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# Aromatization of *n*-Hexane by Platinum-Containing Molecular Sieves

## II. *n*-Hexane Reactivity

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Pt/KL, Pt/BaKL, Pt/KBaKL, Pt/NaY, Pt/CsNaY, Pt/NaFAU(C), Pt/hex, Pt/SSZ-24, Pt/silica, and Pt/carbon were tested as catalysts for the aromatization of *n*-hexane at 460–510°C and atmospheric total pressure in order to study the influence of Pt cluster size and support acidity/basicity, microstructure, and chemical composition on activity and selectivity. Analysis of the catalytic and $NH_3$ temperature-programmed desorption results from Pt/KL, Pt/BaKL, and Pt/KBaKL reveals that the presence of any acidity increases hydrogenolysis at the expense of benzene production. In addition, no increase in aromatization selectivity is observed by the addition of base sites to a Pt/zeolite catalyst, confirming that aromatization of *n*-hexane over Pt clusters on nonacidic carriers is monofunctional. High selectivity to benzene over most of the zeolite samples demonstrates that support microstructure does not contribute directly to the aromatization selectivity over Pt catalysts. High selectivity to benzene is observed for a Pt/carbon catalyst suggesting that a zeolitic support is not necessary for good performance. In fact, similar reactivity is obtained from microporous (Pt/SSZ-24) and nonmicroporous (Pt/silica) silica supported platinum catalysts with similar H/Pt values. A clear trend of increasing benzene selectivity with decreasing Pt cluster size is found. These observations suggest that the exceptional reactivity of Pt/KL for the aromatization of *n*-hexane results from the lack of any acidity in the support and the ability of zeolite L to stabilize the formation of extremely small Pt clusters.

## INTRODUCTION

In our accompanying paper, we describe a vapor phase impregnation procedure that enables Pt clusters having nearly every atom exposed to the surface to be incorporated inside the pore structure of various zeolite and zeolite-type materials (*1*). An advantage of the vapor phase Pt incorporation procedure is that the acid–base properties of the support framework are not altered as with the conventional method of ion exchange. In addition, Pt can be incorporated into zeolites without solvation effects that might limit metal accessibility to the intracrystalline volume.

Platinum catalysts prepared by the vapor phase impregnation method have been synthesized in order to study the influence of support structure, chemical composition, acidity, basicity, and microporosity on the aromatization of *n*-hexane in an attempt to elucidate the physicochemical properties of catalysts that are essential to high aromatization activity and selectivity from *n*-alkanes.

## EXPERIMENTAL METHODS

### *Catalyst Preparation and Characterization*

Preparation and characterization of the Pt-containing crystalline molecular sieves used in this work are described in the first

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paper of this series (*1*). In addition to these samples, we synthesized two nonzeolitic reference materials, Pt/$SiO_2$ and Pt/carbon. The $SiO_2$ was a water resistant form of Shell controlled-pore silica spheres having an average pore diameter of about 25 nm and a specific surface area, determined by $N_2$ adsorption, of 294 $m^2g^{-1}$. The carbon support was microporous with a specific surface area of 666 $m^2g^{-1}$. Both silica and carbon were impregnated with an acetone solution of $Pt(acac)_2$ to the point of incipient wetness, dried, and reduced in flowing $H_2$ at 400°C for 5 h. The metal loading determined by elemental analysis of the final materials showed that both samples contained 0.52 wt% Pt. The total H/Pt ratio from $H_2$ chemisorption at room temperature (see Ref. 1 for details) was 0.78 and 0.79 for Pt/$SiO_2$ and Pt/carbon, respectively.

Acidic properties of the molecular sieves were determined by temperature-programmed desorption (TPD) of preadsorbed ammonia. The experiments were carried out in a fixed bed, flow-type apparatus equipped with a thermal conductivity detector. A sample of about 0.32 g was first activated in flowing helium at 400°C for 1 h, then pure ammonia (50 $cm^3min^{-1}$) was passed over the sample at 150°C for 0.5 h. The treated material was subsequently purged with He at the same temperature for 2 h to remove the physisorbed ammonia. The TPD was performed in flowing He (100 $cm^3min^{-1}$) from 150 to 600°C with a heating rate of 10°C $min^{-1}$ and the final temperature was held for 0.5 h.

### *Reaction System*

A conventional continuous flow microreactor was used to carry out the reaction of *n*-hexane over supported Pt catalysts at atmospheric total pressure. Liquid *n*-hexane was pumped into a constant temperature vaporizer (adjusted to 180°C) where it was mixed with $H_2$ to give a reactant stream having a fixed $H_2/C_6H_{14}$ molar ratio of 6. The mixture was fed into a quartz reactor containing the catalyst (−30/+65 mesh) and reaction products were analyzed by online gas chromatography. Catalysts were reduced *in situ* with flowing $H_2$ at 460°C for 2 h before the feed was introduced. All catalytic results are reported after 1 h on stream.

The major reactions of *n*-hexane over Pt-containing catalysts include dehydrocyclization to benzene and methylcyclopentane (MCP), dehydrogenation to hexenes ($n-C_6^=$), skeletal isomerization to 2- and 3-methylpentanes (MP), and hydrogenolysis to form $C_1$–$C_5$ hydrocarbons (paraffins and olefins). Conversion was calculated as the weight percent of *n*-hexane reacted and selectivity was calculated by dividing the yield of a product by the conversion of *n*-hexane.

Aromatization of *n*-hexane is catalyzed by all of the Pt samples at the conditions described above. In the absence of a catalyst, the conversion of *n*-hexane is 0.8% at 460°C and 4.3% at 510°C with $C_1$–$C_5$ hydrocarbons (paraffins and olefins) as main products. Reaction in the presence of pure zeolites (without Pt) also results in conversion of less than 4% with $C_1$–$C_5$ hydrocarbons and *n*-hexenes as major products.

## RESULTS AND DISCUSSION

### *Influence of Temperature on the Acidic Properties of KL and BaKL*

Figure 1 shows the results of the temperature-programmed desorption (TPD) of ammonia from the KL and BaKL (8 wt% K, 10.22 wt% Ba:42% exchanged) samples with and without calcination at 600°C for 15 h after the corresponding cation exchange. The uncalcined KL shows a very small desorption peak in the temperature region of 530 to 540°C. However, the TPD curve of uncalcined BaKL is characterized by two small desorption peaks which appear in the temperature regions of 250 to 260°C and 530 to 540°C. These low and high temperature peaks can be assigned to ammonia desorption from weak and strong acid sites, respectively. The relative area of the peak at 530–540°C of uncalcined BaKL is approximately three times larger than that of uncalcined KL, indicating that BaKL is more

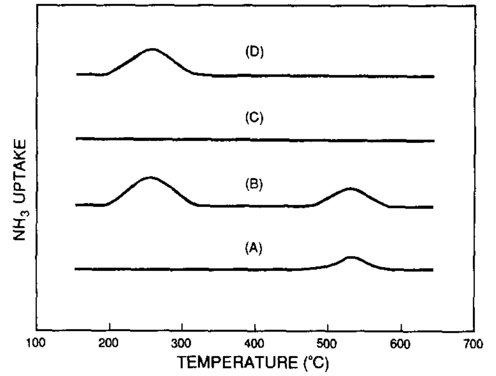

FIG. 1. Ammonia TPD curves from KL and BaKL with and without calcination at 600°C for 15 h: (A) uncalcined KL, (B) uncalcined BaKL, (C) calcined KL, (D) calcined BaKL.

acidic than KL. Another interesting observation is that the high-temperature peak is completely missing in the TPD curves of both calcined KL and BaKL, revealing the absence of strong acid sites associated with the uncalcined samples. These TPD results show that the acidity of zeolite L can be changed by calcination at high temperature as well as by ion exchange and that exchange alone does not produce a zeolite free of acid sites accessible to ammonia. Since ammonia adsorbs on both Bronsted and Lewis acid sites we cannot distinguish the nature of the acid sites on zeolite L. However, it is most likely that the low-temperature desorption is from Bronsted sites. The high-temperature peak is not fully understood, but has been speculated to be the result of some strong Lewis acid sites.

The combination of Ba ion exchange and calcination at high temperature eliminates some acidity. Hughes *et al.* investigated the IR bands of pyridine adsorbed on various alkaline forms of zeolite L (*2*). They reported that calcination at 600°C of the Ba form of zeolite L results in the migration of Ba to "locked" sites in the 8-membered rings of the L structure while the "open" sites in the 12-membered rings become predominantly occupied by K. (See the work of Newell and Rees (*3*) for a full discussion of "open" and "locked" sites in zeolite L.) The TPD of calcined BaKL after re-exchange with K (KBaKL: 11.77 wt.% K, 4.26 wt.% Ba: 17% exchanged) does not show any desorption peak in the temperature region of 250–260°C and is the same as that of calcined KL (Fig. 1C). This indicates that the peak at 250–260°C can be assigned to the "open" acidic sites in the 12-membered rings of BaKL. Thus the calcination conditions used here are not able to place all of the Ba in fully exchanged BaKL into the "locked" sites. These results are important to the interpretation of catalytic data obtained from Pt-containing zeolite L samples.

### *Catalytic Reactions of n-Hexane*

*1. Influence of zeolite acidity and basicity.* The relationship between the conversion of *n*-hexane and the selectivity to benzene formation is shown in Fig. 2. The strong correlation between selectivity and conversion suggests that the most appropriate way to compare different catalysts is to report the selectivity to benzene at the same level of conversion. The product distribution for Pt/KL, Pt/KBaKL, and Pt/BaKL at 460°C and about 30% conversion is shown in Table 1. First, note that Pt/KL prepared by the vapor phase impregnation method yields a catalyst having about the same aromatization selectivity (Fig. 2) as originally reported by Bernard who examined Pt/KL prepared by ion exchange and impregnation of Pt salts in aqueous solution (*4*). Thus, the vapor phase impregnation method is capable of producing Pt/KL that is as selective as one of the best catalysts reported in the literature. Second, Pt/BaKL prepared by vapor phase impregnation shows the same catalytic behavior as Pt/BaKL prepared by ion exchange of Pt. However, the selectivity to benzene is less for Pt/BaKL than for Pt/KL with the major difference being that Pt/BaKL produces a greater amount of cracked products. In addition to producing more $C_1$–$C_5$ hydrocarbons, the selectivity to hexenes is increased over Pt/BaKL compared to Pt/

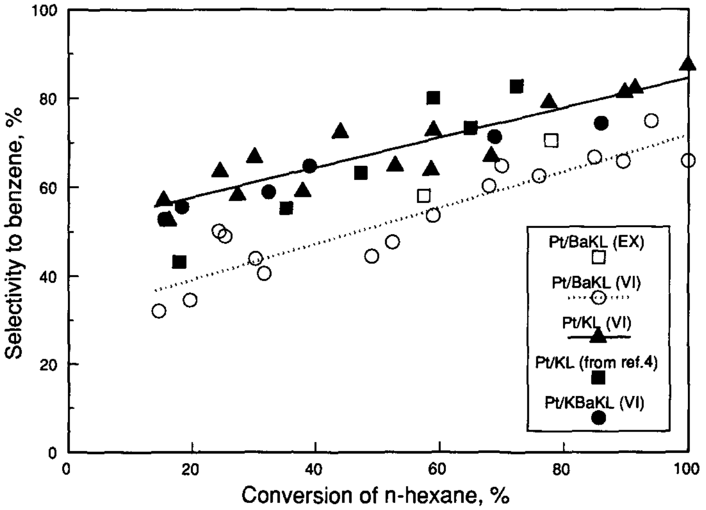

FIG. 2. Selectivity to benzene as a function of *n*-hexane conversion at 460°C, $H_2$/hydrocarbon = 6, and atmospheric total pressure.

KL (Table 1). Significant production of hexenes is not unexpected; in fact, Reagan *et al.* showed a high selectivity for dehydrogenation of *n*-hexane at 475°C that depended strongly on the calcination conditions of a Pt/NaY catalyst containing acid sites (*5*).

The product distributions are changed from those at 460°C over our Pt/L materials for *n*-hexane reaction at 510°C (Table 1). Selectivities to benzene and hexenes over Pt/KL were enhanced at higher temperature while selectivities to methylpentane and methylcyclopentane decreased. This may be due to endothermic dehydrocyclization and dehydrogenation reactions being favored at high temperatures compared to exothermic isomerization reactions. How-

TABLE 1

Conversion and Product Distribution from Reactions of *n*-Hexane on Platinum Catalysts

| | Reaction temp., °C | Conv. to *n*-hexane, % | Select. to $C_1$–$C_5$, % | Select. to MP, % | Select. to MCP, % | Select. to $nC_6^=$, % | Select. to benzene, % | Select. to aromatics[a] % |
|---|---|---|---|---|---|---|---|---|
| Pt/KL | 460 | 27.3 | 4.0 | 20.9 | 15.4 | 1.5 | 58.2 | 0.0 |
| Pt/KBaKL | 460 | 32.4 | 6.5 | 21.9 | 11.4 | 1.2 | 59.0 | 0.0 |
| Pt/BaKL | 460 | 28.1 | 15.4 | 10.9 | 13.4 | 15.1 | 45.2 | 0.0 |
| Pt/KL | 510 | 30.0 | 8.7 | 4.5 | 3.7 | 15.7 | 66.7 | 0.7 |
| Pt/BaKL | 510 | 31.9 | 20.1 | 5.3 | 7.2 | 22.9 | 44.5 | 0.0 |
| Pt/KL[b] | 460 | 100.0 | — | — | — | — | 84.2 | — |
| Pt/BaKL[b] | 460 | 100.0 | — | — | — | — | 72.0 | — |
| Pt/NaFAU(C) | 460 | 100.0 | 19.7 | 0.0 | 0.0 | 0.0 | 79.3 | 1.0 |
| Pt/hex | 460 | 100.0 | 22.6 | 0.0 | 0.0 | 0.0 | 76.6 | 0.8 |
| Pt/carbon | 510 | 90.3 | 18.3 | 3.7 | 2.5 | 6.2 | 68.0 | 1.3 |

[a] Aromatic compounds with $>C_6$.

[b] Extrapolated from data on Figure 2.

ever, cracking is also enhanced at high temperature and we observe a small increase in $C_1$–$C_5$ production at 510°C.

Re-exchange of calcined BaKL to give KBaKL eliminates all acidity as measured by $NH_3$ TPD. Since Pt/KBaKL shows the same selectivity to benzene and other products as Pt/KL (Table 1), we conclude that the presence of any acidity in Pt/L catalysts is severely detrimental to the aromatization selectivity because it produces a greater amount of cracked products (assuming olefinic intermediates react ultimately to benzene). This is in agreement with the work of Bernard who first demonstrated the effects of acid sites on the properties of Pt/L catalysts (*4*). In addition, elimination of acidity prior to Pt loading is critical in this study because the vapor phase impregnation method does not alter the acid/base properties of molecular sieves.

Besoukanhova *et al.* studied the aromatization of *n*-hexane over a series of Pt/L zeolites exchanged with various alkali cations (Li, Na, K, Rb, and Cs) (*6*). They found that the activity and selectivity for aromatization were greater for samples containing heavy cations with Li being the poorest. However, the selectivity to benzene was compared at different levels of conversion, thereby complicating the interpretation as discussed above. The selectivity results for the series of catalysts in Ref. (*6*) nearly superimpose our results in Figure 2 for Pt/KL over the entire range of conversion studied except for the sample containing Li. The low selectivity to benzene associated with a Pt/LiL catalyst may be due to the presence of acid sites generated by Li incorporation (*7*). Thus, the results of Besoukanhova *et al.* are actually consistent with the observation that changing the alkali cation of a *non-acidic* Pt/L catalyst has little or no effect on the *selectivity* to benzene during *n*-hexane aromatization.

Davis and Derouane recently reported that Pt clusters supported on a hydrotalcite-derived magnesia catalyze the aromatization of *n*-hexane with activity and selectivity similar to Pt/KL (*8*). Since the support in that case was highly basic, they speculated that one possible pathway to form aromatics was through a bifunctional mechanism where basic sites on the magnesia supplement Pt metal sites. In order to study the influence of support basicity on *n*-hexane aromatization, we prepared Pt/Y zeolite catalysts in neutral (Pt/NaY) and basic (Pt/CsNaY) forms. Previous work demonstrated that CsNaY zeolite is about two orders of magnitude more active for isopropanol conversion to acetone than NaY zeolite, and is comparable to MgO on a per unit surface area basis (*9*). Details about the synthesis and characterization of these materials can be found elsewhere (*1, 9*). At 460°C and nearly complete conversion of *n*-hexane (99%), the selectivity to benzene was 59.5 and 53.3% for Pt/NaY and Pt/CsNaY, respectively. These results suggest that there is no contribution of a bifunctional mechanism involving support basic sites at the conditions of this study and that the reaction is indeed monofunctional over nonacidic Pt catalysts.

Metal–support interactions have been observed in the Pt/L system by comparing the ratio of toluene and benzene adsorption equilibrium constants, $K_{t/b}$, for samples containing different alkaline earth cations (*10*). The decrease of $K_{t/b}$ with incorporation of heavy alkaline earth cation into the zeolite indicates that Pt clusters become more electron rich, which is consistent with the idea of charge transfer from the zeolite to the cluster. An influence of zeolite basicity on the electronic structure of supported Pt clusters has also been reported to explain the interaction of adsorbed CO with Pt/L as detected by IR (*6*). The decrease in wavenumber of linearly adsorbed CO onto Pt clusters inside the channels of L zeolite may indicate that Pt is more electron rich in L zeolite than other carriers (*6*). In addition, metal–support interactions were speculated to affect *n*-hexane aromatization over nonzeolitic, basic Pt catalysts (*8*). Based on our catalyic results, we cannot exclude the existence of platinum–support interactions; but if they are present, they do not appear to influence the *n*-hexane aromatization reaction.

*II. Influence of support microstructure.* A confinement model involving Van der Waals interactions of reactant *n*-hexane molecules with the channels of zeolite L was developed by Derouane and Vanderveeken to explain the excellent aromatization activity and selectivity of Pt/L catalysts (*11*). They suggest that hexane–framework interactions leading to a cyclic intermediate (that eventually forms benzene) are maximized in zeolite L. Therefore, the unique pore structure and cage dimensions of zeolite L are proposed to enhance conversion of *n*-hexane to benzene over Pt/L catalysts. According to this model, Pt clusters in other zeolite structures would not show the reactivity of Pt/L.

We have studied various Pt/zeolites in order to investigate the influence of support microstrucure on the reactions of *n*-hexane. The reactivity results for Pt/KL, Pt/BaKL, Pt/NaFAU(C), and Pt/hex, at 460°C and 100% conversion are reported in Table 1. All of the samples show very high selectivity to benzene (72–84%) and the only other products are $C_1$–$C_5$ hydrocarbons. Pt/BaKL has the lowest aromatization selectivity for reasons that have already been discussed. Since no special care was taken to ensure that the NaFAU(C) and hex samples were completely nonacidic, we believe that the small differences in benzene selectivity over all of the zeolite samples are due to remaining acidity in the supports other than KL.

We also examined the reactivity of Pt clusters supported on a microporous carbon to test the influence of changing carrier chemical composition and structure. Argon adsorption isotherms for NaY, carbon, KL, and mesoporous silica are plotted in Fig. 3. Earlier work proved that argon adsorption can be used successfully to rank molecular sieves on the basis of pore size (*12*). Figure 3 clearly shows that the carbon used in this work is microporous with pores as small as NaY zeolite. At 510°C, our Pt/carbon catalyst is nearly as selective to benzene as Pt/BaKL (see Table 1); however, Pt/carbon produced a much greater amount of hexenes compared to the zeolite catalysts. Reasons for the lower selectivity to olefins observed with zeolite catalysts will be discussed later. Tennison *et al.* also reported high benzene selectivity for a highly dispersed alkali-promoted Pt/carbon catalyst (*13*). Due to the high dispersion of their catalyst, we speculate that the carbon used was also microporous.

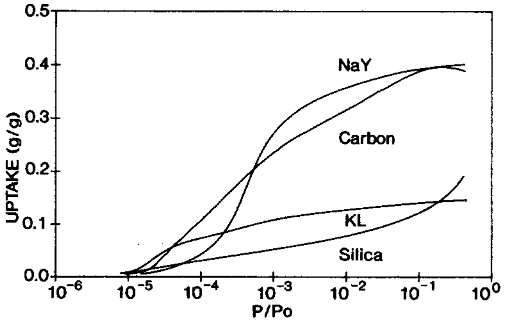

FIG. 3. Argon adsorption isotherms for various catalyst supports. The Ar uptake is plotted versus the ratio of adsorption pressure to the saturation pressure.

Our observations are in agreement with a recent comment made by Tauster and Steger that high aromatization selectivity is not unique to zeolite L catalysts (*14*). They compared the reactivity of dealuminated Pt/faujasite to Pt/KL and found similar aromatization selectivity for both catalysts (*14*). In fact, Bernard reported in his original paper that the benzene selectivity for Pt/NaY is about the same as for Pt/KL when compared at identical conditions and the same level of conversion (*4*). It appears that the confinement model does not account for the performance of Pt/KL as proposed in Ref. (*11*), since other Pt/zeolite materials yield similar results.

A logical next step would be to test two catalysts having Pt clusters supported on a microporous and a nonmicroporous carrier

TABLE 2

Conversion and Product Distribution from Catalysts at Low $n$-Hexane Conversion at 460°C

| Sample | H/Pt | Conversion of $n$-hexane, % | Select. to $C_1$–$C_5$, % | Select. to MP, % | Select. to MCP, % | Select. to $nC_6^=$, % | Select. to Benzene, % |
|---|---|---|---|---|---|---|---|
| Pt/KL | 1.56 | 15.4 | 4.7 | 9.7 | 12.3 | 16.2 | 57.1 |
| Pt/hex | 1.10 | 13.2 | 9.8 | 19.7 | 28.0 | 6.1 | 36.4 |
| Pt/SSZ-24 | 0.72 | 14.3 | 16.7 | 29.4 | 30.8 | 0.0 | 23.1 |
| Pt/silica | 0.78 | 15.3 | 18.9 | 4.6 | 7.8 | 48.4 | 20.3 |
| Pt/carbon | 0.79 | 11.2 | 18.8 | 21.4 | 38.4 | 0.9 | 20.5 |

*Note.* Selectivity to aromatics is zero for all samples.

of the same chemical composition. The Pt cluster size should be identical in both cases to eliminate any ambiguity in the interpretation of catalytic results. To this end, we studied Pt supported on SSZ-24 (a microporous, pure silica, zeolite) and mesoporous silica. The H/Pt ratios for the samples were 0.72 and 0.78 for Pt/SSZ-24 and Pt/silica, respectively, demonstrating a similar average cluster size for the two catalysts. These two materials show about the same selectivity to benzene (see Table 2) which is consistent with the lack of importance of confinement effects during $n$-hexane aromatization over supported Pt. It should be noted that the microporous material produces significant amounts of MP and MCP whereas the nonmicroporous material produces a majority of hexenes. The low production of olefins from Pt/SSZ-24 compared to Pt/silica may be due to a higher rate of hydrogen transfer in the zeolite and/or a stronger interaction of olefins (heat of adsorption) with the zeolite framework. If the desorption rate of olefins is decreased in zeolite catalysts compared to other support materials, then further reaction to aromatics or paraffins is likely to occur (decreases the observed olefin selectivity over zeolite catalysts at identical levels of $n$-hexane conversion).

All of the results presented so far are consistent with the conclusion that the high aromatization selectivities observed over monofunctional Pt catalysts are independent of support microporosity as long as the support is completely nonacidic. As mentioned earlier, the confinement effect does not appear to be a suitable explanation for high benzene selectivity observed over Pt catalysts. Tauster and Steger propose a molecular die effect where the zeolite channel structure collimates a diffusing flux of reactant $n$-hexane so that end-on or terminal adsorption onto the Pt surface is favored (*14*). Terminal adsorption would then lead to 1,6 ring closure and eventually benzene. They report a correlation between the terminal cracking index (TCI) calculated as the $C_5/C_4$ molar ratio and a selectivity parameter representing the tendency of a catalyst to aromatize compared to the tendency to crack $n$-hexane. High values of TCI are found for highly selective, zeolitic, aromatization catalysts, supporting the idea of collimation of $n$-hexane followed by terminal adsorption. We have checked the cracking pattern for catalysts studied in this work and the results are shown in Fig. 4. The spread of points and general trend of increasing aromatization selectivity with increasing TCI is similar to that reported in Ref. (*14*). Since Fig. 4 contains results from microporous and nonmicroporous catalysts, we conclude that even if there is a correlation between aromatization selectivity and TCI, collimation or molecular die effects do not provide a satisfactory explanation of the high aromatization selectivity over supported Pt catalysts. Lane *et al.* arrived at the same conclu-

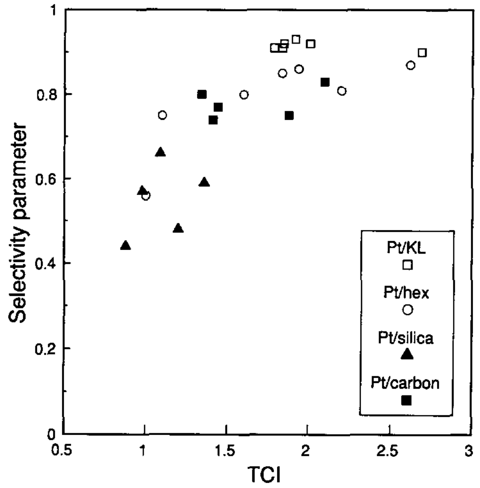

FIG. 4. Aromatization selectivity parameter as a function of terminal cracking index (TCI) at 510°C, $H_2$/hydrocarbon = 6, and atmospheric total pressure.

sion by finding the same TCI for a Pt/KL catalyst (1.8) and a K-promoted Pt/$Al_2O_3$ catalyst (1.7) (*15*). In fact, terminal cracking of *n*-hexane occurs on Pt single crystals with the (111) terraces being the most active for both aromatization and terminal hydrogenolysis (*16*). This intrinsic property of Pt may account for the reported trend of increasing TCI with increasing aromatization over supported Pt catalysts.

*III. Influence of Pt cluster size.* Results obtained at about 15% conversion from Pt supported on zeolitic (Pt/KL, Pt/hex, and Pt/SSZ-24) and nonzeolitic (Pt/silica and Pt/carbon) supports with different pore sizes are reported in Table 2 along with the H/Pt ratio obtained from $H_2$ chemisorption. First, note that the Pt/KL sample with the highest H/Pt ratio, 1.56, is the most selective catalyst for aromatization and produces the least amount of light gases. A clear trend with decreasing H/Pt ratio can be seen by examining the entries in Table 2. As H/Pt decreases, the selectivity to aromatics decreases while cracking increases. The distribution of other products does not show any relation with H/Pt, and may result from different molecule–support interactions among the catalysts studied.

The ratio of H/Pt can be used as a rough guide to the average Pt cluster size. For clusters greater than about 1 nm in average diameter, the stoichiometry of hydrogen to Pt surface atoms is about 1 to 1 (*17*). However, we found H/Pt ratios exceeding unity for several of our catalysts. Vaarkamp *et al.* also found an H/Pt ratio significantly greater than 1 (1.3) for Pt clusters in BaKL (*18*). An average Pt–Pt coordination number of 3.7 determined by EXAFS for the same sample was consistent with Pt clusters composed of only 5 or 6 atoms (*18*). Vaarkamp *et al.* have correlated the H/Pt ratio with average Pt–Pt coordination number and, combined with the data of Kip *et al.* (*19*), show that H/Pt ratios greater than unity contain information on relative cluster sizes (*18*).

We suggest that the low production of light gases from the highly dispersed zeolite catalysts can be explained in terms of an ensemble effect. Hydrogenolysis is known to be a structure-sensitive reaction on metal surfaces requiring at least several adjacent metal atoms to form the active site (*20*). Decreasing the Pt cluster size to contain only a few atoms will inhibit hydrogenolysis activity in the same way as alloying an inactive metal into an active metal dilutes the number of active sites for hydrogenolysis (*21*). Apparently, aromatization requires a smaller ensemble than hydrogenolysis since benzene selectivity does not decrease with decreasing cluster size. Dautzenberg and Platteeuw report that *n*-hexane aromatization is independent of Pt cluster size in the range of 1.5 to 5 nm in diameter (*22*); however, the "best" catalysts used in the present work have clusters less than 1 nm in average diameter so direct comparisons are not applicable. We cannot rule out the possibility that aromatization activity is actually enhanced over extremely small Pt clusters, especially if structure sensitive side reactions that deposit unreactive carbon are suppressed due to an ensemble effect.

### *Unifying Concepts*

A unifying description of monofunctional Pt aromatization catalysts emerges from all of the results presented here. Since the presence of any acidity in these catalysts is severely detrimental to benzene selectivity, the first requirement of preparing an effective catalyst is to eliminate all acid sites on the support material. A second requirement is to incorporate Pt metal in a manner that produces highly dispersed clusters, less than 1 nm in average diameter, without generating acid sites. Therefore, we propose that the uniqueness of Pt/KL catalysts for *n*-hexane aromatization lies not in the geometry of their channel structure but in their ability to stabilize extremely small Pt clusters in a nonacidic environment. This suggests that very highly dispersed Pt clusters on a non-zeolitic, non-acidic support would be as effective as Pt/KL.

Davis and Derouane compared the reactivity of Pt/Mg(Al)O to Pt/KL and found similar results in terms of activity and selectivity for aromatization of *n*-hexane (*8*). The average cluster diameter for Pt/Mg(Al)O was estimated from $H_2$ chemisorption to be 2 nm compared to 1 nm for Pt/KL. Moreover, since their Pt/KL was prepared by ion exchange of aqueous $Pt^{2+}$ some acidity must have been present after metal reduction and may have affected their catalytic results. In addition, their Pt/KL catalyst had an H/Pt ratio of unity suggesting that the Pt clusters were larger than the Pt/KL clusters used in this work having H/Pt = 1.56. However, our results do support the suggestion of Davis and Derouane that the high activity and selectivity to benzene over Pt/Mg(Al)O may result from Mg(Al)O acting as an inert carrier for small Pt clusters (*8*).

Very recently Lane *et al.* explained the unusually high activity and selectivity of Pt/KL by suggesting that the preference for 1,6 ring closure over 1,5 ring closure in L zeolite is related to the optimum pore size of the L zeolite (*15*). This finding is consistent with the confinement model and at the same time in contrast to our results. They studied *n*-hexane reactions over Pt/KL, Pt/KY, Pt/NaY, $Pt/Al_2O_3$ and $Pt/SiO_2$ catalysts at a lower reaction temperature and high dihydrogen to hydrocarbon ratio than in our experiments; yet their results are very similar to ours. For example, ultimate benzene selectivities at low conversion (benzene divided by benzene plus light gases) on their Pt/KL, Pt/NaY, and Pt/KY zeolites were 0.93, 0.87, and 0.73, respectively, which are close to values calculated in this work. We speculate that differences in benzene selectivity observed for the Pt/zeolites of Lane *et al.* may be caused by variation of Pt cluster sizes among the samples. Transmission electron micrographs included in Ref. (*15*) revealed that the Pt clusters in L zeolite were much smaller than in Y zeolite. Also, their turnover frequency (TOF) calculations were based on CO chemisorption results that showed the same CO/Pt ratio on Pt/KL and Pt/KY samples. This calculation assumes that only sites capable of chemisorbing CO are accessible for *n*-hexane reaction. When Larsen and Haller studied Pt clusters on a series of alkaline L zeolites, they found that the CO/Pt ratio varied strongly with cation while the H/Pt ratio remained constant (*10*). Their results clearly show that CO chemisorption should not be used to determine Pt cluster sizes in Pt/L catalysts and cast doubt on the appropriateness of basing TOF's on CO chemisorption.

Up to this point, the issue of absolute activities of the catalysts has not been discussed. In agreement with Lane *et al.*, we observed in general that the Pt/zeolite catalysts are far more active in *n*-hexane conversion per surface Pt atom than Pt/silica. Turnover frequencies were estimated here by calculating the number of *n*-hexane molecules reacted per surface Pt atom per second at 15% conversion (the lowest level of conversion studied) assuming differential conversion. Obviously this assumption is not entirely justified but the calculation provides at least some basis to compare the relative activities of our samples. The TOFs for the catalysts in Table 2 are 0.80, 1.2, 0.07, 0.13 and 0.12 $s^{-1}$ for Pt supported on KL, hex, SSZ-24, silica, and carbon, respectively. Note that Pt/KL and Pt/hex are more active than the other samples and that the trend in activity roughly follows the trend in Pt cluster size. Therefore, both the activity and selectivity results presented in this study are consistent with our conclusion that the formation of extremely small clusters is critical for obtaining an excellent aromatization catalyst.

## CONCLUSIONS

Based on results from $NH_3$ TPD and catalytic reactions of *n*-hexane, we conclude that the presence of any acidity in supported monofunctional Pt catalysts will severely decrease the observed selectivity to benzene by increasing cracking. When special care is taken to eliminate support acidity, no effect of changing the zeolite cation or adding additional basic sites was found for *n*-hexane reactions. Evidently, metal–support interactions and bifunctional catalysis involving basic sites are not important for these reactions.

The confinement model was found to be an unsatisfactory explanation for the excellent performance of Pt/KL since we measured high selectivities to benzene over a series of zeolite catalysts with various framework structures. In addition, a correlation of terminal cracking index with benzene selectivity exists for both microporous and nonmicroporous materials which is in contradiction to the molecular die hypothesis of Tauster and Steger.

A trend of increasing activity and selectivity to benzene with decreasing Pt cluster size is observed, and we propose that the uniqueness of Pt/KL for *n*-hexane aromatization is due to the ability of the L framework to stabilize extremely small Pt clusters (<1 nm) in a completely nonacidic environment.

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