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# Paraffin Dehydrocyclization

## V. The Influence of Pt Loading on the Aromatic Selectivity

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It was observed that the platinum content of Pt-$Al_2O_3$-K and Pt-carbon catalysts determined the aromatic distribution for the dehydrocyclization of *n*-octane and 3-methylheptane. At higher loading (1.2% Pt) the aromatics approached the distribution predicted for an equal contribution of all the cyclization pathways that lead directly to a six-carbon ring. For the low (0.15% Pt) loading the aromatic distribution appeared to be determined by the relative strength of the carbon–hydrogen bonds required to be broken to form the six-carbon ring; the pathway involving the weaker bonds was favored. The relative amount of hydrogenolysis of the reactant and the aromatic products to form lower carbon number aromatics increased as the platinum loading increased.

## INTRODUCTION

The fraction of a surface that is catalytically active has been a concern of investigation for many years. Taylor (*1*) summarized the early results in 1925 and proposed that the amount of surface which is catalytically active is determined by the reaction catalyzed. Numerous studies of supported metals since then have been interpreted to show the existence of special arrangements of atoms that provide a specific site for adsorption (*2*). Recently, the selectivity for isomerization vs hydrogenolysis of neopentane has been interpreted to require isomerization on one type of site and hydrogenolysis on another type of site (*3*). Boudart (*2c, 3*) has proposed that a reaction showing selectivity dependent on the catalytic function be called a *demanding* reaction and a reaction whose selectivity is independent of the catalytic function be called a *facile* reaction. Examples of facile reactions are the hydrogenolysis of cyclopropane (*4*) and the hydrogenation of ethylene (*5*). On the other hand, there are reports that the catalytic action of metals is influenced by the support implying that selectivity is determined by an electronic factor (*6*). Thus, it appears that the question of the catalyst property that is responsible for catalytic selectivity is still unresolved.

In this paper we present results of an aromatic selectivity for paraffin dehydrocyclization that is dependent on the Pt metal function. However, this selectivity appears to differ from the demanding reaction as defined by Boudart (*3*).

## EXPERIMENTAL

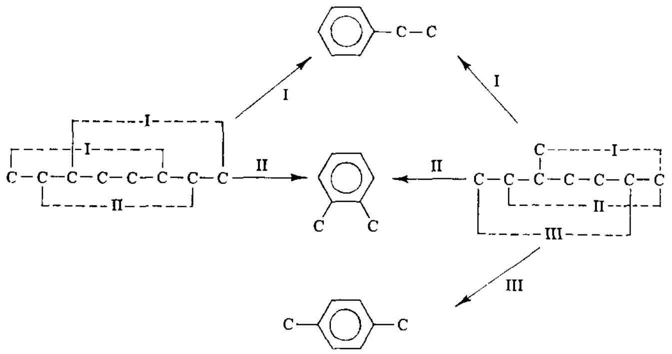
*Catalysts. Pt-$Al_2O_3$-K.* Catalysts prepared by impregnating "nonacidic" alumina with chloroplatinic acid were washed with ammonium hydroxide after reduction at 500°C to remove chlorine (*7*). *Pt-C.* Graphatized carbon (from the Cabot Corp.) was impregnated with an acetone solution of chloroplatinic acid. The chlorine associated with the chloroplatinic acid was lost during the reduction step.

*Methods.* All dehydrocyclization reactions were run at 482°C. A continuous-flow apparatus was used for the runs (*7*). Catalysts were reduced *in situ* for 3 hr in a 5 $cm^3$/min stream of hydrogen. The liquid products were analyzed by glc using Carbowax 20M to obtain the total conversion and a Bentone 3,4-diiso-decylphthalate column for the $C_8$-aromatic isomer distribution.

*Metal crystal size.* For the Pt-C catalysts, the average metal crystallite size was estimated by X-ray line broadening. The catalyst was reduced at 550°C and, since the Pt lines are not masked by the carbon, the line broadening was determined directly on the Pt-C catalyst. The intensity of the {111} line for the 0.15% Pt crystals was insufficient to determine the crystallite size. The other three crystals had a crystallite size near the limit of X-ray determination: 0.6% Pt, 35 Å; 1.2% Pt, 45 Å; 2.2% Pt, 48 Å.

## RESULTS

The aromatic products which should result from a direct $C_6$ ring formation for the dehydrocyclization of *n*-octane and 3-methylheptane are:



Most of the pioneer investigators favored a mechanism involving equal probability for the formation of all possible six-carbon rings. The results in Fig. 1 show that the Pt loading determines the $C_8$-aromatic distribution from the dehydrocyclization of 3-methylhephtane. The catalysts used to obtain the distribution in Fig. 1 were reduced in a hydrogen flow of 5 $cm^3$/min at 550°C. Over the lowest Pt loading the EB:OX:PX (ethylbenzene:*ortho*-xylene:*para*-xylene) ratio was about 1:1.5:3 and changed with Pt loading to give a ratio of about 1:1:1 for the 1.2% Pt loading. This change was primarily caused by a decrease in the amount of PX with a corresponding increase in the amount of EB. This change in selectivity is more evident if we assume that the MX (*meta*-xylene) results from 2- or 4-methylheptane formed by a methyl migration from the 3-position to the 2- or 4-position and should not be included in the $C_8$-aromatic selectivity distribution; this selectivity is presented in Fig. 2 for the three Pt loadings. It appears that the amounts of EB, OX, and PX do not change appreciably at longer time-on-stream. Figure 3 presents the aromatic distribution vs Pt loading using the aromatic distribution at later time-on-stream from Fig. 2. Although it is shown later in this section that catalysts reduced at 550 and 650°C had different hydrogenolysis and MX selectivity, the reduction temperature did not alter the selectivity for the formation of the three aromatic isomers expected from direct $C_6$ ring formation.

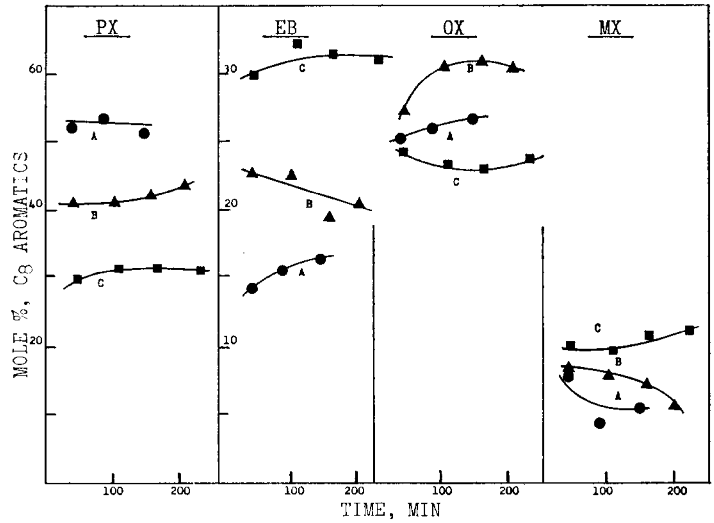


FIG. 1. $C_8$-aromatic distribution from the dehydrocyclization of 3-methylheptane over Pt-C catalysts (reduced 550°C; run 482°C). (A), 0.15% Pt; (B), 0.6% Pt; (C), 1.2% Pt.

The hydrogenolysis of $C_8$-aromatics was carried out over the Pt-carbon catalysts under the same conditions as those of the dehydrocyclization reaction except the initial hydrogen pressure was that expected if 50% of the alkane was connected to aromatics and hydrogen during the dehydrocyclization reaction (Figs. 4–6). Comparing the amount of hydrogenolysis of the aromatic charge to benzene and toluene with the amount of benzene and toluene formed from 3-methylheptane (Fig. 4)

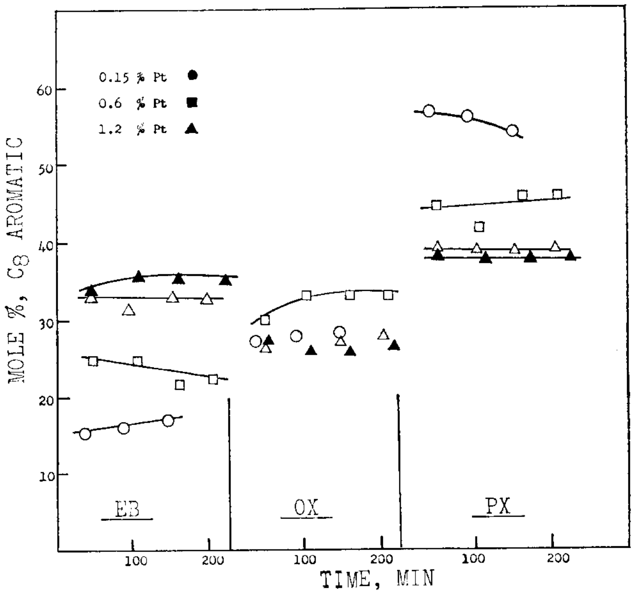


FIG. 2. $C_8$-aromatic distribution from the dehydrocyclization of 3-methylheptane (*meta*-xylene was neglected in this distribution; open symbols, reduced at 550°C; closed symbols, reduced at 650°C).

suggests that these aromatics come from two sources: (a) hydrogenolysis of $C_8$-aromatics and (b) hydrogenolysis of the charge prior to cyclization. The amount of $C_6$ and $C_7$ paraffins in the liquid product was very small in comparison to the amount of benzene and toluene formed from the hydrogenolysis; hence, the 3-methylheptane charge undergoing "hydrogenolysis" is apparently converted to benzene and toluene without desorption to the gas phase. Over the three lower Pt loadings, 0.15, 0.6, and 1.2% Pt, the hydrogenolysis appears to be a selective hydrogenolysis of the EB; OX and PX undergo little, if any, hydrogenolysis (Fig. 5). Over the highest Pt loading, 2.2% Pt, the hydrogenolysis is more severe; EB still underwent hydrogenolysis more rapidly but the OX and PX also underwent hydrogenolysis. The aromatics were also isomerized to MX over the 2.2% Pt-loaded catalyst.

In Table 1 the effect of reducing the 1.2% Pt catalyst at 550 and 650°C is shown. The ratio $(C_7)/(C_6 + C_7)$ aromatic is the same for both catalysts but the ratio $(C_6 + C_7)/(C_6 + C_7 + C_8)$ aromatic is higher for the 550°C reduction. Apparently the hydrogenolysis selectivity to $C_6$ and $C_7$ carbon products is the same over both catalysts but the hydrogenolysis activity is higher for the 550°C-reduced catalyst than the 650°C-reduced one (Fig. 6).

TABLE 1

Hydrogenolysis of Aromatic Products (and Charge, 3-Methylheptane) to Lower Carbon Number Aromatics over the 1.2% Pt-Catalyst[a]

| Time-on-stream (min) | $C_6+C_7$ / Total aromatics | $C_7/(C_6+C_7)$ / Aromatics | Conversion to $C_8$-aromatic (mol%) |
|---|---|---|---|
| 550°C reduction | | | |
| 49 | 0.57 | 0.70 | 21 |
| 96 | 0.48 | 0.72 | 16 |
| 149 | 0.55 | 0.68 | 11 |
| 196 | 0.53 | 0.70 | 10 |
| 650°C reduction | | | |
| 45 | 0.41 | 0.73 | 26 |
| 85 | 0.39 | 0.79 | 16 |
| 152 | 0.42 | 0.80 | 10 |
| 190 | 0.38 | 0.71 | 12 |

[a] 482°C, LHSV 0.3, no added hydrogen, 1 atm.

The $C_8$-aromatic distributions from *n*-octane over Pt-C catalysts are presented in Fig. 7. For the catalysts reduced at 500°C it is noted that the amount of OX decreased and EB increased as the Pt loading

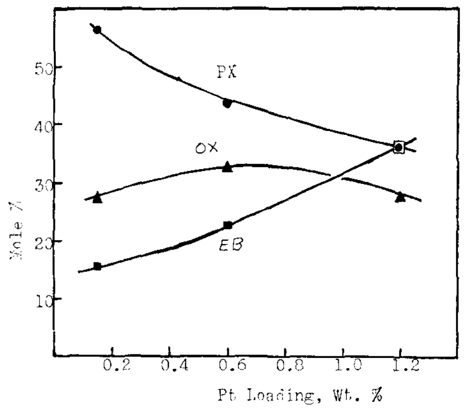


FIG. 3. $C_8$-aromatic distribution over Pt-C catalysts with increasing Pt content (plotted points refer to conversions at longer times-on-stream and neglecting *meta*-xylene).

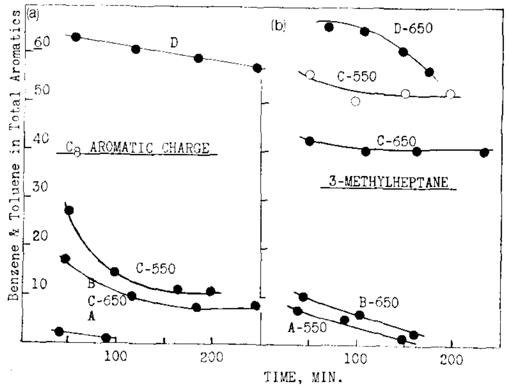


FIG. 4. (a), Mole percentage of benzene and toluene in the total aromatic fraction (EB and OX charge; $H_2$:hydrocarbon, 2:1; temperature, 482°C). (b), Ratio of toluene to benzene and toluene in the aromatics from the conversion of 3-methylheptane at 482°C and no added hydrogen.

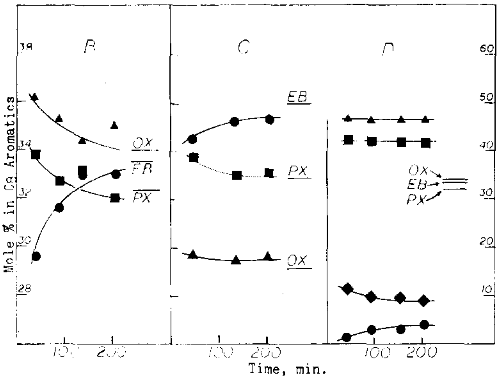


FIG. 5. Hydrogenolysis of $C_8$-aromatic mixtures over 0.6, 1.2, and 2.2% Pt catalysts (temperature 482°C; 1 atm pressure; $H_2$:hydrocarbon = 2:1 mole ratio; LHSV 0.32). The aromatic charge composition for each run is shown to the right of the conversion points for each run.

increased from 0.15 to 1.2%. While the amount of OX formed over each of the three catalysts decreased with time-on-stream and the amount of EB increased, it appears that the ratio OX:EB is approaching a constant value for each catalyst at later time on stream. This constant value decreased from about 1.1 for the 0.15% Pt catalyst to about 0.75 for the 1.2% Pt loading (Fig. 8). Since over the 1.2% Pt loading only EB underwent appreciable hydrogenolysis, the initial ratio was probably smaller than 0.75. The reduction

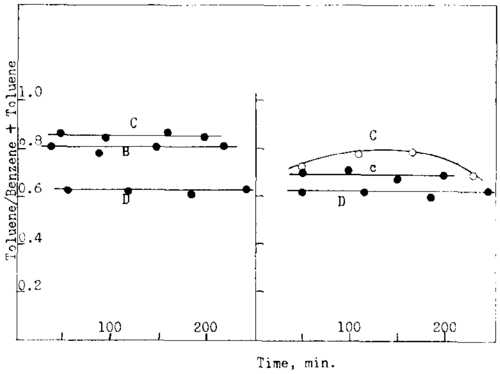


FIG. 6. (Toluene)/(benzene + toluene) ratio for the conversion of $n$-octane (left) and 3-methylheptane (right) over 0.6, 1.2, and 2.2% Pt catalysts.

temperature did not appear to influence the OX/EB ratio. Likewise, the amount of the isomers not allowed by direct $C_6$ ring formation, MX and PX, increased with Pt loading (Figs. 8, 9). The catalyst pretreated at 650°C produced considerably less of the MX and PX isomers than the same catalyst pretreated at 500°C. The ratio $(C_6 + C_7)/(C_6 + C_7 + C_8)$ aromatic also increased by greater than an order of magnitude as the Pt loading increased from 0.15 to 1.2%.

It was not possible to obtain a reliable $C_8$-aromatic distribution for the conversion of 3-methylheptane over the 2.2% Pt-C catalyst. For this Pt loading the hydrogenolysis of the aromatic products was so severe that practically all of the EB and much of the xylenes were converted to benzene and toluene.

A change in selectivity is observed for Pt-$Al_2O_3$-K catalysts as the Pt loading increased. In Table 2 the results for the conversion of $n$-octane over increasing Pt loading on the "nonacidic" alumina support are shown. For the three lower loadings, 0.05 to 0.22%, the aromatic selectivity definitely favors the formation of OX. However, as the Pt loading was increased to 0.6%, the selectivity changed to equal amounts of OX and EB.

The amount of hydrogenolysis increased as the platinum loading increased. Over the 0.15% Pt there was little hydrogenolysis, but increasing the loading to 1.2% Pt resulted in about 20–30% of the aromatics from the conversion of 3-methylheptane being benzene and toluene. The amount of hydrogenolysis over the 0.15, 0.5, and 1.2% Pt catalysts decreased with time-on-stream but the relative amounts of benzene and toluene was constant with time-on-stream. For $n$-octane, benzene and toluene comprised a larger fraction of the aromatics over the same catalyst than was obtained from 3-methylheptane even though the conversion to aromatics was similar. This suggests that benzene and toluene result from two pathways: hydrogenolysis of the

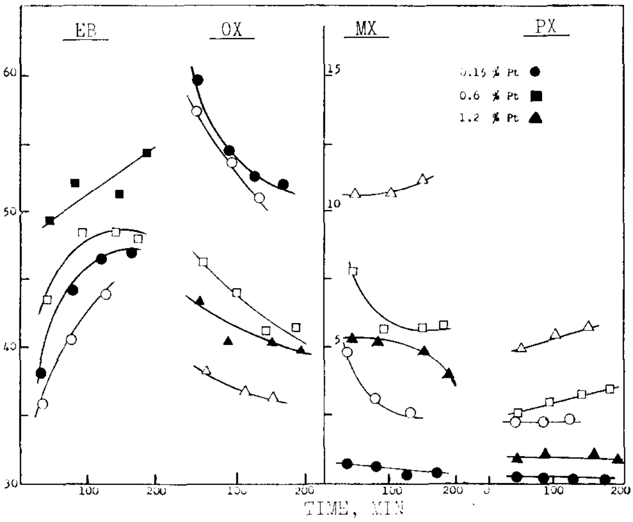


Fig. 7. $C_8$-aromatics from the dehydrocyclization of *n*-octane at 482°C (open symbols, reduced at 500°C; closed symbols, reduced at 650°C).

$C_8$-aromatic and hydrogenolysis of the paraffin charge prior to or during cyclization Since *n*-hexane and *n*-heptane are not formed in nearly as large amounts as toluene and benzene, the $C_6$ and $C_7$ paraffins formed by hydrogenolysis of the $C_8$ charge are converted directly to aromatics without the intermediate step of alkane desorption to the gas phase. Previous studies had shown that the conversion of each component of an alkane or an alkane:cycloalkane mixture was approx-

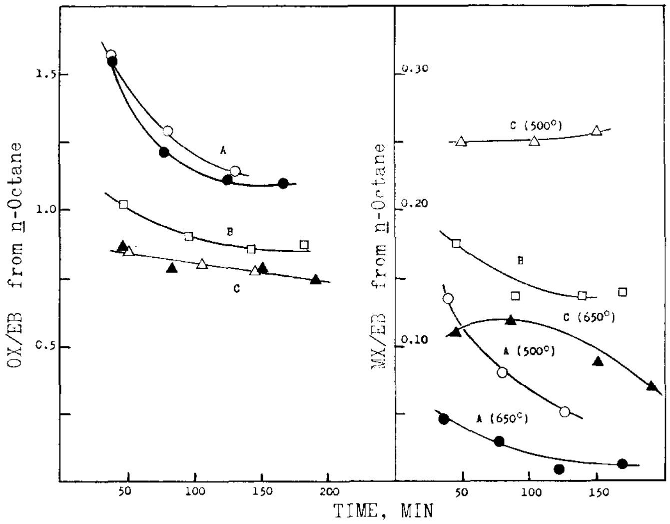


Fig. 8. Influence of metal loading on the $C_8$-aromatic ratio OX/EB and MX/EB for the dehydrocyclization of *n*-octane (run 482°C; open symbols, reduced at 500°C; closed symbols, reduced at 650°C).

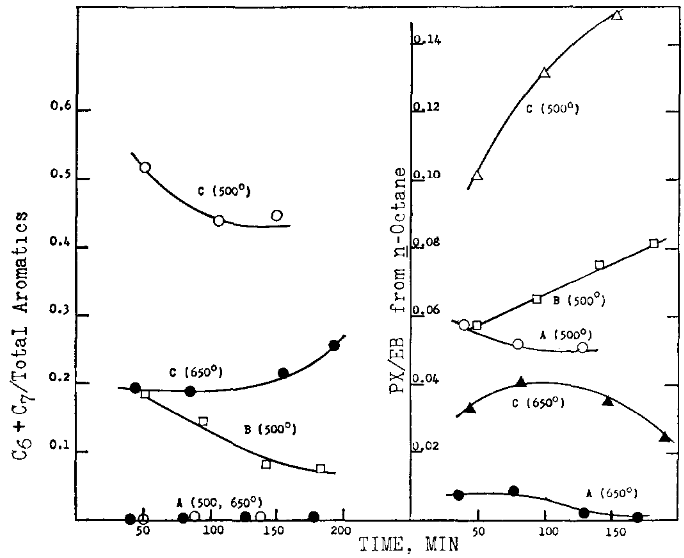
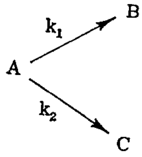


Fig. 9. Influence of Pt loading on the "hydrogenolysis," ($C_6 + C_7$)/total aromatics, and "isomerization" (PX/EB) from the dehydrocyclization of *n*-octane. Numbers in the parentheses are the reduction temperatures.

imately in the same proportion as their molar concentration in the reaction mixture (*7a*).

## DISCUSSION

According to Wheeler's classification (*8*) the dehydrocyclization of *n*-octane and 3-methylheptane is a type II selectivity:



For this type of selectivity diffusion of the reactant will not alter the product distribution. Since the $C_8$-aromatics do not undergo isomerization after formation, diffusion will not alter the aromatic selectivity after the aromatics are formed.

The conversion of *n*-octane to aromatics was approximately the same over all four Pt-C catalysts. Thus, the olefin intermediate required for dual functional acid–metal catalyzed isomerization should be present in nearly equal amounts for all four catalyst loadings. Over the two lower Pt loadings, less than 2% of the aromatics not allowed by direct six-carbon ring formation, MX and PX, were formed. Thus, isomerization to the methylheptane skeletons does not occur by an acid-catalyzed pathway over the two lower loaded catalysts. Therefore, we believe acid-catalyzed mechanism for MX and PX formation can also be eliminated for the higher platinum loadings since any acidity of the support should be present in all four catalysts.

TABLE 2

The Selectivity (OX:EB) for the Conversion of *n*-Octane over Pt-$Al_2O_3$-K Catalysts Containing Various Pt Loading[a]

| Pt loading (wt%) | *ortho*-Xylene/ethylbenzene | | |
|---|---|---|---|
| | 1[b] | 2[b] | 3[b] |
| 0.05 | 1.4 | — | — |
| 0.14 | 1.3 | 1.3 | 1.2 |
| 0.22 | 1.4 | 1.2 | 1.3 |
| 0.35 | 1.6 | 1.0 | 1.0 |
| 0.6 | 1.0 | 1.0 | 1.0 |

[a] 482°C, LHSV 0.3, no added hydrogen, 1 atm.
[b] Sample numbers.

The selectivity change does not appear to be due to an isomerization of the reactant prior to cyclization. A 1,2-methyl shift to 2- or 4-methylheptane would cause a corresponding increase in the amount of MX (*meta*-xylene) (*7*); this does not occur. Likewise, a methyl insertion-type isomerization as proposed by Pines and co-workers (*9*) to form *n*-octane would require an increase in OX paralleling the increase in EB; inserted, the amount of OX remained nearly constant while the EB increases by a factor of two. Thus, we conclude that the aromatic selectivity is determined by the metal function.

Boudart *et al.* (*3*, *4*) have proposed that reactions which show no dependence on the metal function other than surface area be classified as *facile* and those which show a selectivity dependent on the metal be classified as *demanding*. To date only the isomerization–hydrogenolysis of neopentane over metal catalysts has been found to be a demanding reaction. Boudart *et al.* have proposed that this demanding reaction requires the two reactions to be catalyzed by a different arrangement of the surface metal atoms to form specific "active sites." The change in aromatic selectivity with platinum loading for the present study would suggest that dehydrocyclization may be a demanding reaction. However, it is very difficult to visualize a geometric configuration demanding enough to control the EB:OX ratio.

Boudart (*3*) also reported that the hydrogenolysis activity of a Pt-C catalyst pretreated at 900°C was less than one reduced at 500°C even though the metal dispersion, measured by hydrogen chemisorption, was the same for both pretreatment temperatures. Boudart attributed this to the fact that platinum develops (111) facets when heated above 900°C *in vacuo*; these (111) facets provide for more abundant triadsorption of the neopentane which is the intermediate he proposed to be required for isomerization. While dispersion was the same for both temperature pretreatments, the activity for isomerization of the 900°C treated catalyst was less than the 500°C treated one by the factor of nearly four ($8.4 \times 10^{-2}$ for 500°C and $2.6 \times 10^{-2}$ for 900°C). If the dispersion remains the same and more (111) facets are developed by heating at 900°C than at 500°C, the absolute rate of isomerization should increase rather than decrease for higher pretreatment temperature. In fact, both isomerization and hydrogenolysis decreased for the higher pretreatment temperature but the hydrogenolysis reaction decreased more rapidly than isomerization.

In the present study, both the hydrogenolysis and isomerization activity is lower for the 650°C pretreated catalyst than the 550°C pretreated one. This agrees with the experimental observation of Boudart (*3*, *4*). However, EB and MX cannot be triadsorbed as was the case with neopentane. Thus, we observe the same activity change with EB as Boudart observed with neopentane but the triadsorbed intermediate cannot apply in our case. We believe the change in hydrogenolysis activity and aromatic selectivity is better explained by carbon atoms migrating from the support to the metal. These carbon atoms would not have their valence satisfied by bonding as is the case in the bulk carbon support. Thus, the carbon atom would be expected to "donate" electrons to the metal in forming bonds with the surface metal atoms. Somorjai (*10*) has observed that on large Pt crystallites the formation of an ordered carbon containing layer on the stepped surface with (111) orientation plays an important role in maintaining catalytic activity for *n*-heptane dehydrocyclization.

Dehydrocyclization must begin with a carbon–hydrogen bond rupture. The carbon–hydrogen bond strength for a primary hydrogen ($-CH_3$) is about 3 kcal/mol greater than for secondary hydrogens ($-CH_2-$). For sufficiently electron-deficient metal crystallites there will be no discrimination between these two types of hydrogen. However, as the metal becomes less electron deficient we would expect a point to be reached where the chemical potential for adsorption due to metallic holes would decrease to the point where the 3 kcal/mol bond strength would become significant. A preferential adsorption by breaking secondary C–H bonds would lead to a relative increase in the amount of OX from *n*-octane and in OX and PX from 3-methylheptane. This is the change in aromatic distribution which we observe.

Thus, the change in aromatic selectivity with metal loading can be explained by changes in the electron concentration in the metal. However, dehydrocyclization is a very complicated reaction and the electron deficiency will not be able to account completely for the aromatic selectivity. Certainly the amount of OX and PX from 3-methylheptane shows that other factors are also important. We would expect equal amounts of OX and PX since both involve the rupture of the same type of C–H bonds for direct six-carbon ring formation. However, as the Pt loading is decreased from 1.2 to 0.15% Pt, the amount of PX doubles but OX remains constant. Apparently, the steric effort of the two methyl groups on adjacent carbons also influences the selectivity.

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