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THE EFFECTS OF CATALYST MODIFICATION ON THE CATALYTIC ACTIVITY IN THE DEHYDROCYCLIZATION OF PARAFFINS OVER Pt/γ-Al_2O_3

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Abstract—In the dehydrocyclization of n-octane over Pt-Sn/γ-Al_2O_3, the bimetallic Pt-Sn catalyst prepared by simultaneous impregnation as a complex showed higher activity than the catalyst prepared by successive impregnation with $SnCl_2$ and H_2PtCl_6, and the suspended Pt-Sn catalyst showed more enhanced catalytic behaviors in C_8-aromatics formation than the normal one. The geometric factor was an important parameter for the positive effect on the catalytic activity in the n-octane conversion, while the electronic factor, the electron density of the metal, was that in the aromatization of n-hexane.

INTRODUCTION

Catalytic reforming is a refining process to transform straight-run naphthas into gasolines with high both octane and aromatics. In addition to its importance in providing the world with motor fuels of high octane numbers, the catalytic reforming process has been the primary instrument in the synthesis and supply of the basic aromatics - benzene, toluene, and xylene [1].

The first generation of the reforming catalyst involved platinum metal dispersed on a porous carrier and needed high pressure ($\simeq$30 bar), thus giving low gasoline and hydrogen yields with short runs. In the 1970's the discovery of bimetallic catalyst has been one of the major technical developments in heterogeneous catalysts, and nowadays interests are focussed on the studies of the effect of the second metal on the catalytic reforming reaction and of the chemical state of the second metal [2-4]. The application of Pt-Sn/γ-Al_2O_3 as a reforming catalyst has given rise to many studies concerning the role of Sn and its effect on the catalytic properties of Pt. The conclusions which find general agreements are that tin improves the stability of the catalyst and enhances the selectivity for aromatization.

In the 1920's, Taylor suggested the concept of "active sites" as the seat of activity for heterogeneous catalysis. Since then, many researches have been performed to interpret this point of view. Though there have been many attempts to relate catalytic activity with electronic characteristics of the solid d-band holes, conductivity or work function [5-8], a matter of relating catalytic behavior either to surface geometry or to electronic structure is not yet well-established because the electronically controlled chemical properties of the surface atoms are dependent on the particle size at some size range [9].

In the present work, the catalyst modification is developed for enhancing the catalytic activity for the conversions of paraffins to productive aromatics.

EXPERIMENTAL

The catalysts were prepared by impregnation of γ-Al_2O_3 with the solutions containing the calculated amounts of $H_2PtCl_6 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$ and KNO_3. The solutions were aqueous for K and Pt components, and acetonic for Sn component. For the catalyst containing K, the support was impregnated firstly to the aqueous potassium nitrate solution followed by drying at 393 K and calcining at 873 K for 3 hours, and then to Pt and Sn dissolved in water and acetone, respectively. Otherwise bimetallic catalysts containing both Pt and Sn were impregnated simultaneously with the form of acetonic solution followed by evaporation of acetone with a rotary evaporator at room temperature. They

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were dried overnight at 393 K and calcined for 3 hours at 673 K. The specific surface areas of the catalysts were measured by BET method using N_2 at 77 K with a surface analyzer (Quantachrome Co., Quantasorb M), and were 142-200 m^2/g. Before any examination they were reduced in a hydrogen flow (5-10 cc/min) for 2 hours at 773 K. The loading of Pt was fixed by 0.75 wt%, and the amount of Sn was designated by mole ratio in a pair of brackets. The catalytic measurements were performed in a flow reactor, and the gas products were analyzed by a GC (Yanaco G80). However, because there were some difficulties in analyzing the C_1-C_4 cracked products individually, the yield in the present work was represented by the sum of mole% of all the products passing through the catalyst layer.

The reaction was carried out at atmospheric pressure and 773 K, a typical temperature for catalytic reforming process. The mole ratio of H_2 (used as a carrier gas)/hydrocarbon was maintained at 2, and the LWHSV (liquid weight hourly space velocity) was 0.54 for n-hexane and 0.56 for n-octane.

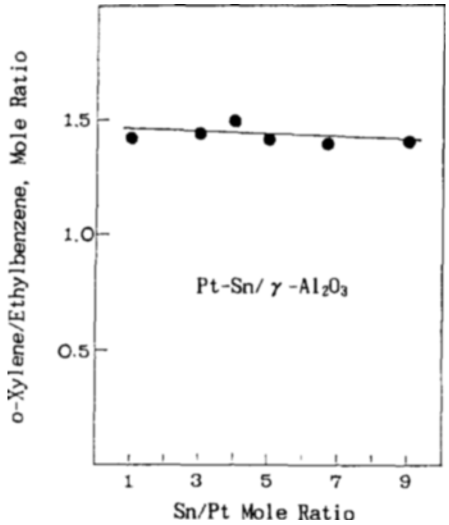

Fig. 1. o-Xylene/ethylbenzene mole ratio vs. Sn/Pt mole ratio in the dehydrocyclization of n-octane over Pt-Sn/γ-Al_2O_3.

RESULTS & DISCUSSION

1. n-Octane: geometric factor

According to Davis et al. [11], electron transfer from Sn to Pt is responsible for enhancing the catalytic behaviors of Pt-Sn/γ-Al_2O_3 catalysts in the dehydrocyclization of alkanes. This interpretation has also been favored by Burch and Galar [12]. However, in our study this point of view does not seem to be appropriate for the interpretation of the obtained experimental data for the following reasons. First, the K-modified catalyst did not show the improved catalytic effect for n-octane conversion in spite of strong electropositivity of K [13]. At this time, of course, the possibility cannot be excluded that K might donate excessive electrons to Pt. Second, the mole ratio of o-xylene/ethylbenzene in the conversion of n-octane over various Pt-Sn catalysts with different mole ratio of Sn/Pt was shown to be almost constant, and it is shown in Fig. 1. That is, the added Sn did not effect electronically on Pt.

Markedly different catalytic behaviors were shown in various Pt-Sn catalysts regardless of almost same o-xylene/ethylbenzene mole ratio. As reported earlier [13], the mole ratio of o-xylene/ethylbenzene may be an indirect index indicating the electron density of Pt. However, it is not reasonable to concentrate on the electronic factor only in order to explain the enhanced catalytic properties for n-octane conversion.

Generally, dehydrocyclization depends on the size of dispersed metal particles. It has been known that the cyclic-type reactions occur favorably on well-dispersed metal crystallites and that bond-shift and skeletal rearrangement reactions do on large metal particles of the catalyst [14, 15]. Therefore, the remarkable increases in catalytic activity and selectivity of the dehydrocyclization are rather interpreted by the structural change of Pt by adding Sn. That is, the existence of Sn around Pt leads to the increase of the number of small ensembles composed of Pt, which causes rapid change in activity and selectivity of the catalyst [16-18].

Provided that two metals are mixed, the average size of surface-exposed "ensembles" of contiguous active atoms will decrease upon dilution. The interpretation of the catalytic properties in terms of the formation of small ensembles has been proposed by Dautzenberg and Platteeum [19] and Völter et al. [20].

According to their theory, the dilution of an active metal with an inactive one causes the strongest blocking in the biggest ensembles. As a consequence, the selectivity in a parallel reaction is shifted from the reaction which is more sensitive to larger ensembles toward the less sensitive reaction. It is known that hydrogenolysis requires bigger ensembles than both dehydrocyclization and dehydrogenation [21]. In the present case the active Pt is diluted by the inactive Sn. Therefore, the selectivity is shifted from hydrogenolysis which is more sensitive reaction to bigger ensembles, towards dehydrocyclization.

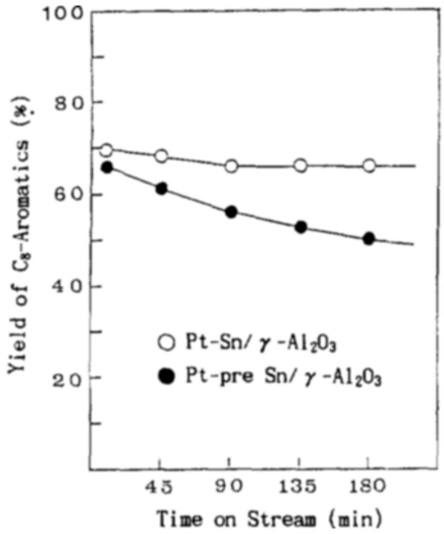

Fig. 2. Yield of C_8-aromatics vs. time-on-stream over Pt-Sn [1 : 4]/γ-Al_2O_3 and Pt-pre Sn [1 : 4]/γ-Al_2O_3.

The following experiments were performed to support that the geometric effect is responsible for the enhanced catalytic behavior. First, the bimetallic Pt-Sn catalyst as a complex prepared by simultaneous impregnation showed higher activity than the catalyst prepared by successive impregnation with $SnCl_2$ and H_2PtCl_6. The results are shown in Fig. 2. This suggests that the Pt-Sn complex which is different from the successive impregnated catalyst in a structural sense plays an important role in enhancing the catalytic activity. In the case of simultaneous impregnation, the Pt-Sn complex is expected to give a uniform distribution with a high dispersion resulting in a higher catalytic activity due to the geometric effect. Second, a Pt-Sn catalyst was prepared by impregnating alumina with an acetone solution containing $PtSnCl_8^{2-}$ and excess $SnCl_2$ (Sn/Pt=5). This impregnated Pt-Sn catalyst had a characteristic brown color, whereas the addition of suspended solution of tin chloride to platinum solution produced a deep red color suggesting that two different Pt-Sn complexes were formed. Tin (II) chloride stock solution was prepared by dissolving $SnCl_2 \cdot 2H_2O$ in acetone. At initial time the stock solution showed a suspended state, but after one or two days the solution turned to a transparent state, a perfectly dissolved state. Hereafter, the Pt-Sn catalyst prepared with the deep red solution shall be designated to "suspended catalyst". From Fig. 3, the suspended catalyst showed much more enhanced catalytic behavior in C_8-armotics formation from n-octane than the normal Pt-Sn catalyst. These different catalytic activities can be interpreted by different Pt-Sn complexes due to the different colors of the two impregnating solutions [22]. Though it is not obvious whether the higher activity of the suspended Pt-Sn catalyst comes from the higher stability of the Pt-Sn complex ion and/or the other advantageous properties or not, it is possible to assume that the suspended catalyst has a high concentration of the complex and/or an appropriate ensemble structure for n-octane conversion. Therefore, the enhanced catalytic properties might be explained by the geometric effect of the ensemble structure in Pt and Sn, and it can be confirmed by the yield of C_8-aromatics as products.

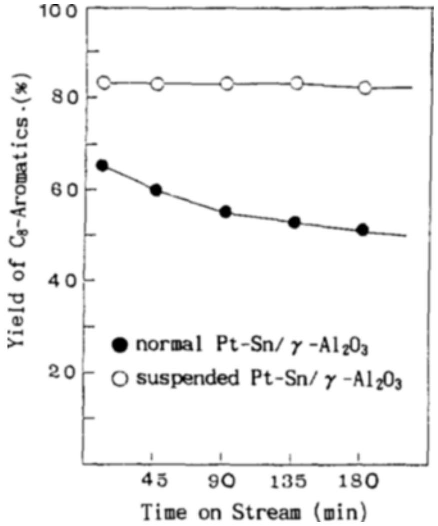

Fig. 3. Yield of C_8-aromatics vs. time-on-stream in the dehydrocyclization of n-octane over the normal Pt-Sn [1 : 5]/γ-Al_2O_3 and the suspended Pt-Sn [1 : 5]/γ-Al_2O_3.

It is known that the formations of p- and m-xylenes are more favorable than those of o-xylene and ethylbenzene with the increase of acidic strength of the reforming catalyst [23]. As shown in Fig. 4, on the suspended Pt-Sn/γ-Al_2O_3, the formations of p- and m-xylenes decreased, whereas the formations of o-xylene and ethylbenzene increased a little in comparison with the results in ref. 13. Fig. 4 suggests that the added Sn changed the geometric structure of Pt resulting in the increase of the activity in the dehydrocyclization of n-octane over the suspended catalyst because the amounts of o-xylene and ethylbenzene were increased. That is, for the suspended catalyst in which Sn may have almost the same electronic factor as in the normal catalyst, the electronic effect of Sn on Pt was negligible, and the amount of acidic centers of alumina

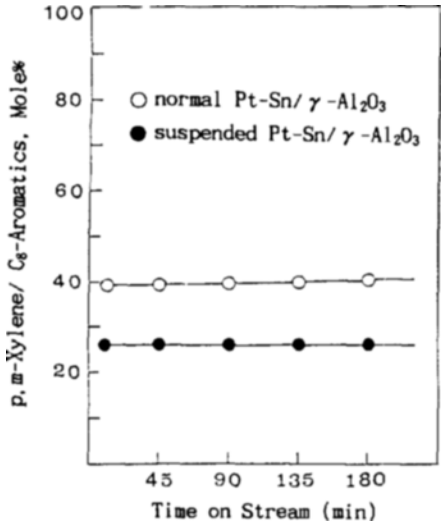

Fig. 4. p-, m-Xylene/C_8-aromatics vs. time-on-stream in the dehydrocyclization of n-octane over the normal Pt-Sn [1 : 5]/γ-Al_2O_3 and the suspended Pt-Sn [1 : 5]/γ-Al_2O_3.

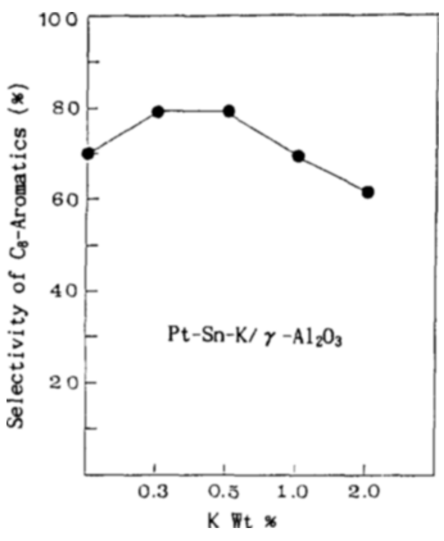

Fig. 5. Selectivity for C_8-aromatics vs. K-content in the dehydrocyclization of n-octane over various Pt-Sn-K/γ-Al_2O_3.

around Pt, where isomerization takes place was decreased.

Fig. 5 shows the selectivity for C_8-aromatics vs. K-content in the dehydrocyclization of n-octane over various Pt-Sn-K/γ-Al_2O_3. The selectivity for C_8-aromatics as a reference of catalytic activity was not increased steadily with the increase of K-content in the catalyst.

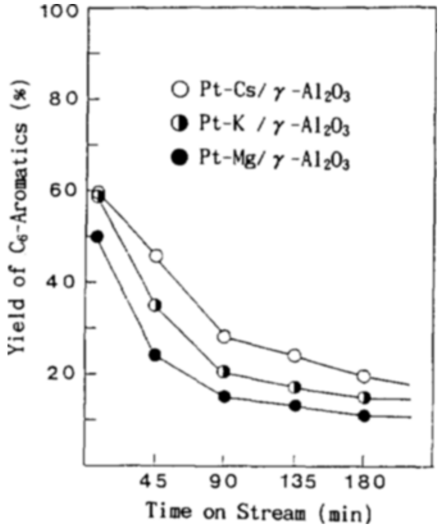

Fig. 6. Yield of C_6-aromatics vs. time-on-stream in the dehydrocyclization of n-hexane over Pt-Cs (K, Mg) /γ-Al_2-O_3.

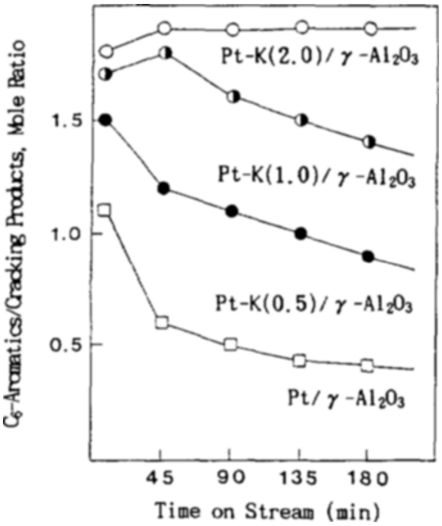

Fig. 7. C_6-aromatics/cracking products vs. time-on-stream in the dehydrocyclization of n-hexane over various Pt-K/γ-Al_2O_3.

That is, the added K which has a strong electron-donating capability, was not directly responsible to the catalytic activity, suggesting that the electronic effect did not contribute so much to this reaction. But this result was not matched in the case of n-hexane. The details on this will be shown in Figs. 6 and 7.

In conclusion, to obtain the positive effect of the catalytic behavior for the dehydrocyclization of n-octane, the geometric factor should be primarily considered as an important parameter in the modification of reforming catalysts.

2. n-Hexane: electronic factor

In n-hexane conversion, which is the dominating factor in geometric factor and electronic factor for enhancing the catalytic behavior? As reported previously by Lee and Lee [13], the K-modified catalyst made a positive effect on n-hexane conversion, but a negative effect on n-octane conversion. If this kind of K-effect on n-hexane and n-octane conversions is interpreted as electronic factor, the following explanation is possible; the aromatization of n-hexane needs stronger adsorption sites by metal than that of n-octane. Dehydrocyclization of n-hexane involves only primary C-H bonds in -CH_3 groups, but for n-octane there must be two direct six ring closure pathways involving at least a secondary C-H bond in a -CH_2-group, which is lower than primary C-H bond in bond energy. Therefore K, compared with Sn, contributed more electron-donating effect on Pt, which might produce the positive effect on n-hexane conversion involving only primary C-H bond breaking.

Besides, the addition of Cs, Mg to Pt/Υ-Al_2O_3 catalyst gave the similar effect on n-hexane conversion as shown in Fig. 6. In Fig. 6, the Cs-added catalyst showed the best activity for C_6-aromatization, which tells us the catalytic activity is related with the electron-donating capability of the added metals. Fig. 7 shows the C_6-aromatics/cracking products vs. time-on-stream in the dehydrocyclization of n-hexane over various Pt-K/Υ-Al_2O_3. The mole ratio of C_6-aromatics to cracking products was increased steadily with the increase of K-content in the catalyst unlike Fig. 5. It suggests that the electron density of the main metal was increased resulting in the decrease of the acidic strength of the catalyst. Therefore, it is reasonable to concentrate on the electronic factor, the electron density of the metal, in order to increase the aromatization of n-hexane.

CONCLUSION

For the dehydrocyclization of n-octane over Pt-Sn/Υ-Al_2O_3, the enhanced catalytic properties of the bimetallic catalysts were mainly attributed to the geometric factor of the catalysts, whereas for n-hexane, mainly to the electronic one.

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