration of hexyl cations, minimizing oligomerization/cracking reactions that give rise to cracked products. Finally, the ability of Pt to facilitate hydrogen activation is determined by measuring the extent of deuterium uptake during hexane isomerization in D_2.

It should be noted that the role of the secondary metal (Fe) has not been clearly described in these systems. We have observed that Fe enhances the paraffin isomerization activity of these catalysts. A detailed description of the role of iron is lacking; however, elucidation of this important issue is outside the scope of this paper.

II. EXPERIMENTAL

Catalyst Synthesis

The $FeO_y/WO_x/ZrO_2$ catalyst was prepared by a method similar to the co-precipitation procedure described elsewhere (4). In brief, an aqueous solution containing ammonium metatungstate and ammonium hydroxide was added to a solution containing iron sulfate and zirconyl chloride. The precipitate was filtered, washed, and dried overnight at 85°C and calcined in dry air at 825°C for 3 h. At room temperature, Pt was added via incipient wetness with $H_2PtCl_6 \cdot 6H_2O$ (from Aldrich) dissolved in distilled water. The Pt-containing catalyst was air-dried at 120°C for 1 h, then air-calcined at 300°C for 2 h. The elemental composition of the catalyst was 0.5 wt.% Pt/0.6 wt.% Fe/15 wt.% W/ZrO_2, with a BET surface area of 62 m^2/g.

Catalytic Data Collection

The hexane isomerization reaction over both Pt-free and Pt-containing $FeO_y/WO_x/ZrO_2$ catalysts was carried out in a down-flow, fixed-bed reactor. Typically, 4 cc ($\sim$5.0 g) of 14/30-mesh catalyst was charged into the reactor. The catalyst was positioned in the central region of the reactor between two layers of sand, and pretreated in flowing nitrogen (GHSV = 2300 h^{-1}) at 300°C for 1 h to ensure removal of adsorbed water from the reactor and catalyst. After catalyst pretreatment, the reactor was cooled to reaction temperature, then pressurized with hydrogen at 450 psig. Hexane (Aldrich) was slowly fed into the reactor using a standard high-pressure ISCO pump while maintaining a high hydrogen flowrate (>1500 GHSV); then hydrogen and *n*-hexane flows were adjusted to give a $2H_2/n\text{-}C_6$ mol ratio. After passing through a back-pressure regulator downstream of the reactor, the effluent was diluted with nitrogen, and the combined stream was sent to on-line gas chromatography sampling for analysis. Heating and insulating tapes were wrapped around the stainless steel lines connecting the reactor exit and the gas chromatograph sampling valve to maintain temperature around 160°C to avoid condensation of the reaction products in the transfer line. A fused silica capillary column (DB-1, 60 m) run at 28°C isothermal was used to determine the reaction product composition.

Deuterium Uptake Measurements

The fixed bed reactor was initially lined out, as described above, at 18–20% overall hexane conversion with a

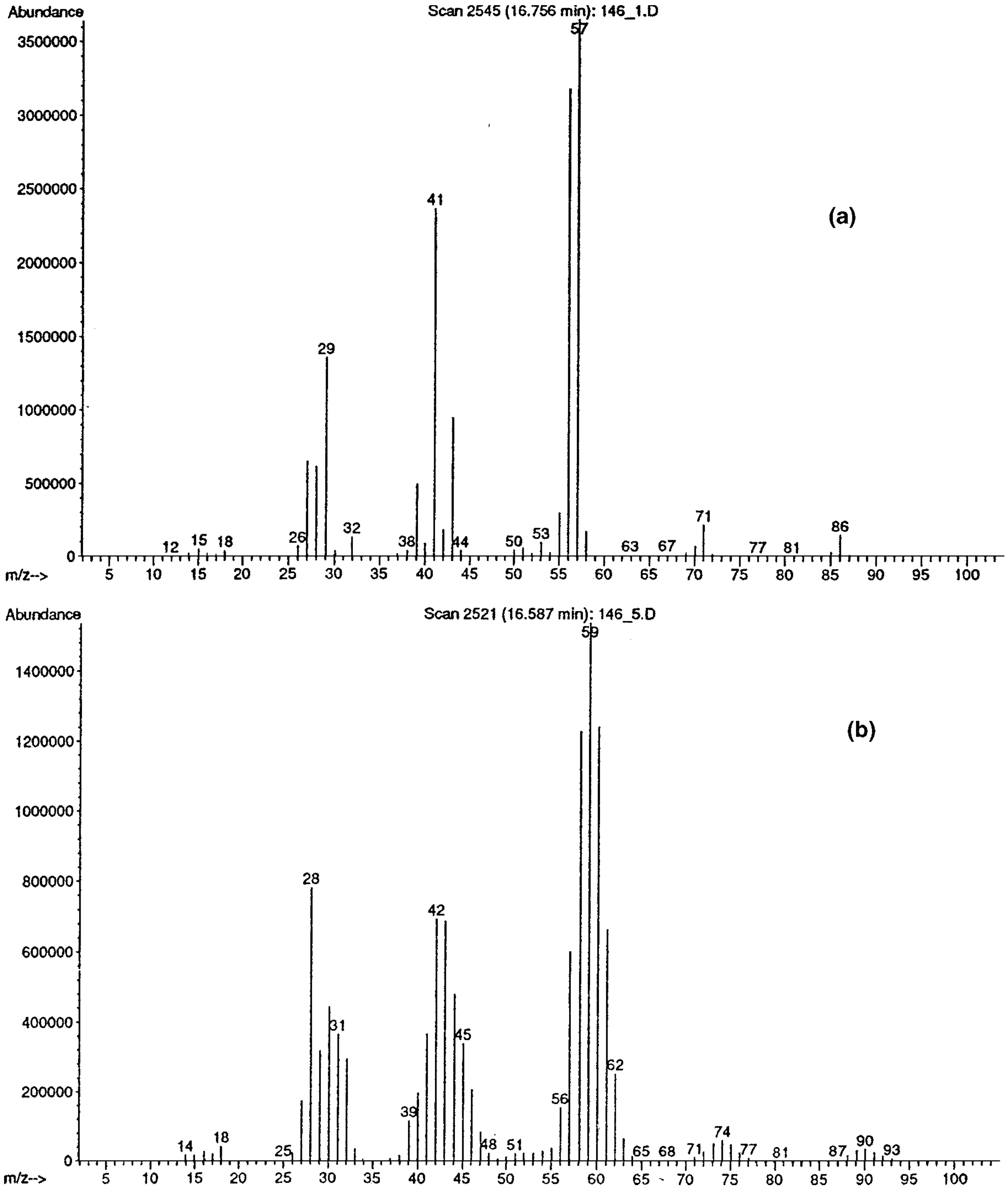


FIG. 1. Mass ion fragmentation pattern of 3-methylpentane product formed in (a) H_2 and (b) D_2.

hydrogen co-feed. Once stable operation was achieved, the reactor effluent was redirected through a dry ice trap for manual collection. After collecting hourly liquid product samples for several hours, feed hydrogen was replaced with deuterium. Deuterium feed was maintained for 2–3 h to completely purge hydrogen from the reactor system, whereupon several hourly liquid products were again collected. Finally deuterium was replaced with hydrogen and, after sufficient purging, liquid product sampling was repeated to determine if the product deuterium returned to its baseline level in hydrogen. All liquid samples were analyzed by GC and GC/MS using HP5890 and HP5890/5971A instruments, respectively.

Figure 1 compares typical fragmentation patterns for 3-methylpentane from liquid products collected in the presence of H_2 and D_2. The incorporation of deuterium is evidenced by the conversion of distinct, relatively isolated weight loss lines in H_2, to envelopes of lines extending to high m/z in D_2. The deuterium content of each isomer, except 2,2-dimethylbutane, was determined from the relative abundance of the 86 m/z parent ion peak ($C_6H_{14^+}$) within the envelope of deuterated parent ions. Since 2,2-dimethylbutane did not exhibit a parent ion peak, the intense 71 m/z methyl-loss peak ($C_5H_{11^+}$) was used.

The intensity of the 86 m/z line indicates the amount of deuterium-free $C_6H_{14^+}$ present in a given isomer. Deuterium incorporation could increase this ion mass to a potential maximum of 100 m/z ($C_6D_{14^+}$), with all intermediate masses included in the deuterated envelope. Therefore, the percentage of the 86 m/z intensity to the cumulative intensity over the 86–100 m/z range was taken as the relative concentration of $C_6H_{14^+}$,

$$\%\chi_{86} = \left(\frac{I_{86}}{\sum_{n=0}^{14}(I_{86+n})}\right)100, \quad [1]$$

where, for example, I_{86} equals the measured intensity at 86 m/z. As stated above, the 71 m/z peak was used for determining deuterium incorporation into 2,2-dimethylbutane. In this case, the relative concentration of the undeuterated $C_5H_{11^+}$, $\%\chi_{71}$, was calculated from

$$\%\chi_{71} = \left(\frac{I_{71}}{\sum_{n=0}^{11}(I_{71+n})}\right)100, \quad [2]$$

The incorporation of deuterium into the product would decrease the $C_6H_{14^+}$ fragment concentration as reflected in a decreased $\%\chi_{86}$ value.

III. RESULTS AND DISCUSSION

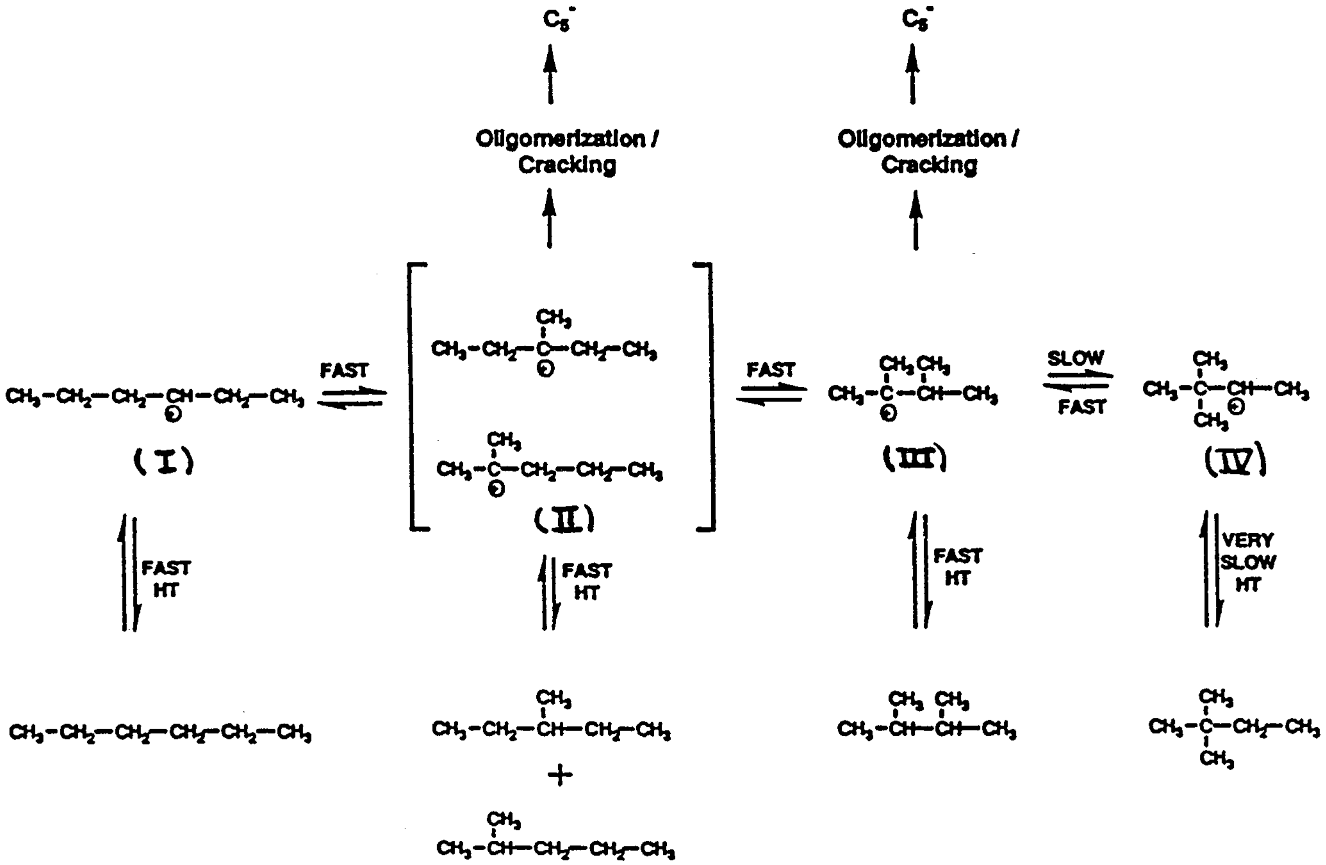
The hexane isomerization results obtained over the Pt-free and Pt-containing $FeO_y/WO_x/ZrO_2$ catalysts are shown in Table 1. Although Pt plays a critical role in the generation of olefinic intermediates in the classical dual functional mechanism, this is not nearly as important in strong acids, such as WO_x/ZrO_2, as in relatively weak acids, such as amorphous silica alumina and zeolites. Accordingly, the Pt-containing $FeO_y/WO_x/ZrO_2$ catalyst exhibits only slightly higher overall hexane conversion than the Pt-free catalyst. Table 1 also indicates that under identical reactor conditions, $Pt/FeO_y/WO_x/ZrO_2$ favors the formation of much more 2,2-dimethylbutane and much less cracked products (C_{5^-}), than its Pt-free analogue. The product distribution obtained on the monofunctional Pt-free $FeO_y/WO_x/ZrO_2$ catalyst can be rationalized in terms of a hydride transfer mechanism along with ß-scission of large (C_{6^+}) carbenium ion intermediates. The cracked product (C_{5^-}) distribution obtained over this monofunctional catalyst consists primarily of isobutane and isopentane with very small amounts of ethane and methane. These cracked products are formed by isomerization and ß-scission of large carbenium ion intermediates that may be formed from oligomerization of surface hexyl cations. The ß-scission of carbenium ions favors the formation of stable tertiary carbenium ion fragments that are precursors of branched alkanes, isobutane and isopentane, and disfavors the formation of primary carbenium ion precursors of methane and ethane (13). The data obtained over the Pt-free catalyst also indicates that, unlike the other C_6 isomers, the yield of 2,2-dimethylbutane is uniquely far away from its thermodynamic value.

TABLE 1

Hexane Isomerization over Pt-Free and Pt-Containing $FeO_y/WO_x/ZrO_2$ at 210°C, $2H_2/n\text{-}C_6$ Molar Ratio, 450 psig, 2 LHSV (ml $n\text{-}C_6$ Feed per ml Catalyst per Hour). Data Obtained after Five Days on Feed

	Catalyst	
Prod. Dist. (wt.%)	Pt-free	Pt-containing
$C_1 + C_2$	0.03	0.6
C_3	1.3	1.2
i-C_4	9.3	0.9
n-C_4	0.9	0.9
i-C_5	5.6	1.0
n-C_5	0.9	0.4
2,2-DMB	5.3	24.4
2,3-DMB	9.0	9.1
2-MP	30.0	29.6
3-MP	18.6	18.2
n-C_6	18.4	13.4
C_{7+}	Tr	Tr
n-C_6 conv., wt.%	81.6	86.6
C_5-, wt.%	18.0	5.0
2,2-DMB/Total C_6's, %	6.5	25.8
2,2-DMB thermo. equil., %	25.9	25.9

Scheme 1 summarizes the various reaction pathways that are proposed to give rise to the observed product distribution. The first step is the generation of a secondary n-hexyl cation, for example 3-hexyl carbenium (I). In addition to direct protolysis, hydride abstraction, C–H oxidation, or protonation of trace olefins (14), (I) may also form stepwise via minor acid cracking of hexane to generate carbenium ions (15), which then undergo rapid intermolecular hydride transfer with hexane to give the secondary n-hexyl cation (I). Regardless of how they are formed, these secondary linear cations rapidly isomerize and equilibrate with the monobranched tertiary 2- and 3-methyl-pentyl cations (II), which subsequently equilibrate with the di-branched, tertiary 2,3-dimethyl-2-butyl cation (III). The tertiary 2,3-dimethyl-2-butyl cation (III), in turn, equilibrates with the secondary 3,3-dimethy-2-butyl cation (IV), with the equilibrium favoring the more stable tertiary ion. In addition to these relatively rapid skeletal rearrangements, the surface hexyl cations may undergo two other reaction



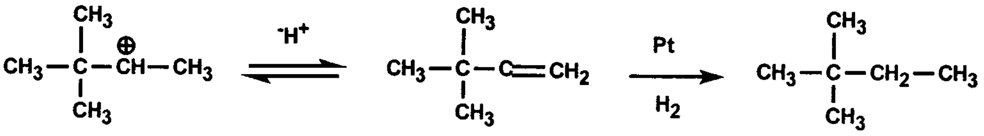
SCHEME 1

pathways; (a) intermolecular hydride transfer to complete a surface turnover and form the corresponding alkane product, or (b) oligomerization/cracking reactions that give rise to C_{5^-} products. The relative rates of these two reaction pathways and the thermodynamic limitation imposed on the hexane isomer concentrations, dictate the product distribution. The observed thermodynamic yields of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane indicate that their hexyl cation precursors, surface species (II) and (III), respectively, are at equilibrium, and undergo rapid intermolecular hydride transfer. On the other hand, the low yield of 2,2-dimethylbutane, as noted above, suggests that its formation proceeds over a high kinetic barrier.

With a t-butyl group alpha to the charged center, IV is the most sterically protected carbenium ion in Scheme 1. Therefore, formation of the bimolecular hydride transfer transition state with a neutral molecule would be most hindered. This is illustrated by comparing the relative reaction rates of S_N2-type reactions of ß-substituted alkyl halides, where neopentyl halides (as in IV) react about three orders of magnitude slower than isobutyl halides (16). It is likely that the suppressed formation of 2,2-dimethylbutane is due to the hindered intermolecular hydride transfer of the 3,3-dimethyl-2-butyl cation with a paraffin molecule. Thus, on the Pt-free FeO$_y$/WO$_x$/ZrO$_2$ catalyst, rearrangement of the secondary 3,3-dimethyl-2-butyl cation (IV) to form the more stable tertiary 2,3-dimethyl-2-butyl cation (III) is preferred relative to the sterically hindered intermolecular hydride transfer.

Overall, for the Pt-free catalyst, one may conclude that thermodynamic limitations on the concentration of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, along with the high kinetic barrier involved in the formation of 2,2-dimethylbutane, give rise to a relatively large concentration of surface hexyl cations. These cations may undergo oligomerization/cracking reactions to give C_{5^-} products.

Now, let us turn our attention to the bifunctional (metal/acid) Pt/FeO$_y$/WO$_x$/ZrO$_2$ catalyst for hexane isomerization. The results presented in Table 1 indicate that the addition of Pt to the catalyst has a striking effect on the product distribution. Platinum decreases the formation of cracked products, C_{5^-}, and greatly enhances the formation of 2,2-dimethylbutane to give equilibrium concentrations of this high octane isomer. Therefore, while all of the other C_6 isomers shown in Scheme 1 readily form via a monofunctional acid mechanism, 2,2-dimethylbutane formation alone is only facile in the presence of a metal function.



IV

SCHEME 2

As stated above, it has been proposed that the role of Pt in these highly acidic, modified zirconia catalysts is hydrogen activation (9–11). The Pt-catalyzed hydrogen activation, provides a ready source of H^- for the hydride transfer reactions in Scheme 1 which yield the observed C_6 isomers. Accordingly, it has been proposed that the greater selectivity of $Pt/WO_x/ZrO_2$ for C_{7+} alkane isomerization (as opposed to cracking) relative to $Pt/SO_4/ZrO_2$ is due to its greater effectiveness at generating and storing spillover (activated) hydrogen (17).

While this proposed Pt role would be expected to enhance overall isomerization selectivity, it also provides an explanation for the specific enhancement in 2,2-dimethylbutane formation for the Pt-containing catalyst. Since 2,2-dimethylbutane is formed via the most sterically hindered carbenium ion, its formation would benefit the most by the increased presence of a hydrogen transfer reagent substantially smaller than hexane. The generation of highly reactive free hydride via the Pt catalyzed heterolytic cleavage of H_2 to H^+ and H^-, eliminates the rate-limiting, high-energy intermolecular hydride transfer between the 3,3-dimethyl-2-butyl cation (IV) and a paraffin molecule.

Another possible pathway to 2,2-dimethylbutane, which avoids this high kinetic barrier, might involve the Pt-catalyzed hydrogenation of surface olefinic intermediates which are in equilibrium with the 3,3-dimethyl-2-butyl cation (IV), as shown in Scheme 2.

The residence time or concentration of these surface olefinic intermediates is expected to be rather small at the low temperature and high hydrogen pressure used in this study (12). Nonetheless, the ability of Pt to rapidly hydrogenate trace olefins might shift the above equilibrium sufficiently to the right to substantially increase 2,2-dimethylbutane production.

Even with the addition of Pt, the approach of 2,2-dimethylbutane to equilibrium is the slowest among the hexane isomers. Figure 2 summarizes the hexane isomer yields obtained as a function of temperature. The data clearly indicate that 2,2-dimethylbutane requires the highest temperature to reach its equilibrium concentration. 2-Methylpentane, 3-methylpentane, and 2,3-dimethylbutane easily achieve their equilibrium compositions at a temperature of about 302°F. The yield of cracked products (C_{5^-}) increases significantly as 2,2-dimethylbutane approaches equilibrium (∼30% at 350°F). As discussed above, the slow approach of 2,2-dimethylbutane to equilibrium is due to the low surface concentration of its energetically unfavored secondary 3,3-dimethyl-2-butyl cation precursor relative to the more stable tertiary hexyl cation precursors of the other hexane isomers, and the high kinetic barrier to intermolecular hydrogen transfer with this cation. The surface concentration of the secondary 3,3-dimethyl-2-butyl cation is expected to increase only after the tertiary hexyl cations are at thermodynamic equilibrium with their corresponding isomer products, consistent with recent findings that 2,2-dimethylbutane is a secondary isomerization product (12).

The Effect of Pt on Gas Phase Deuterium Incorporation During Hexane Isomerization

In order to further probe the effect of platinum, hexane isomerization was conducted in both hydrogen and deuterium atmospheres over both Pt-free and Pt-containing catalysts. It was anticipated that Pt-catalyzed hydrogen activation would increase the extent of deuterium incorporation via easy deuteride ($D:^-$) transfer with the carbenium ions shown in Scheme 1.

Product samples were collected at ∼20% hexane conversion during the initial unit lineout in H_2, after switching to

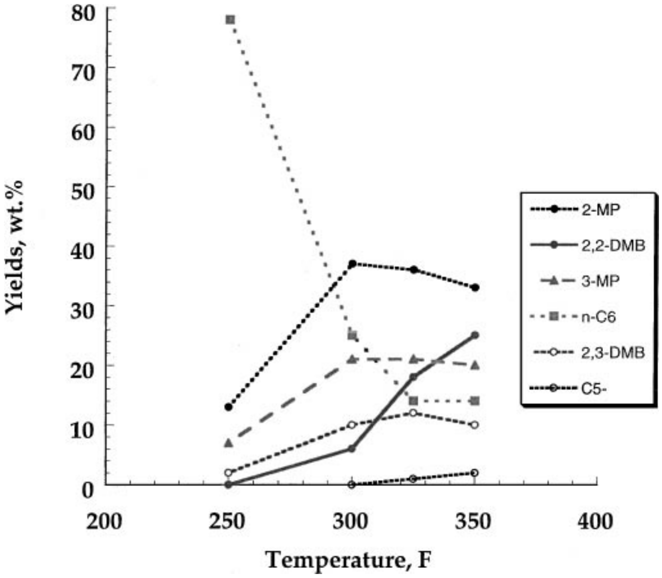


FIG. 2. Temperature dependence of C6 isomer distribution obtained with $Pt/FeO_y/WO_x/ZrO_2$.

TABLE 2

Deuterium Incorporation during Hexane Isomerization

Catalyst:	$FeO_y/WO_x/ZrO_2$				$Pt/FeO_y/WO_x/ZrO_2$			
	$\%C_6H_{14}$				$\%C_6H_{14}$			
Cofeed gas: Isomer	H_2 (init.)	D_2	H_2 (final)	% loss C_6H_{14}	H_2 (init.)	D_2	H_2 (final)	% loss C_6H_{14}
n-C_6	93.2	88.9	93.3	4.6	93.3	2.8	92	97.0
2-MP	93.8	15.7	93.5	83.3	93.4	2.11	91.5	97.7
3-MP	93.9	14.7	93.9	84.3	93.6	0.58	92.6	99.4
2,3-DMB	94.1	6	93.9	93.6	92.7	0.33	90.4	99.6
2,2-DMB	94.4	21.2	94.7	77.5	94.8	0.12	92.7	99.9

D_2 cofeed, and finally after switching back to H_2 for the conclusion of the run, as described above. Using Eqs. [1] and [2], the GC/MS fragmentation intensity data obtained on these samples was used to calculate an approximate percent of each isomer present as un-deuterated $C_6H_{14^+}$ ($\%\chi_{86}$ or $\%\chi_{71}$). These results are shown in Table 2.

Two noteworthy observations in this data are that (1) even in H_2 none of the isomers are present as 100% $C_6H_{14^+}$, according to this simple calculation, and (2) the calculated values in H_2 before and after D_2 cofeed agree very well. The latter indicates that sufficient gas phase purging had taken place between liquid sampling to assure a steady-state gas phase composition and that this is well reflected in the calculated $\%\chi_{86}$. The deviation from 100% for the $C_6H_{14^+}$ parent ion in H_2 can be attributed to the presence of ^{13}C (approx. $100 - [6 \times 1.11] = 93.34$).

Taking the calculated $\%\chi_{86}$ in H_2 as the nondeuterated reference point, the percent loss in $C_6H_{14}^+$ in D_2 was calculated for each isomer as the percent decrease in $\%\chi_{86}$ between samples collected in hydrogen and deuterium (Table 2 and Fig. 3). While this simple normalization corrects for the presence of ^{13}C, it does not consider errors in the $m/z = 86$ intensity in the deuterated samples due to the concomitant loss of H (or D) during ionization, i.e., $m/z-1$, $m/z-2$, etc. This causes an overestimation of $C_6H_{14^+}$ (underestimation of % loss) since multiple ions can contribute to the $m/z = 86$ intensity. Methods are available which correct for these contributions (18); however, we did not employ them since the estimated error is small relative to the magnitude of the effects we observed.

Figure 3 shows the degree of deuteration (as % loss of C_6H_{14}) for all of the C_6 isomers. The results show that a higher percentage of all of the product isomer molecules contain at least one deuterium atom when Pt is present, consistent with Pt-catalyzed hydrogen activation. Nonetheless, with the exception of *n*-hexane, the degree of deuteration decreases only slightly in the absence of Pt. For $Pt/FeO_y/WO_x/ZrO_2$, 95–100% of the product contains at least one deuterium per molecule, whereas with Pt-free $FeO_y/WO_x/ZrO_2$, this number only drops to 75–90% for the isohexanes, but is very low (4.6%) for *n*-hexane. These results suggest that more than one mechanism for deuterium incorporation is operable in this system. In addition to enhanced deuteride transfer via Pt-catalyzed D_2 activation, another pathway is needed to explain the substantial degree of deuteration in the Pt-free case.

The deuteration of isoparaffins in the absence of isomerization or cracking has been observed with previously D_2O-exchanged zeolite and SO_4/ZrO_2 catalysts (19). The authors propose a carbenium ion mechanism with an olefinic intermediate which is deuteronated by a deuterium-exchanged acid site, AD, enhanced by proximate nucleophilic centers on the solid acid surface (bifunctional Lewis base-assisted Brønsted acidity) (14, 20). Interestingly, normal paraffins are *not* deuterated over D–Y zeolite (21), possibly due to an unfavorable surface configuration (electronic and/or steric) with regard to Lewis base assistance (20). If we assume gas phase D_2 exchange with the Brønsted acid sites in

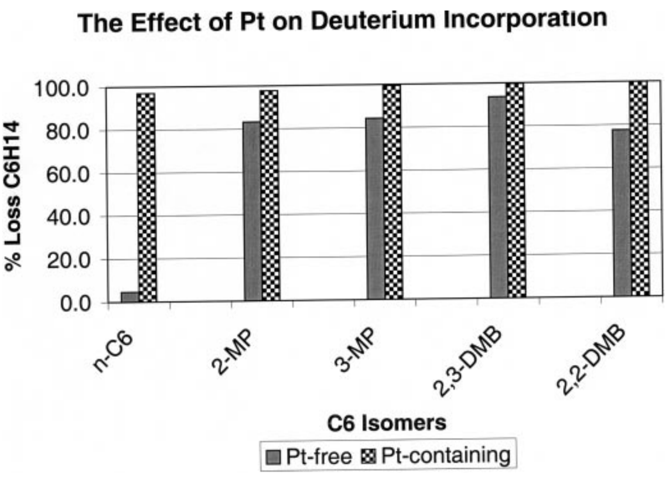


FIG. 3. The effect of Pt on the extent of deuterium incorporation into the product isomers with D_2 cofeed.

TABLE 3

Hexane Isomerization Products Obtained During Deuterium Exchange Experiments at Low Conversion

Catalyst	H_2/D_2	°C	$\%C_5-$	%2,2-DMB	$\%C_6$ conv.
$FeO_y/WO_x/ZrO_2$	H_2	197	0.35	0.44	22
	D_2	197	0.28	0.35	18.9
$Pt/FeO_y/WO_x/ZrO_2$	H_2	165	0.04	0.4	20.8
	D_2	165	0.06	0.25	15.9

WO_x/ZrO_2, as observed in zeolites (22), this acid-catalyzed deuterium exchange mechanism would incorporate deuterium into the isohexanes but not the unreacted *n*-hexane, as observed in Fig. 3.

The data in Fig. 3 were obtained at low (16–22%) hexane conversions. The product selectivities for these runs are shown in Table 3. In contrast to the results obtained at much higher conversions (Table 1), the addition of Pt has no effect on the formation of 2,2-dimethylbutane, but is still seen to reduce the amount of cracking. Thus, at ~20% conversion, Pt has a much reduced impact on product selectivity and incorporates modestly more deuterium into the isomerized products. Clearly the most pronounced effect Pt has at low conversion is the dramatic increase in the deuterium content of the *n*-hexane.

The extensive deuteration of *n*-hexane by the $Pt/FeO_y/WO_x/ZrO_2$ catalyst could occur via two metal-assisted pathways. As stated above, Pt-catalyzed H_2 (D_2) activation should enhance the rates of all of the hydride (deuteride) transfer steps in Scheme 1, including that of the 3-hexyl cation (I) to regenerate deuterated *n*-hexane. However, for this to explain the almost complete loss of C_6H_{14} hexane with the $Pt/FeO_y/WO_x/ZrO_2$ catalyst (Fig. 3), it would require that all of the feed be converted to the 3-hexyl cation (I), of which only ~20% proceeds on to isomerize, while the remaining 80% reverts via deuteride transfer to linear $C_6H_{14-x}D_x$. Thus the pool of spillover deuterium generated by Pt(20), would have to provide enough of a driving force to shift the kinetics to greatly favor the deuteride transfer reaction relative to the facile conversion of the highly reactive sec-3-hexyl carbenium ion to the more stable tertiary intermdiates (II & III), and on to the isomerized products. This is unlikely.

It has been reported that H–D exchange between *n*-C_7H_{16} and D_2 occurs much more rapidly than *isomerization* on $Pt/WO_x/ZrO_2$ (17, 23). This requires an alternative exchange pathway which does not require a carbenium ion intermediate, such as the direct deuteration of the *n*-hexane feed via C-H bond activation by Pt (24, 25). Deuterium exchange with alkane adsorbed on metal surfaces is known to be very easy (24). The rate of exchange between the pool of H atoms bound on the surface of the Pt particles, and the H atoms of the chemisorbed hydrocarbon radical, is very fast relative to the hydrocarbon desorption rate (25). If so, a considerable yield of multideuterated molecules would be expected, consistent with the envelope of high mass parent and fragment ion peaks observed in Fig. 1. In the case of $Pt/FeO_y/WO_x/ZrO_2$, the presence of spillover hydrogen (17, 26) may supplement the chemisorbed hydrogen to maintain a large inventory of activated H (D) atoms for ready exchange with the surface-bound hydrocarbon species.

It is important to note that the metal-assisted deuterium exchange described above is indiscriminate with respect to the source of the C–H bond. Assuming no significant difference in the chemisorption tendencies among the C_6 isomers, this pathway would incorporate deuterium comparably for all of the product isomers, as observed.

Overall, the results in Fig. 3 suggest the following. Pt-catalyzed deuterium activation results in greater deuterium incorporation in the presence of Pt than in its absence. Deuterium exchange via deuterated bronsted acid sites could explain the still high degree of deuteration with the Pt-free catalyst. Based on previous observations on D–Y zeolite (21), this might also explain the conspicuous lack of exchange with *n*-hexane in the absence of Pt. Finally, nonselective, metal-assisted, C–H bond activation provides an explanation for the uniformly high degree of reactant and product deuteration even at low hexane conversion.

IV. CONCLUSIONS

Our results indicate that paraffin isomerization on WO_x/ZrO_2-based catalysts takes place mostly on monofunctional acid sites via intermolecular, hydride-transfer reactions between neutral molecules and carbenium ions. The highly acidic character of this material is such that high conversions are achieved without the need for a hydrogenation/dehydrogenation component.

The presence of Pt is found to specifically facilitate the approach to equilibrium of the 2,2-dimethylbutane isomer. This isomer is shown to form from the most sterically hindered carbenium ion intermediate. The results suggest that Pt-catalyzed hydrogen activation generates substantial amounts of surface atomic hydrogen which readily undergoes hydrogen transfer with this hindered intermediate, which would otherwise undergo very slow hydrogen transfer with neutral molecules. Our results also suggest that Pt-catalyzed hydrogen activation may play a more classical role in keeping the surface concentration of hexyl cations low, and consequently secondary reactions, oligomerization/cracking, that give rise to cracked products, are inhibited.

The results of deuterium exchange measurements in D_2 at low conversion are best explained by invoking both acid- and metal-facilitated deuteration pathways. The presence of Pt results in a moderately higher level of deuterium exchange in the isohexane products, but a large increase in the deuteration of the normal hexane starting material. At ∼20% conversion, nearly all of the *unreacted* normal hexane molecules contain at least one deuterium atom over Pt/FeO$_y$/WO$_x$/ZrO$_2$, while only 4–5% of the hexane is deuterated over Pt-free FeO$_y$/WO$_x$/ZrO$_2$. These results can be attributed to branched isomer exchange with deuterated Brønsted sites, supplemented by non-isomer-selective C–H bond activation by Pt.

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