

A Study on the Catalytic Property of Pt/ γ -Al₂O₃ on the Dehydrocyclization of Paraffins

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포화탄화수소의 탈수소고리화 반응에 관한 촉매특성 연구

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Abstract: The addition of Sn to Pt/ γ -Al₂O₃ catalyst greatly enhanced the activity and decreased the deactivation rate for the dehydrocyclization of paraffins. For the dehydrocyclization of n-octane, there appeared to be an optimal ratio of Pt:Sn=1:4 for 0.75 wt% Pt/ γ -Al₂O₃ catalyst. The addition of K to Pt/ γ -Al₂O₃ also produced a similar effect on the dehydrocyclization of n-hexane. In the case of n-octane, the addition of K led to a less selective catalyst.

요 약: 담지된 백금촉매에 주석의 첨가는 포화탄화수소의 탈수소고리화 반응에 대한 촉매의 활성 및 안정도의 현저한 증가를 가져왔다. n-octane의 탈수소고리화 반응에서 0.75wt%의 Pt에 대해 주석의 몰비가 약 4일 때 가장 높은 촉매적 활성을 나타냈다. 또한 K의 첨가도 n-hexane의 탈수소고리화 반응에 대해 주석과 비슷한 효과를 나타내었다. n-octane의 전환반응의 경우에는, K의 첨가 효과가 적게 나타났다.

1. Introduction

Naphtha is a compound composed of 22~74% paraffins, 19~56% naphthenes, some unsaturated cyclic hydrocarbons, and cyclic compounds with sulfur and/or nitrogen. So, most of reactions in the catalytic reforming process are conversions of saturated hydrocarbons to aromatics such as dehydrocyclization and naphthene dehydrogenation.

Since the catalytic reforming process was first developed in 1940's employing the supported monometallic catalysts[1], bimetallic catalysts with greatly improved catalytic properties have been introduced in 1970's. The application of bimetallic catalyst provides significant improvements; the bimetallic catalyst can work more efficiently under mild conditions (low pressure and low temperature), and give higher yields of gasoline and hydrogen than the

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monometallic catalyst[2]. Recent works have also demonstrated that the catalytic reforming performance could be significantly improved by addition of alkali metals or alkaline earth metals. However, the origin of these beneficial effects remains controversial.

The purpose of the present work is to investigate the dependences of dehydrocyclization rate on the amount of the second metal and to clarify the fundamental role of the second metal.

2. Experimental

The catalysts were prepared by impregnation of γ - Al_2O_3 with the aqueous solutions containing the calculated amounts of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and KNO_3 . They were dried overnight at 393K and calcined for 3 hours at 673K. Before any examination they were reduced in a hydrogen flow (5~10cc/min) for 2 hours at 773K. The content of Pt was fixed by 0.75wt%, and the amounts of Sn and K added were designated by mole ratio in a pair of brackets and wt% in a pair of parentheses, respectively. The catalytic measurements were performed in a flow reactor, and the gas products were analyzed by a GC(Yanaco G80).

All dehydrocyclization reactions were run at the condition of 500°C of temperature, 1 atm of pressure, 2 of mole ratio of $\text{H}_2/\text{H.C.}$, and 0.54(n-hexane)/ 0.56(n-octane) of LWHSV(liquid weight hourly space velocity).

3. Results & Discussion

3. 1. Addition of the second metal

3. 1. 1. Addition of Sn

Dehydrocyclizations of n-octane and n-hexane were studied at 773K, a typical temperature for the reforming process. The activity as a function of reaction time for n-octane is shown in Fig. 1. In the case of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, the yield of C_8 -aromatics was much lower at first, which is probably due to the effect of cracking; at the beginning of the reaction,

the amounts of benzene and toluene productions were large as reported by Babu et al.[3]. After about 30 minutes, the maximum yield was obtained because as the reaction proceeded the strong acidic sites of $\gamma\text{-Al}_2\text{O}_3$ were poisoned by the reaction products and it had some moderate acidic sites only. The corresponding figure for n-hexane is shown in Fig. 2. The $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst suffered a severe deactivation at this temperature, and the conversion of n-hexane to aromatics decreased very quickly at the beginning, and leveled off after about 3 hours to rather a low value.

On the other hand, the bimetallic catalysts behaved quite differently. In the case of n-octane, the activity was considerably high and remained nearly constant with time-on-stream, and the decreasing rate of the activity for n-hexane was much lower. Fig. 3 shows the yield of C_8 -aromatics from n-octane as a function of mole ratio of Sn/Pt over $\text{Pt-Sn}/\gamma\text{-Al}_2\text{O}_3$. For the dehydrocyclization of n-octane, the catalytic activity was maximum when the mole

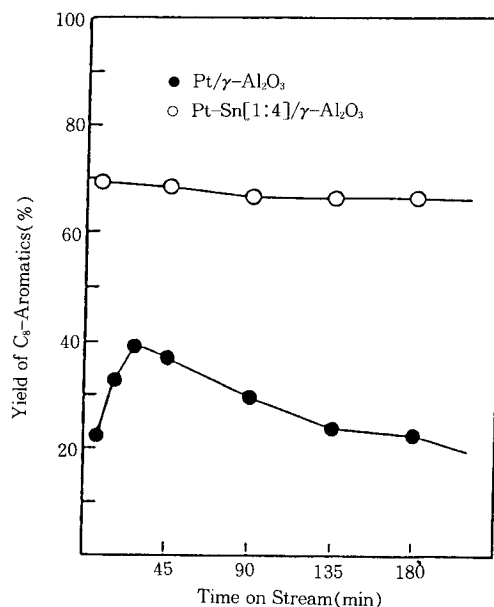


Fig. 1. Yield of C_8 -aromatics vs. time-on-stream in the dehydrocyclization of n-octane over $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Pt-Sn}[1:4]/\gamma\text{-Al}_2\text{O}_3$.

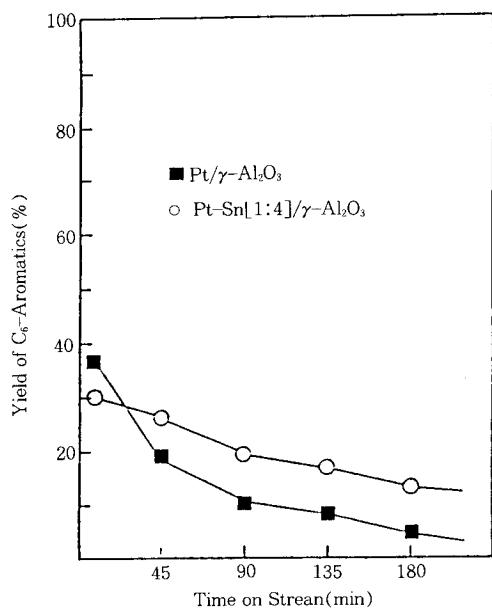


Fig. 2. Yield of C₆-aromatics vs. time-on-stream in the dehydrocyclization of n-hexane over Pt/ γ -Al₂O₃ and Pt-Sn[1:4]/ γ -Al₂O₃.

ratio of Sn/Pt was 4. When the Sn/Pt was greater than 5, the activity rather decreased, which is probably because poisoning of Pt by Sn became predominant[4].

The bimetallic effects are clearly evident in the dehydrocyclization of the paraffins. The observed results were well conformable with the general agreement that Sn improves the stability of the catalyst by decreasing coke deposition and enhancing the selectivity for aromatization.

3. 1. 2. Addition of K

The positive effect of alkali doping has long been known for such reactions as synthesis of ammonia, oxidation of sulfur dioxide to sulfur trioxide, and dehydrogenation of ethylbenzene to styrene. A number of authors have postulated the reasons for the positive effects of alkali doping, and the improvements of catalytic behavior are frequently attributed to the electronic factors—especially electron donating factor[5]. In the reforming catalyst, the

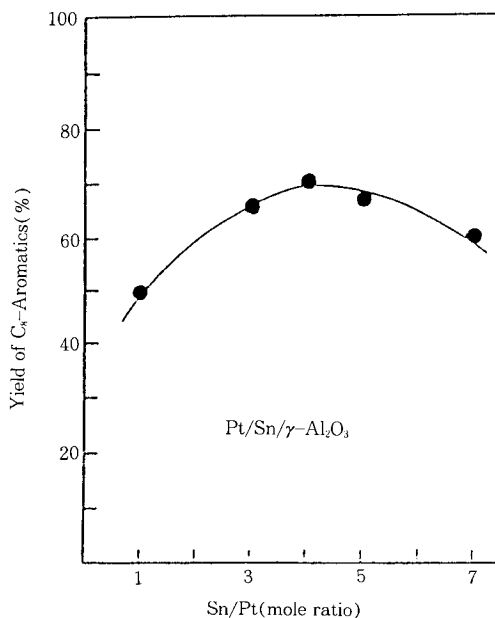


Fig. 3. Yield of C₆-aromatics vs. mole ratio of Sn/Pt in the dehydrocyclization of n-octane over Pt-Sn/ γ -Al₂O₃.

function of the alkali metal is, at least in part, to neutralize the acidic centers.

The influence of K doped on Pt/ γ -Al₂O₃ catalysts upon the aromatization of paraffins was studied, and the results for n-octane and n-hexane are shown in Fig. 4 and Fig. 5, respectively. In contrast to the effect of added Sn, the doped K produced the mixed effects on the aromatization of paraffins. For the dehydrocyclization of n-octane, the activity and the stability were rather decreased. In the case of 0.5wt% K-doped catalyst, the amount of C₈-aromatics produced increased a little probably because the doped K blocked the acidic centers of γ -Al₂O₃, which are the active sites for cracking reactions[6]. For the dehydrocyclization of n-hexane, the activity increased as the amount of K doped increased up to 3.0wt%. From these results, the positive effects of K and Sn dopings should be interpreted differently in consideration of fundamental properties such as the electronic structure of the solid or surface geometry.

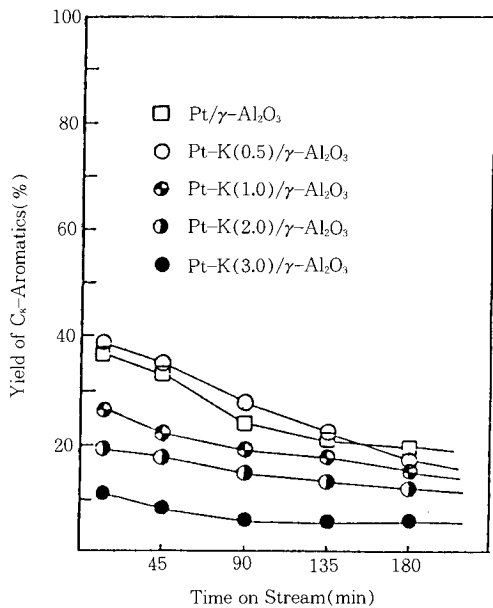


Fig. 4. Yield of C₈-aromatics vs. time-on-stream in the dehydrocyclization of n-octane over Pt/γ-Al₂O₃ and various Pt-K/γ-Al₂O₃.

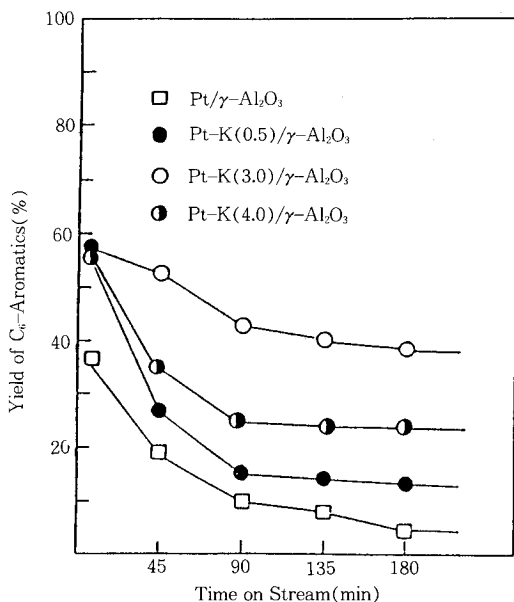


Fig. 5. Yield of C₆-aromatics vs. time-on-stream in the dehydrocyclization of n-hexane over Pt/γ-Al₂O₃ and various Pt-K/γ-Al₂O₃.

3. 2. The conversion of n-octane

When two elements with different electronegativity are bonded, the more electronegative atom attracts the bonding electrons more closely than the less electronegative atom does. Considering the different electronegativities of added elements, the electron density of Pt supported on γ-Al₂O₃ is expected to increase in the order of Pt+Cl<Pt<Pt+Sn<Pt+K.

In recent years, it has been established that Lewis acid on alumina contributes significantly as a source of acidic centers for reforming reactions. Therefore, the strength of acid site is predicted by the same concept based on electronegativity. According to this, the increasing order of acidic strength on various catalysts is as follows; Pt-K/γ-Al₂O₃<Pt-Sn/γ-Al₂O₃<Pt/γ-Al₂O₃<Pt-Cl/γ-Al₂O₃.

Fig. 6 shows the change of selectivity for C₈-aromatics upon adding promoters(Sn, K). It was shown that the formations of ethylbenzene and o-xylene were more favorable than those of p-xylene and m-xylene with the decrease of acidic strength of the reforming catalyst. In contrast to the acidic Pt/γ-Al₂O₃, where about 50% of the aromatic products was predicted by direct six-membered ring formation, the non-acidic Pt-K/γ-Al₂O₃ catalyst produced more than 95% of the o-xylene and ethylbenzene isomers. Thus, the formations of o-xylene and ethylbenzene are supposed to be controlled by the metal function only. Fig. 7 presents the o-xylene/ethylbenzene vs. time-on-stream over two different catalysts, showing that the mole ratio of o-xylene/ethylbenzene decreased with the increase of electron density of Pt.

The mechanism of the catalytic aromatization of alkanes has been the subject of the considerable interest for the last several decades[7-9]. A primary concern is the number of carbons which make up the ring that is initially formed. As discussed earlier, o-xylene and ethylbenzene are the aromatic products predicted by the direct six-membered ring formation and are formed by the metal function(not acidic function). A probable source of the small

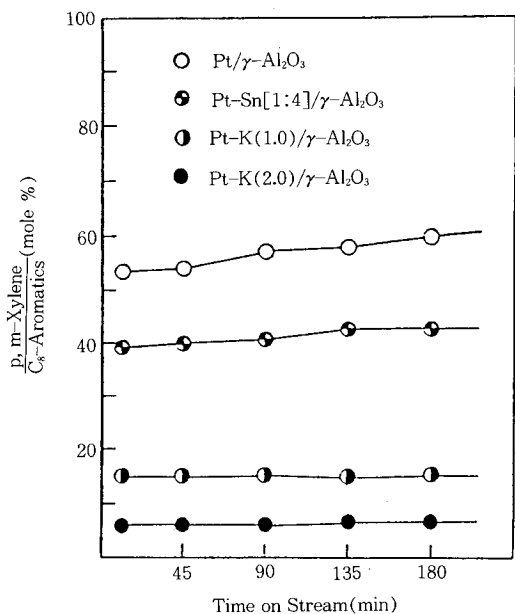


Fig. 6. p-, m-xylene/C₈-aromatics vs. time-on-stream in the dehydrocyclization of n-octane over various catalysts.

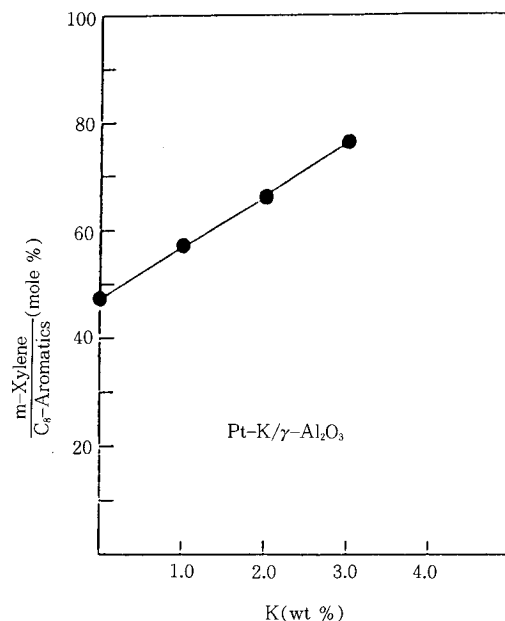


Fig. 8. m-xylene/C₈-aromatics vs. K wt% in the dehydrocyclization of 4-methylheptane over various Pt/K/ γ -Al₂O₃.

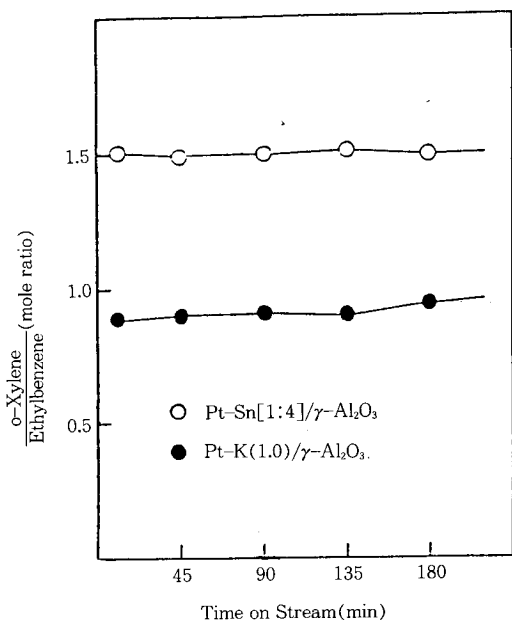


Fig. 7. o-xylene/ethylbenzene vs. time-on-stream in the dehydrocyclization of n-octane over Pt-Sn[1:4]/ γ -Al₂O₃ and Pt-K(1.0)/ γ -Al₂O₃.

amount of aromatic isomers over non-acidic catalyst would be through the isomerization of the reactant by a small amount of residual acidity not neutralized by the alkali, prior to or during the cyclization step. For 4-methylheptane, m-xylene is the only C₈-aromatic isomer allowed by direct six-membered ring formation. Fig. 8 shows the formation of m-xylene in the dehydrocyclization of 4-methylheptane as a function of the amount of K doped on the catalyst. From Fig. 8, m-xylene was shown to be the major product according to the increase of added K. Therefore, in our reaction conditions, the formation of aromatics from the dehydrocyclization of C₈-paraffins would mostly follow six-membered carbon ring mechanism.

For n-octane there are two direct six-membered ring closure pathways as shown in Fig. 9. Ring closure by the pathway(a) involves only secondary C-H bonds in -CH₂- groups and that by the pathway(b) must involve a primary C-H in a -CH₃ group[10]. It is well known that dehydrocyclization

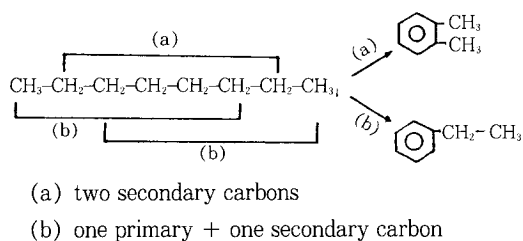


Fig. 9. The function of metal on the dehydrocyclization of n-octane.

must begin with a carbon-hydrogen bond rupture and that the bond strength for a primary hydrogen is about 3 kcal/mol greater than that for a secondary hydrogen. The data presented in Fig. 2 may be used in correlating the two types of C-H bonds with the electron density of metal crystallites. For example, for a slightly electron-deficient metal crystallite, there might be no discrimination between these two types of hydrogen. However, as the metal becomes more electron-deficient, a preferential adsorption by breaking secondary C-H bonds would lead to a relative increase of the ratio o-xylene to ethylbenzene. Finally, our results strongly suggest that the electron density of metal crystallites has a close connection with the selectivity to C₈-aromatics based on the energetic favorability existing between these two types of C-H bonds. The effect of temperature on the mole ratio of o-xylene/ethylbenzene over Pt-Sn[1:4]/ γ -Al₂O₃ is shown in Fig. 10. With the increase of reaction temperature, the formation of less favored ethylbenzene reached to almost the same amount as that of o-xylene. Thus the change in aromatic selectivity with the added promoters can be explained by the changes in the electron density 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. Even though our results were not supported by surface characterization studies, we believe that the strength of the Pt-C bond induced by an electronic modification dominates the feasibility of C-H bond breaking. Indeed, the in-

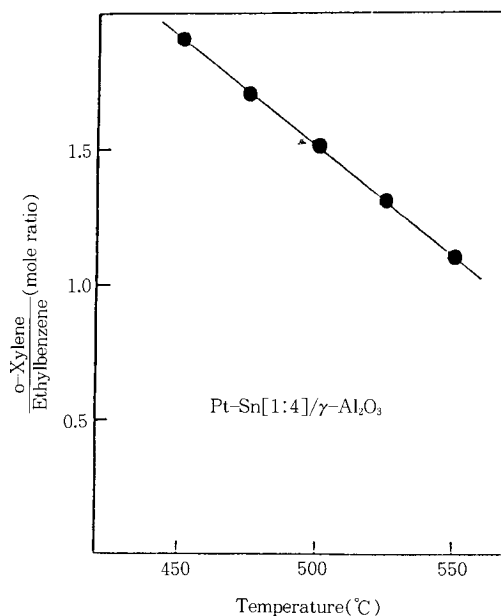


Fig. 10. o-xylene/ethylbenzene vs. reaction temperature in the dehydrocyclization of n-octane over Pt-Sn[1:4]/ γ -Al₂O₃.

creased Pt-C bond strength with electronic modification caused by the addition of alkali metal is known to induce the weakening the C-H bond strength[11, 12]. So, for a slightly electron deficient metal, it can be expected that the energy difference in the two types of C-H bonds becomes less important in the initial reaction pathways, and so the feasibility of the primary C-H bond breaking in comparison with the secondary C-H bond will be lessened to some extent. On the other hand, for a sufficiently electron-deficient metal the decrease in Pt-C bond strength by Cl addition will raise the importance of the energetic favorability in the initial reaction pathways. Our results show that for a sufficiently electron-deficient metal the production of energetically favored o-xylene almost doubles up that of ethylbenzene(Fig. 7).

To sum up, all our experimental results point out that the mole ratio of o-xylene/ethylbenzene can be an indirect index indicating the degree of electronic modification of Pt/ γ -Al₂O₃, and that excessive elec-

tron density of Pt is not appropriate for the aromatization of n-octane.

3.3. Conversion of n-hexane

Up to now, the suggested mechanisms for the dehydrocyclization of n-hexane are largely classified as two different routes; i) via formation of six-membered carbon ring (C₆-ring) intermediates, ii) via ring expansion of five-membered carbon ring (C₅-ring) intermediates. If dehydrocyclization of n-hexane proceeds along C₅-ring intermediates, the acidic function of reforming catalyst is indispensable for the predominant path of C₅-ring intermediate enlargement. However, with increasing content of K, the conversion for benzene increased (Fig. 4). The fact that a neutralized catalyst produced much more C₆-aromatics than a normal catalyst provides a reasonable ground to expect ii) pathway as a minor contributor for the aromatization of n-hexane.

In contrast to a great advantageous Pt-K/ γ -Al₂O₃ catalyst, the addition of Sn to Pt/ γ -Al₂O₃ catalyst did not improve the initial activity for n-hexane conversion, but the continuous deactivation was retarded. Therefore, during the reaction Pt-Sn catalyst maintained higher activity and selectivity in aromatization for a longer time.

4. Conclusions

1. The addition of Sn to Pt/ γ -Al₂O₃ catalyst enhanced the activity and decreased the deactivation rate for dehydrocyclization of paraffins. For the dehydrocyclization of n-octane, there appeared to be an optimal ratio of Sn/Pt=4 for the 0.75wt% Pt/ γ -Al₂O₃ catalyst.

2. The addition of K to Pt/ γ -Al₂O₃ also produced a positive effect on the dehydrocyclization of n-hexane, but in the case of n-octane the addition of K led to a less selective catalyst.

3. For n-octane conversion the formations of o-xylene and ethylbenzene were more favorable than those of p-xylene and m-xylene with the decrease

of acidic strength of the reforming catalyst by adding promoters, and the mole ratio of o-xylene/ethylbenzene decreased with the increase of electron density of Pt.

4. For the slightly electron deficient metal, it had no effect on the production ratio of o-xylene/ethylbenzene, but when the electron deficiency of the metal was sufficient, the production of energetically favored o-xylene almost doubled up that of ethylbenzene.

5. In the case of dehydrocyclization of n-hexane, the conversion via formation of six-membered carbon ring intermediates predominated the mechanism via ring expansion of five-membered carbon ring intermediates.

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