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Hydroisomerization of *n*-Hexane on Platinum Zeolites

I. Kinetic Study of the Reaction on Platinum/Y-Zeolite Catalysts: Influence of the Platinum Content

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The transformation of *n*-hexane has been carried out under hydrogen pressure on a series of platinum-stabilized Y-zeolites with platinum contents varying from 0 to 17.7 wt% (platinum area ranging from 0 to 10 $m^2 g^{-1}$). The conventional bifunctional mechanism accounts for the change in the isomerization activity and selectivity with the platinum area and with various operating conditions (temperature, *n*-hexane and H_2 pressures, H_2S and NH_3 poisoning). Moreover, the cracking mechanism shifts from a carbonium ion one on small platinum area catalysts to hydrogenolysis on large platinum area catalysts.

INTRODUCTION

Light alkane (C_5–C_6) isomerization which leads to a cut of high octane number can be carried out on various bifunctional catalysts: the hydrogenating–dehydrogenating function is provided by noble metals and the acid function by highly chlorinated alumina, or by amorphous silica-alumina or crystalline aluminosilicates. In accordance with the thermodynamics of the isomerization, the lower the reaction temperature the greater the increase in the octane number (*1*, *2*). The best bifunctional catalysts are therefore the chlorinated alumina-base catalysts which can be operated at the lowest temperature (110–180°C). However, these catalysts are very susceptible to deactivation and their utilization requires careful feed pretreatment. The noble-metal-loaded acid zeolites do not have this drawback. They are more stable and they operate also at relatively low temperatures (about 250°C (*3*)).

Concerning the alkane isomerization mechanism on supported noble metals, the following three typical situations can be encountered depending on the acid strength of the carrier.

(1) With catalysts of very strong acidity, isomerization occurs on acid sites, the only role of the metal being to limit the coke formation and the deactivation of acid sites. This is the situation found on platinum/chlorinated-alumina (*4*).

(2) With catalysts of very low acidity, isomerization occurs only on metal sites and the mechanism depends on the size of the crystallites (*5*).

(3) With catalysts of average acidity such as platinum on amorphous silica-alumina, isomerization occurs through the conventional bifunctional mechanism (*6*): the metal sites catalyze the formation of intermediate olefins and the acid sites catalyze their skeletal isomerization. The relative importance of the metal and of the acid activities determines which step is rate-limiting (*7*).

With noble-metal-loaded acid zeolites,

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mechanisms of the first and of the third types as well as a combination of the two have been proposed. Thus, in a study of PdH-mordenite catalysts, Chick *et al.* (*8*) concluded in favor of a purely acid mechanism, the main role of the metal being to control the surface acidity of the mordenite. On the other hand, Jacobs *et al.* (*9*) interpreted the results of the *n*-decane isomerization on Pt/ultrastable Y-zeolite by the bifunctional mechanism. Finally, a combination of both mechanisms was suggested by Kouwenhoven (*2*) to explain *n*-pentane isomerization on PtH mordenite.

This paper reports on the isomerization of *n*-hexane on a series of platinum catalysts prepared by cationic exchange of a Y-zeolite stabilized by wet air treatment (*10*). The aim of this investigation is to determine the influence of the metal area (varying over a very wide range) on the mechanism of this reaction.

EXPERIMENTAL

Seven catalyst samples of different platinum contents were prepared as follows.

(1) Preparation from Union Carbide NaY zeolite (SiO_2/Al_2O_3 = 4.75) of a $(NH_4)_{0.93}$ $Na_{0.07}$ Y-zeolite by ion exchange with ammonium nitrate solutions (five times at 20°C and four times at 100°C).

(2) Dilution of the zeolite in an alumina gel (67 wt% calculated on materials calcined at 800°C) and extrusion (extrudates 0.15 × 0.5–1 cm).

(3) Stabilization of the zeolite (*10*) by calcination in a wet air flow at 500°C for 4 hr with steam introduction from 400°C upward.

(4) Exchange by ammonium nitrate solutions leading to a $(NH_4)_{0.96}Na_{0.04}$ Y-zeolite.

(5) Exchange by $Pt(NH_3)_4^{2+}$ in competition with NH_4^+ according to the method previously described (*11*). This technique produces a homogeneous macroscopic platinum distribution on the zeolite surface.

(6) Calcination in a dry air flow at 500°C for 2 hr, then 2 hr reduction at 450°C in hydrogen (30 bars; flow rate, 60 liters/hr).

Benzene hydrogenation has been carried out as previously described (*12*) (temperature, 100°C; pressure, 1 bar; benzene partial pressure, 0.1 bar; conversion <5%).

The experiments with *n*-hexane (Carlo Erba >99% purity) were carried out in a flow-type fixed bed (weight of catalyst, 20 g). The liquid condensates and the gaseous effluents were analyzed by GLC (100 m squalane capillary column).

RESULTS

Seven catalyst samples were prepared with platinum contents varying from 0 to the value obtained by zeolite exchange carried out to saturation. The samples will be designated as PtHY followed by the mass platinum content of the zeolite in parentheses, e.g., PtHY (*17.7*) is a catalyst sample with a 6.7 wt% platinum content in which the zeolite has a 17.7 wt% platinum content. Their physicochemical properties (BET surface area, acidity, platinum dispersion) have already been reported (*13*). The samples used for the catalytic study had a benzene hydrogenation activity which was practically proportional to their metal surface area: the number of benzene molecules hydrogenated per second and per accessible platinum atom was approximately equal to 0.6 for all the catalysts.

All the catalysts were first aged for 16 hr under the following standard conditions: $t = 300°C$, p_{H_2} = 24 bars, $p_{n\text{-hexane}}$ = 6 bars, WHSV (weight of *n*-hexane per hour and per unit weight of zeolite) = 8.6 hr^{-1}. During this conditioning the conversion was generally high (*13*). The kinetic properties of the reaction were then determined under operating conditions where the conversion was always less than 10%.

Aging Period

n-Hexane was isomerized into methylpentanes and dimethylbutanes and also led to light alkanes from C_1 to C_5. There was no formation of products heavier than C_6.

At the start and at the end of the aging period, the isomerization conversion increases strongly for low platinum contents and then decreases, whereas the cracking conversion, after a slight decrease, increases with the platinum content (*13*).

There is a greater difference between the light products formed on low platinum (≤0.09%) and on high platinum content catalysts (≥2.95%).

With PtHY(*0*) and with low platinum content catalysts, the C_1 and C_2 molar fractions are considerably lower (about 10 times) than the C_5 and C_4 molar fractions whereas they are almost equal in the case of high platinum content catalysts, as can be expected from a simple scission of C_6 alkanes.

The molar ratio $(C_1 + C_2)/C_3$, very low (about 0.1) for low platinum content catalysts, increases rapidly with the platinum content. With high platinum content catalysts, it equals 1 (*13*).

C_4 and C_5 isoalkanes are formed three to four times faster than the corresponding *n*-alkanes on low platinum content catalysts, but at practically the same rate as the latter on high platinum content catalysts.

Reaction Rates and Selectivities

Table 1 gives the values of the *n*-hexane isomerization and cracking rates at temperatures ranging from 230 to 325°C. The influence of the platinum content of the catalysts on these rates does not depend on the temperature. The isomerization rate increases very rapidly with low metal contents to reach a maximum for PtHY(*2.95*) and then decreases (*13*). The apparent activation energy ranges from 117 kJ $mole^{-1}$ for PtHY(*0*) to 155 kJ $mole^{-1}$ for catalysts having a platinum content higher than 0.09%. The cracking rate decreases until the platinum content is 0.5%, and then increases proportionally to the content. The apparent activation energy is 184 kJ $mole^{-1}$ for PtHY(*0*) and about 146 kJ $mole^{-1}$ for all the other catalysts.

Figure 1 shows that the metal area of the catalysts (and consequently their hydrogenating activity) has the same influence on the isomerization and cracking rates as the platinum content.

With all the catalysts, 2- and 3-methylpentanes are formed practically in their thermodynamic equilibrium quantities. On the other hand, the quantity of 2,3-dimethylbutane in the mixtures of methylpentanes and 2,3-dimethylbutane, equal to its equilibrium value for PtHY(*0*), decreases very rapidly to about 10% of this value when the platinum content increases from 0 to 0.09%; it then remains constant. The 2,2-dimethylbutane content in the isomer mix-

TABLE 1

Isomerization (r_I) and Cracking (r_C) Rates of *n*-Hexane (10^{-4} mole hr^{-1} g^{-1} PtHY) on PtHY Catalysts at Various Temperatures

T(°C)	PtHY catalysts													
	(*0*)		(*0.03*)		(*0.09*)		(*0.5*)		(*2.95*)		(*6.0*)		(*17.7*)	
	r_I	r_C	r_I	r_C	r_I	r_C	r_I	r_C	r_I	r_C	r_I	r_C	r_I	r_C
230							39	0.15	57	0.4	48	0.7	34	1.8
250			80	2.9	108	1.2	180	0.7	247	1.6	191	2.8	151	8.2
260							317	1.2	481	3.2	379	5.6	268	14.8
270			261	9.2	354	5.2	613	2.4	853	6.0	698	10.4	531	30.6
280			434	18										
290	18	1.1	739	35.2	924	13.2								
300	30	2.9	1177	60	1329	21								
310	44	4.9												
325	75	12.6												
Apparent activation energy (kJ $mole^{-1}$)	117	184	134	146	134	146	155	146	155	146	155	146	155	146

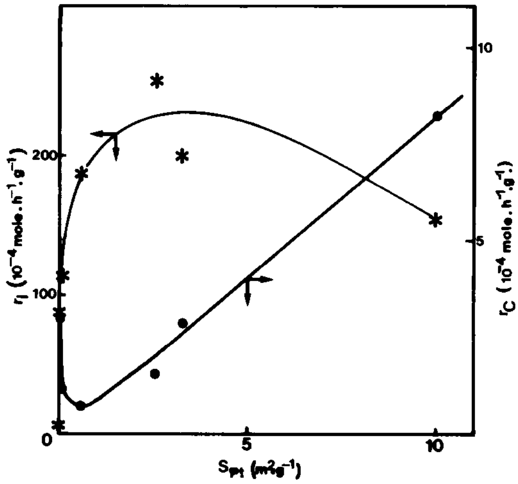


FIG. 1. Rates of *n*-hexane isomerization (r_I) and cracking (r_c) against the metal surface area of the samples (S_{Pt}).

ture of the *n*-hexane is always very low; it decreases when the platinum content of the catalysts increases.

Influence of n-Hexane and Hydrogen Pressures on the Isomerization Rate

This study was carried out on PtHY(*6.0*), at 250°C and a total pressure of 40 bars, helium being using as a complementary gas. Since preliminary measurements showed that the deactivation degree of the catalysts was very dependent on the operating conditions, an experimental procedure maintaining the catalyst in the same state was employed. In this procedure, the catalyst sample was calcined before each experiment for 3 hr at 450°C in a hydrogen flow under a pressure of 40 bars. The reaction rate was then determined under specific pressure conditions, by extrapolating to zero working-time the change of this rate as a function of time. The apparent hydrogen and hexane orders determined by these experiments were −0.85 and 0.6–0.8, respectively.

Influence of Sulfur and Nitrogen Poisons on the Isomerization Rate

These experiments were carried out on PtHY(*6.0*) at 250°C, p_{H_2} = 24 bars, $p_{n\text{-hexane}}$ = 6 bars using H_2S as the sulfur poison and NH_3 as the nitrogen poison. These two compounds were produced *in situ* by the decomposition of dimethyldisulfide and *n*-butylamine, respectively.

Figure 2 shows the change against working-time of the conversion of an *n*-hexane feedstock containing 220 wt ppm of dimethyldisulfide. At first the conversion decreases rapidly, while the proportion of 2,3-dimethylbutane in the mixture of methylpentanes and 2,3-dimethylbutane increases. After 3 hr, the conversion and the isomerization selectivity no longer vary. A treatment of 8 hr at 500°C in a hydrogen flow under pressure restores the initial activity and selectivity of the catalyst.

The conversion of an *n*-hexane feedstock containing 800 wt ppm of *n*-butylamine decreases rapidly without reaching a plateau. The isomerization selectivity is not modified. A treatment of 8 hr at 500°C in a hydrogen flow under pressure restores the initial activity of the catalyst.

DISCUSSION

Isomerization Mechanism

The conventional mechanism (*6*) described below offers a good explanation for the change in the isomerization activity and selectivity with the platinum surface area,

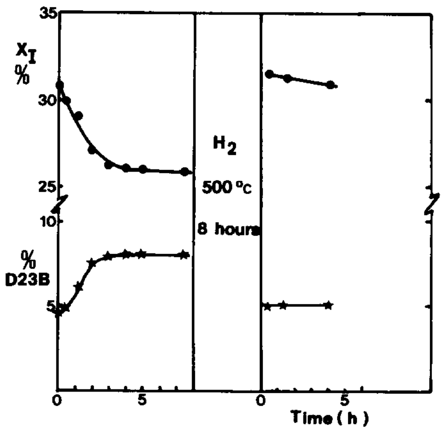
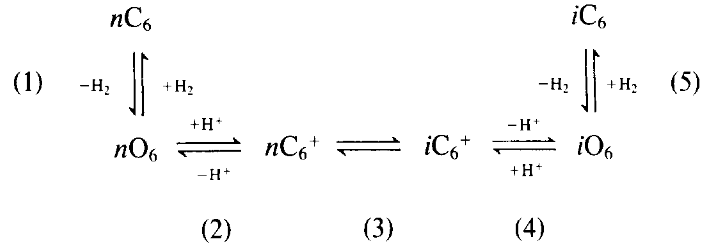


FIG. 2. Influence of dimethyldisulfide on the isomerization conversion (X_I) of *n*-hexane and on the 2,3-dimethylbutane (D23B) content in the methylpentane and 2,3-dimethylbutane mixture.

with poisoning and with *n*-hexane and H_2 pressures.



Bifunctional mechanism of *n*-hexane isomerization: nC_6, nO_6, and nC_6^+, respectively, represent *n*-hexane, *n*-hexenes, and carbonium ions with an *n*-hexane skeleton and iC_6, iO_6, and iC_6^+ isohexanes, isohexenes, and carbonium ions with an isohexane skeleton.

Isomerization activity and platinum surface area. For small metal surface areas, dehydrogenation and hydrogenation reactions (1) and (5) limit the bifunctional process; the isomerization activity is proportional to the metal surface area. Above a certain value of the metal surface area, these reactions become faster than the skeletal isomerization of olefins on the acid sites (steps 2, 3, 4). Then, isomerization activity no longer depends on the metal area. It is roughly what can be seen on PtHY catalysts (Fig. 1). However, for very high values of metal area, a decrease of the isomerization activity can be observed. It is probably a definite poisoning of the acid sites of large metal surface area catalysts by the coke formed during the aging period that is responsible for this decrease (*13*). The value of the platinum area required to obtain the acid reaction as the limiting step is smaller than 0.5 $m^2 g^{-1}$ (platinum content between 0.1 and 0.5%, i.e. comparable to the value found by Lanewala *et al.* (*14*) with PtLaY catalysts). It is considerably higher (two to three times) than the value found on platinum/silica-alumina (*7*). It should be pointed out, however, that the maximum value of the isomerization activity was about 100 times lower than that of PtHY catalysts. These observations can be easily explained if we consider that the acidity of the Y-zeolite is considerably higher than that of silica-alumina.

Isomerization selectivity and platinum surface area. The isomerization selectivity is quite different from that which can be expected with the bimolecular mechanism proposed by Bolton and Lanewala (*15*): namely the formation of products heavier than hexanes is not observed and the direct formation of 2,3-dimethylbutane from *n*-hexane is very low, at least on large platinum area samples.

On large metal area catalysts the isomerization of *n*-hexane leads almost selectively to methylpentanes. This selectivity is identical to that found for platinum/silica-alumina catalysts for which the isomerization of *n*-hexane occurs via the bifunctional mechanism with the skeletal isomerization of intermediate olefins as its limiting step (*16*). This selectivity is quite different from that observed on platinum catalysts (*5, 17*) and on acid catalysts such as PtHY(*0*) and chlorinated alumina (*4*).

The selectivity of small metal surface area catalysts is intermediate between the selectivities of PtHY(*0*) (acid mechanism) and of large metal surface area catalysts (bifunctional mechanism with step 3 as limiting step): there is an appreciable direct formation of 2,3-dimethylbutane. Consequently, it could be explained by the simultaneous participation of an acid mechanism and a bifunctional mechanism. However, a bifunctional mechanism in which the steps on platinum sites and the steps on acid sites occur at similar rates is sufficient to account for this selectivity. Indeed, the selectivity of a bifunctional isomerization, with as limiting step the reaction on platinum sites (reactions 1 and 5), must be identical to that resulting from an acid reaction: due to the low rate of reaction (5), the transformation of carbonium ions iC_6^+ into isohexanes (by the succession of steps 4 and 5) is, as in the acid mechanism, much slower than the carbonium ion isomerization (step 3).

Poisoning effects. Poisoning experiments on PtHY(*6.0*) confirm the participation of acid and metal sites in the isomerization of *n*-hexane (and hence of the bifunctional mechanism). Indeed, H_2S as well as NH_3 reduce the activity of this catalyst. Modifications in activity and in selectivity caused by the poisonings are those expected from the bifunctional mechanism as follows.

(i) H_2S, a platinum poison, reduces the active part of the metal area. Thus, the poisoned catalyst will act like a catalyst with a smaller platinum content than PtHY(*6.0*). This is observed. The poisoned catalyst has the isomerization selectivity (formation of 2,3-dimethylbutane) and activity of a catalyst with a 0.09 to 0.5% platinum content. Thus, the introduction of dimethyldisulfide considerably reduces the PtHY(*6.0*) metal area, from 3.5 $m^2\ g^{-1}$ to less than 0.5 $m^2\ g^{-1}$.

(ii) The basic poison NH_3 reduces the number of the acid sites. Since on PtHY(*6.0*) the acid step is the slow one in the bifunctional process, there should be a decrease in activity with no modification in selectivity. This is effectively what is observed.

Kinetic study. The results of the kinetic study also agree with the bifunctional mechanism. Namely, the value of the apparent activation energy of isomerization for platinum content ≥0.5% is higher than for acid catalysts (18) (particularly for PtHY(*0*)) (Table 1) and lower than for platinum (*19*). Slightly higher than for the platinum/silica-alumina previously examined (*7*), it is close to that found for other bifunctional zeolite catalysts (*8*). For PtHY(*6.0*), the apparent hydrogen order is different from the one that can be expected for a reaction on metal sites (-2 by the bond-shift mechanism and -3 to -4 by the cyclic mechanism (*19*)) as well as for an acid mechanism (zero order). It also differs from the order obtained on high platinum content platinum/silica-alumina (order = −1) (*19*) where the reaction occurs through a bifunctional mechanism in which the limiting reaction is the acid isomerization of olefins (steps 2, 3, 4). This hydrogen order as well as the *n*-hexane order can however be explained by this mechanism. Since the formation of carbonium ions from olefins is much faster than their rearrangement, it is the rearrangement which limits the bifunctional process. At low conversion, the reverse reaction can be neglected, and the isomerization rate of *n*-hexane can be written:

$$r = k_3 C_m K_1 K_2 \frac{p_{nC_6}}{p_{H_2} + K_1 K_2 p_{nC_6}} \quad (1)$$

where k_3 is the isomerization rate constant of carbonium ions, C_m the concentration of Brønsted sites of the zeolite, and K_1 and K_2, respectively, the equilibrium constants of the dehydrogenation of *n*-hexane (reaction 1) and of the carbonium ion formation (step 2). The fractional orders obtained show that the product $K_1 \cdot K_2 \cdot p_{nC_6}$ is of the same order of magnitude as p_{H_2}, whereas it was negligible with platinum/silica-alumina for similar p_{H_2}/p_{nC_6} ratios. This can result from a higher value of the protonation equilibrium constant K_2 of olefins on Y-zeolite, due to the greater strength of its acid sites.

The validity of the bifunctional mechanism can be checked by plotting the linear transform of Eq. (1): $1/r$ against p_{H_2}/p_{nC_6}. Figure 3 shows that an acceptable straight line is obtained provided that the results obtained for values of p_{H_2}/p_{nC_6} higher than 10 are neglected. This straight line allows us to determine the values of k_3 C_m and K_1K_2,

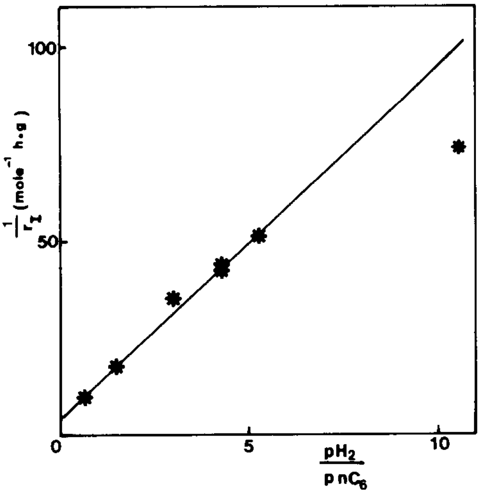


FIG. 3. Check of the kinetic equation linked to the bifunctional mechanism with the skeletal isomerization of olefins as the limiting step.

i.e., $k_3C_m = 0.25$ mole hr^{-1} g^{-1} of PtHY and $K_1K_2 = 0.4$. A value of K_2 of about 10,000 bar^{-1} is obtained using the value of K_1 calculated from thermodynamic tables (*20*) and with the assumption that the dehydrogenation of *n*-hexane leads to a mixture of linear hexenes in equilibrium. This high value of K_2 indicates that the olefin protonation equilibrium is entirely displaced toward the formation of carbonium ions.

Mechanism of Light Products

The formation of light products probably occurs through two reactions.

On PtHY(*0*) and on small metal area catalysts, the distribution of light products is typical of a mechanism with carbonium ion intermediates: the formation of methane and of ethane is much slower than the formation of propane and there is a considerably larger number of C_4 and C_5 molecules (mainly branched) than of C_1 and C_2 molecules. These C_4 and C_5 products cannot result from a simple scission of *n*-hexane or of its isomers; rapid bimolecular secondary reactions between primary cracking products and eventually the reactant can explain their formation (*21*). Introduction of platinum in the zeolite inhibits this cracking reaction. According to Chick *et al.* (*8*) this inhibition could be the result of a reduction in the carbonium ion lifetime. Indeed, in the presence of platinum, the desorption of alkanes from carbonium ions occurs more rapidly (by steps 4 and 5) than in the absence of platinum (formation of alkane by hydride transfer). This desorption becoming faster than the carbonium ion cracking, the cracking rate decreases whereas the isomerization rate increases (*21*). A reduction of the number of cracking sites could also explain this inhibition: cracking sites, which would be Lewis acid sites, would combine with monohydrogen species spilling over from the metal on to the zeolite surface (*22*).

On large metal surface area catalysts, a hydrogenolysis reaction is responsible for the formation of light products. Their distribution is the one that can be expected from a simple hydrogenolysis reaction, namely an important formation of methane and ethane and a $(C_1 + C_2)/(C_4 + C_5)$ molar ratio of about 1; the greater the metal area the greater the activity. The constant ratio activity for hydrogenolysis (a structure sensitive reaction (*23*))/platinum area, can be explained by the fact that all PtHY catalysts, having platinum crystallites of practically the same size, only differ by the number of these crystallites.

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