June, 1994] © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **67**, *1553—1559(1994)* 1553

Studies on the Surface Property of Pt/KL Zeolite Catalysts

Lian-Xin DAI, Haru SAKASHITA, and Takashi TATSUMI*
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113

(Received December 28, 1993)

Pt/KL catalysts prepared by ion exchange (IE), ion exchange followed by the addition of KCl (IE-KCl), incipient wetness impregnation (IWI), and coimpregnation with KCl (IWI-KCl) were compared regarding the aromatization of hexane, and were characterized by transmission electron microscopy, the chemisorption of H_2 and NH_3, the competitive hydrogenation of toluene and benzene, and the infrared spectroscopy of adsorbed CO. The majority of Pt particles on the various Pt/KL catalysts seem to be highly dispersed inside the zeolite channels. The presence of KCl in the Pt/KL catalysts resulted in a decrease in the acidity of zeolite, giving rise to a reduction in the C_1–C_5 selectivity, regardless of the method of catalyst preparation. The competitive reaction of toluene/benzene and FT-IR results consistently show that the Pt particles on the IE-KCl catalyst have the most electron-rich sites among the Pt/KL samples examined. The high specific activity for benzene production of the IE-KCl catalyst should be attributed to these Pt particle sites with high electron-donating ability. It is proposed that the terminal adsorption of hexane, resulting in the formation of primary alkyl species, is favorable on electron-rich Pt particles, leading to a 1,6-ring closure, and eventually benzene.

Platinum supported on KL zeolite exhibited excellent activity and selectivity for the aromatization of hexane.[1,2] There was evidence for both geometric[3—5] and electronic[6,7] effects concerning reactions on the Pt/KL zeolite catalyst. The catalytic performance of the Pt/KL zeolite catalyst also appeared to be a function of the preparation method.[8—11] It has been proved that the treatment of KL zeolite with CF_3Cl prior to its impregnation with $[Pt(NH_3)_4]Cl_2$ results in enhanced activity and selectivity for hexane aromatization and stabilization of the catalytic performance.[8] Poeppelmeier et al.[9] have claimed in a patent that the coimpregnation of KL zeolite with a solution containing $[Pt(NH_3)_4]Cl_2$ and KCl gives rise to an increase in selectivity for benzene formation. Ostgard et al.[10] have compared the properties of Pt/KL catalysts prepared by ion exchange (IE), incipient wetness impregnation (IWI), and coimpregnation with KCl (IWI-KCl) by employing various techniques, and have pointed out that IWI and IWI-KCl catalysts are less acidic, less active for hexane conversion, and more selective for benzene production than is the IE catalyst.

We recently reported a novel method for preparing a Pt/KL catalyst; in this method potassium chloride acts as an effective additive to a Pt/KL catalyst prepared by ion exchange, resulting in an enhancement in both the catalytic activity and selectivity in hexane aromatization.[11]

The overall objective of this study is to investigate the effect of the preparation method regarding the Pt/KL catalytic behavior. Special emphasis is placed on the characterization of surface sites. The size of Pt particles, the acidity of Pt/KL zeolites, and the relative adsorption equilibrium constants of toluene and benzene on Pt particles have been determined. The infrared spectra of CO adsorbed on the Pt surface have been compared. Furthermore, attempts are being made to relate any differences in the reaction performance to the electronic properties of the Pt/KL catalysts.

Experimental

Catalyst Preparation and Catalytic Reaction. Zeolite KL-supported Pt catalysts were prepared by ion-exchange and impregnation methods. A sample prepared by the ion exchange of KL with $[Pt(NH_3)_4]Cl_2$ (designated as an IE catalyst) was impregnated with KCl to incipient wetness to afford IE-KCl catalysts. For the IWI catalyst, platinum was introduced into the KL zeolite by incipient wetness impregnation with $[Pt(NH_3)_4]Cl_2$. The IWI-KCl catalyst was prepared in a similar manner with the exception that the impregnating solution contained additional KCl (KCl/Pt molar ratio = 2). After calcination in air at 573 K for 2 h, the catalysts were reduced in situ in flowing H_2 at 773 K for 0.5 h. The Pt loadings of the catalysts were determined using an ICP spectrometer, and were found to be 0.44 wt% for the IE series catalysts and 0.50 wt% for the IWI series samples, respectively. A reaction of hexane was carried out using a conventional fixed-bed reactor. The typical experimental conditions were as follows: a reaction temperature of 743 K, a total pressure of 0.5 MPa, a WHSV (weight hourly space velocity) of 2.4 h^{-1}, and an H_2 to hexane molar ratio of 6.0.

Transmission Electron Microscopy. Platinum particle distributions were examined with a Hitachi Model H-600A electron microscope operated at 100 KV with a magnification of 100000.

H_2 Chemisorption. Hydrogen chemisorption measurements were carried out at room temperature by using a conventional glass-made static vacuum system. The catalyst (0.50 g) was outgassed at room temperature in a vacuum and then pretreated in flowing He. The temperature was raised to 373 K at a heating rate of 6 K min^{-1} and held at 373 K for 0.5 h. The catalyst was then reduced in flowing H_2 while the temperature was raised from 373 to 773 K at a rate of 6 K min^{-1} and held at 773 K for 0.5 h. After reduction, the sample was evacuated ($<10^{-4}$ Torr, 1 Torr = 133.322 Pa) at 773 K for 1 h and cooled to room temperature in a vacuum; the isotherms were then recorded. The total amount of chemisorbed H atoms was obtained by extrapolating the linear higher pressure part of the adsorption isotherm to zero pressure. The platinum dispersion was conventionally defined as being the ratio of the chemisorbed H atoms to the loaded platinum atoms.

NH_3 Chemisorption. Chemisorption of NH_3 was carried out in order to determine the concentration of acidic sites by using the same system used for H_2 chemisorption. In a similar way to H_2 chemisorption, a first NH_3 adsorption isotherm was recorded at pressures within the range of 0—100 Torr at room temperature. The sample was then evacuated ($<10^{-4}$ Torr) at 373 K for 5 min to eliminate the weakly bound NH_3; a second adsorption curve at room temperature was then determined. The amount of chemisorbed NH_3 was obtained by subtracting the two isotherms and extrapolating the results to zero pressure.

Competitive Hydrogenation of Toluene and Benzene. Competitive hydrogenation reactions of toluene and benzene were carried out in a conventional flow, fixed-bed microreactor system. The partial pressure of toluene and benzene was set by changing the molar ratio of toluene to benzene in the liquid reactants. The experimental conditions were as follows: a reaction temperature of 353 K, atmospheric pressure, a WHSV of 6.5 h^{-1}, and an H_2 to aromatics molar ratio of 12.

Fourier-Transform Infrared Spectroscopy. The infrared spectra of adsorbed CO were taken on a Perkin–Elmer 1600 FT-IR instrument. The spectra were collected over the range of 1000—4000 cm^{-1} using 64 scans and at a resolution of 4 cm^{-1}.

About 50 mg of crushed powder, which had been prereduced at 773 K for 0.5 h and passivated in flowing 1% O_2 (Ar balance) from 373 K to room temperature, was pressed into a thin self-supporting wafer with a diameter of 20 mm under a pressure of 20 MPa. The wafer was placed in a typical home-made IR cell with CaF_2 windows, evacuated at room temperature for 15 min, and purged in flowing He at a flow rate of 80 ml min^{-1} with the temperature ramped from 298 to 393 K with a hold at 393 K for 0.5 h. After the system was again evacuated the catalyst wafer was reduced in situ in flowing H_2 at a flow rate of 80 ml min^{-1} and a temperature ramped from 393 to 673 K with a hold at 673 K for 0.5 h. Thereafter, the cell system was evacuated to less than 10^{-5} Torr at 673 K for 1 h. The wafer was lowered into the infrared beam and cooled to room temperature. High-purity grade CO was admitted into the IR cell system to a pressure of 30 Torr at ambient temperature for 0.5 h. The IR spectra were taken at ambient temperature after heating the samples to 373 K for 0.5 h in a vacuum.

Results and Discussion

Aromatization of Hexane. The product distribution for the IE, IE-KCl (KCl/Pt=4.5), IWI, and IWI-KCl (KCl/Pt=4.0) catalysts at about 80% conversion is shown in Fig. 1. The benzene selectivities observed over these catalysts were in the following order: IE-KCl>IWI>IWI-KCl>IE. The sequence of selectivity for benzene production on the IE and IWI series catalysts are quite similar to those found by Ostgard et al.[10] The lower benzene selectivity for the IE catalyst was due to the higher C_1–C_5 selectivity. The IE-KCl catalyst exhibited lower C_1–C_5 selectivity, leading to higher benzene selectivity. The IE-KCl and IWI (or IWI-KCl) catalysts were different in their selectivities for methylcyclopentane and hydroisomerization products. Although the selectivity for C_1–C_5 over the IWI or IWI-KCl catalyst was significantly low, the selectivities for methylpentanes and methylcyclopentane were considerably high. It is particularly noteworthy that in terms of the activity based on catalyst weight, the IE-KCl was 5-times as high as the IWI-KCl. Although the IE-KCl (KCl/Pt=4.5) and IWI-KCl (KCl/Pt=4.0) catalysts have a similar chemical composition, subtle variations in the method for loading platinum and adding KCl resulted in marked differences in the performance of the catalysts for the aromatization of hexane.

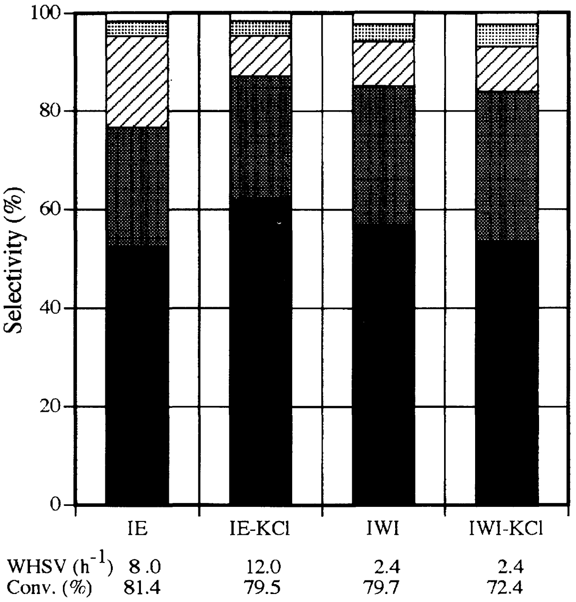


Fig. 1. Effect of preparation methods on the catalytic performance. (■) Benzene; (■) *i*-C6; (▨) C1–C5; (□) MCP; (□) Others.

Analysis of the Size of Pt Particle. Transmission electron microscopy observations revealed that Pt particles of 2—5 nm in diameter were present on a few spots of the Pt/KL samples. Typical micrographs for the IE and IE-KCl samples are shown in Fig. 2. Since these Pt particles are larger than the size of the L zeolite channel of its widest point 1.1 nm, they must be outside the zeolite.

Measurements using a JEM-4000EX high resolution transmission electron microscope at 400 KV showed that most of the zeolite regions contained extremely small Pt clusters, although no metal particles larger than 1 nm were evident.[12] By also taking into account the results of H_2 chemisorption (as described below), the overwhelming majority of Pt particles would be highly dispersed and the catalyst should have a bimodal distribution of platinum particle size, consisting of a small number of large particles outside the zeolites and small clusters inside the zeolites.

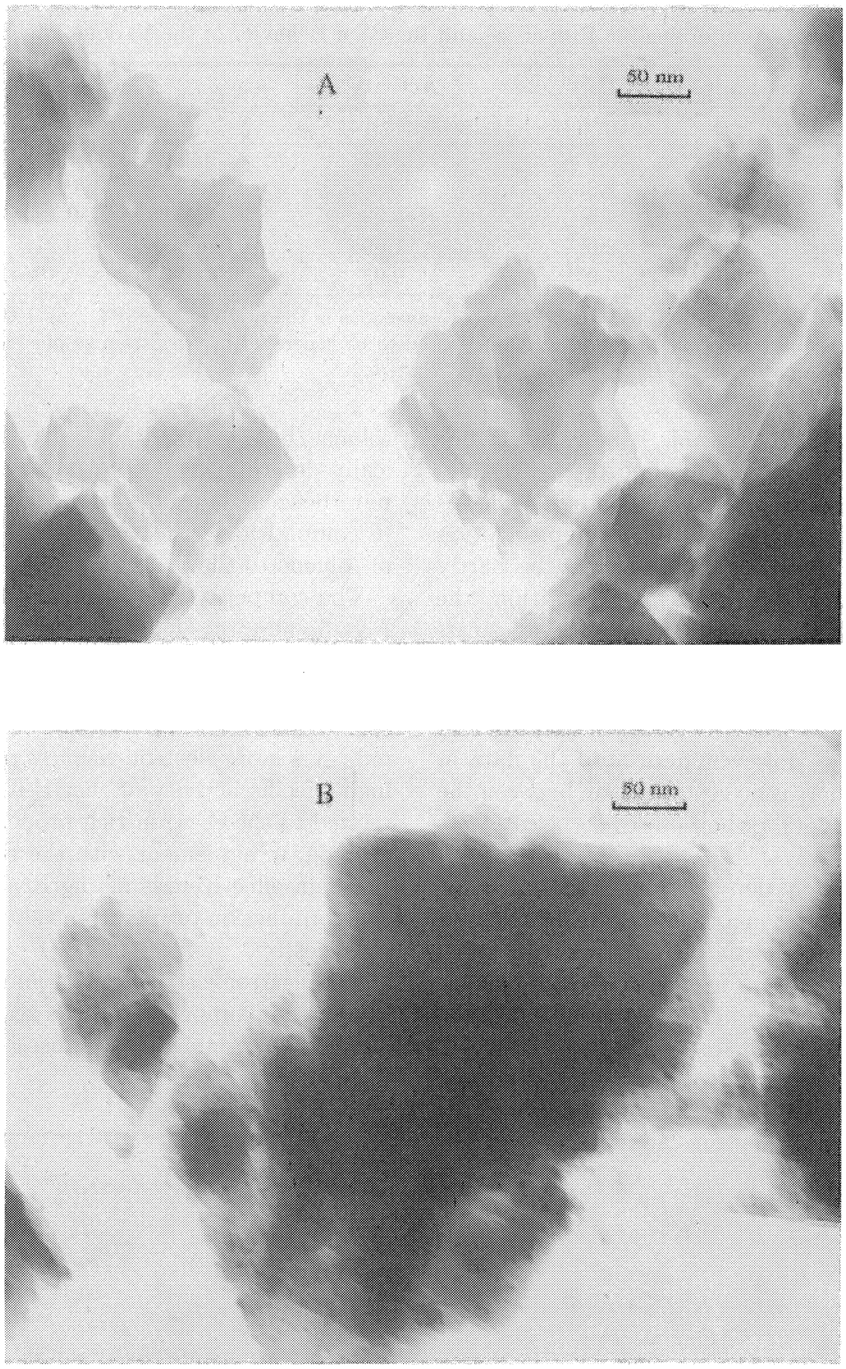


Fig. 2. Transmission electron micrographs of the various Pt/KL catalysts. (A) IE; (B) IE-KCl.

The H/Pt ratio of the Pt/KL catalysts with different preparations is summarized in Table 1. Due to the bimodal distribution of the platinum in zeolite, the dispersions shown in Table 1 cannot be used to estimate metal particle sizes. However, it is evident that most of the platinum was well dispersed on the samples examined.

The H/Pt ratio of the IE-KCl (or IWI-KCl) sample was significantly lower than that of the IE (or IWI) sample. This might mean that the size of particles slightly increased when KCl was externally introduced into the Pt/KL catalysts. However, as shown in Table 1, there is no clear correlation between the H/Pt ratio and the catalytic performance. Hence, the enhancement of benzene production due to the addition KCl to the IE catalyst was not due to an increase in the Pt dispersion. It is thus suggested that the catalytic performance of hexane aromatization was mainly affected by the electronic state of platinum.[6,7]

Analysis of the Electronic Property of Platinum Surface. It is generally recognized that Pt/KL catalysts are monofunctional, with only the metal (platinum) centers acting as active sites.[1,2,6] A small amount of acidity is sufficient to decrease the ben-

Table 1. Comparison of Surface Properties and Reaction Behavior of the Various Pt/KL Catalysts

Catalyst	Pt loading	KCl/Pt[a)]	Activity[b)]	H/Pt	NH_3	$K_{T/B}$
	wt%	molar ratio	g-benzene g-cat^{-1} h^{-1}		mmol g-cat^{-1}	
IE	0.44	0.0	3.42	1.11	0.22	7.7
IE-KCl	0.44	2.3	—	1.03	0.17	—
IE-KCl	0.44	4.5	5.92	1.00	0.15	6.4
IWI	0.50	2.0[c)]	1.09	1.03	0.21	—
IWI-KCl	0.50	4.0[d)]	0.93	0.94	0.19	15.5

a) Molar ratio of added KCl to loaded Pt. b) Conversions in the range of 72—81%. c) KCl supposed to be generated by ion exchange. d) KCl supposed to be generated by ion exchange plus additional 2 moles of KCl introduced.

zene yield. The data given in Table 1 indicate that for the IE series catalysts the amount of adsorbed NH_3 decreased with an increase in the KCl content. The increased activity and selectivity for benzene production found with the IE-KCl series catalysts may be partly attributed to the decreased acidity. In addition, the smaller NH_3 adsorption amount on the IWI series catalysts accounts for the low C_1–C_5 selectivity compared to that of the IE sample. These results indicate that there is an obvious correlation between the acidity and the C_1–C_5 selectivity. However, perusal of the data in Table 1 shows that there is no clear relation between the acidity and the selectivity for benzene over the catalysts prepared in different ways.

Competitive hydrogenation of aromatics is governed by their relative adsorption coefficients, and these in turn reflect the local electronic charge on the metal particle. In the competitive hydrogenation of toluene and benzene, toluene is the better electron donor and is therefore expected to form stronger π-bonds with Pt.

Assuming a competitive adsorption of toluene and benzene for the same sites on the metal surface, the rates of benzene hydrogenation can be given by the Langmuir rate lows:[13)]

$$R_B{}^* = (k_B K_B P_B)/(1 + K_B P_B) = k_B \qquad (1)$$

and

$$\begin{aligned} R_B &= (k_B K_B P_B)/(1 + K_B P_B + K_T P_T) \\ &= (k_B K_B P_B)/(K_B P_B + K_T P_T), \end{aligned} \qquad (2)$$

where k, K, and P are the rate constant, adsorption coefficient, and partial pressure, respectively, of benzene (B) and toluene (T). R_B^* is the rate of benzene hydrogenation in the absence of toluene and R_B is the rate of hydrogenation of benzene in competition with toluene.

The ratio of these two rates gives

$$R_B{}^*/R_B = 1 + (K_T/K_B)(P_T/P_B) = 1 + K_{T/B} P_{T/B}. \qquad (3)$$

If $K_{T/B}$ and $P_{T/B}$ are defined as the ratio of the adsorption constants and partial pressures for toluene to benzene, respectively, then a plot of R_B^*/R_B against $P_{T/B}$ is linear with $K_{T/B}$ as the slope.

The ratio of the adsorption equilibrium constants for toluene/benzene on Pt particles ($K_{T/B}$) can be kinetically determined by plotting the ratio of the rates of pure benzene hydrogenation to benzene hydrogenation in competition with toluene as a function of the ratio of toluene to the benzene partial pressure.

The competitive hydrogenation results are shown in Fig. 3, and the $K_{T/B}$ values are also shown in Table 1. It is conspicuous that $K_{T/B}$ was dependent on the preparation method, increasing in the following order: IE-KCl<IE<IWI-KCl. Since a lower $K_{T/B}$ value indicates more electron-richness of the Pt particles, the high specific activity of the IE-KCl catalyst should be related to the electron-rich property of the Pt particles thereon, in agreement with the previous proposal that the high effectiveness of the Pt/KL catalysts for benzene production results from the electron-richness of Pt particles.[1,2,6,7,11,14)]

The electronic structure (or ionization potential: I.P.) of platinum supported on the zeolite is affected by the support environment and cluster size, etc. The I.P. of

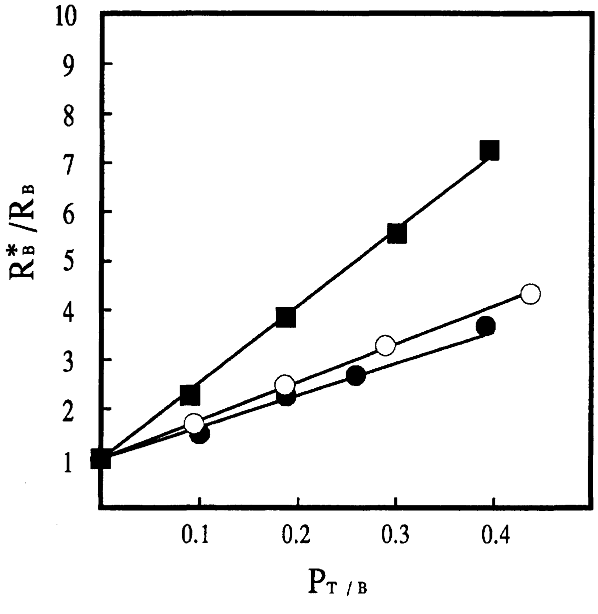


Fig. 3. Competitive hydrogenation toluene and benzene on the various Pt/KL catalysts. (○) IE; (●) IE-KCl; (■) IWI-KCl.

the Pt particles decreases with lowering acidity (or electrophilic character) of the support, leading to more electron-richness of the platinum clusters and higher activity in the aromatization of hexane. It is suggested that there is a close correlation between the $K_{\mathrm{T/B}}$ value and the activity for benzene formation. Although the IWI-KCl catalyst had lower acidity, as is evidenced by the decrease in the amount of adsorbed NH_3 than did the IE catalyst (Table 1), it showed a higher $K_{\mathrm{T/B}}$ than did the IE sample, being consistent with the low aromatization activity. Thus, competitive hydrogenation is a suitable method for directly determining the electronic property of platinum induced by the introduction of KCl to the Pt/KL catalyst, in contrast to the NH_3 adsorption method, which only determines the support acidity. Since the interaction between the zeolite and Pt particles is affected by the catalyst preparation method, it is possible that the electronic structure of Pt may not directly reflect the acidity of the zeolite support.

FT-IR spectroscopic measurements were also carried out using CO adsorption as a probe molecule to investigate any changes in the electronic state of the platinum particles. Figure 4 shows typical spectra of chemisorbed CO on various Pt/KL catalysts.

In accord with previous studies of adsorbed CO on Pt-L zeolite catalysts,[6,15—19] all samples exhibited a typical CO adsorption spectrum with bands in the range of 2070—1900 cm^{-1} owing to the linear-bonded CO, and a broader band located at around 1800 cm^{-1} due to bridge-bonded CO.

For the IE-KCl catalyst, at least four CO bands were observed. Bands at 2050, 1995, and 1970 cm^{-1} predominated. Furthermore, it is noteworthy that only the IE-KCl sample showed a very low-frequency band at 1935 cm^{-1} compared to the other samples. The Pt particles on the IE-KCl sample seem to have the most electron-rich sites among the Pt/KL catalysts examined. The electron-rich platinum atoms back donate electrons into the CO π^* orbital, and shift the infrared bands to a lower frequency. We have also found that this special band disappeared and, concurrently, the activity and selectivity for benzene formation sharply decreased when KCl was removed from the IE-KCl catalyst by washing.[20] It is thus indicated that the high specific activity of the Pt particles on the IE-KCl catalyst is due to this kind of highly electron-rich sites.

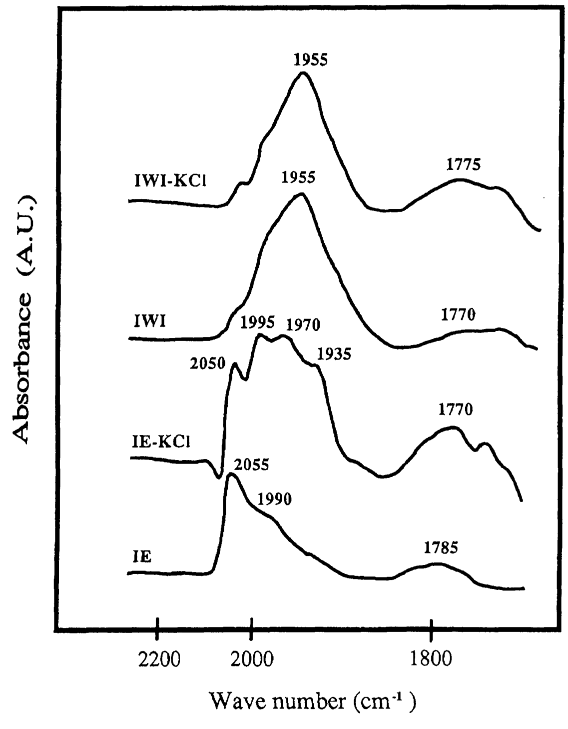


Fig. 4. FT-IR spectra of CO adsorbed on the various Pt/KL catalysts.

A strong CO band at 2055 cm^{-1} and a shoulder peak near 1990 cm^{-1} were observed for the IE sample. A dominant peak at 1955 cm^{-1} was found for both the IWI and IWI-KCl catalysts. If we compare the wavenumbers on these catalysts, the Pt particles on the IWI series samples are apparently more electron-rich than those on the IE catalyst. However, the decrease in the wavenumber of the IWI series samples might be not due to the increased electron density of Pt particles thereon. It is well known that the C–O stretching frequency is lowered due to an electrostatic interaction of the oxygen atom of adsorbed CO with the alkali cation.[21—25] Therefore, the presence of additional K cations on the IWI and IWI-KCl catalysts may account for their lower CO stretching frequency compared to the IE sample, whereas the $K_{\mathrm{T/B}}$ values suggest that the former were less electron-rich than the latter.

Barthomeuf et al.[6] originally suggested that the low-frequency bands in the 2000—1960 cm^{-1} range are due to CO adsorbed on very small Pt clusters embedded in the framework; later, however, they concluded that[16] these bands should be assigned to CO adsorbed on Pt atoms interacting strongly with the negatively charged framework oxygen atoms of the zeolite. This interaction is supposed to transfer electrons to the platinum atoms. In the case of the IE-KCl catalyst, it can be expected that the Cl^- anion associated with K^+ may donate electrons to the Pt particles, resulting in a highly active Pt species.

Mechanism for Benzene Formation on Pt/KL Catalyst. Pt/KL zeolite catalysts have a unique activity for hexane aromatization to benzene. The initial proposal was that the interaction of the Pt particles with the basic L zeolite walls caused the particles to be electron-rich.[6,7] Alternative explanations based on the confining structure of the undulating parallel channels of the L zeolite were proposed by Tauster and Steger[3,4] as well as Derouane and Vanderveken.[5] The former proposal suggested that the high aromatization selectivity of Pt supported on the L zeolite was caused by the ability of the channels to collimate the flux of hexane molecules, leading to end-on adsorption at the Pt surface. The latter authors suggested that the non-binding interaction of hexane with the active site environment led to the preorganization of hexane as a pseudo-cycle. However, Davis and Derouane[26] found that the hexane aromatization selectivity on Pt/MgO was similar to that on Pt/KL. They thus ruled out any effects of microporosity, but instead speculated on metal-support interactions between Pt clusters and a high surface-area basic support. Therefore, the geometric hypothesis concerning the L zeolite seems to be inconceivable. However, none of the previous proposals account for the increased selectivity for benzene production on electron-rich Pt particles.

The "terminal cracking index" (TCI), defined as the C_5/C_4 molar ratio in the cracking products, was proposed by Tauster and Steger.[4] They found that the TCI value increases paralleled the benzene selectivity. If a hexane molecule is coordinated through its terminal carbon atom, the selectivity for 1,6-ring closure will increase, leading ultimately to benzene. Nonterminal adsorption cannot lead to aromatization, but results in methylcyclopentane (MCP) formation followed by conversion to methylpentanes (MPs).[27] It is intuitively obvious that terminal adsorption favors terminal cracking versus nonterminal cracking. The benzene selectivity observed for the IE-KCl series catalysts with different KCl/Pt molar ratios is plotted against the TCI value in Fig. 5. It is clear that the benzene selectivity increased monotonically with the TCI value. This finding means that the addition of KCl to the IE catalyst effectively promoted the probability of the terminal adsorption of hexane and the following formation of benzene via 1,6-ring closure and dehydrogenation.

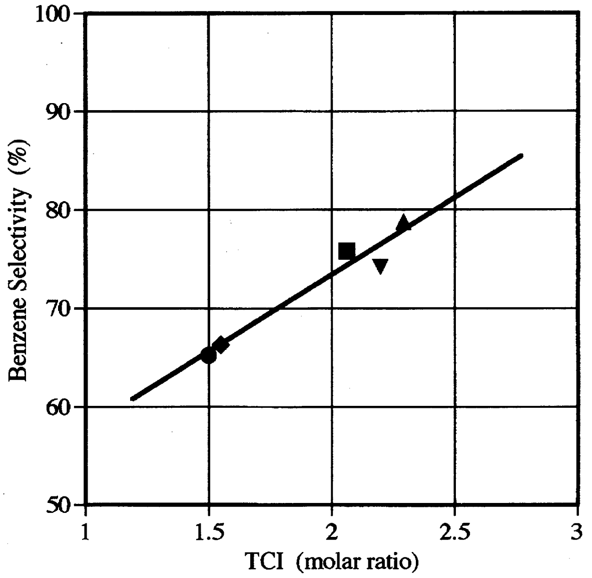


Fig. 5. Effect of terminal cracking index on benzene selectivity over the IE-KCl series catalysts. (●) KCl/Pt=0; (◆) KCl/Pt=1.1; (■) KCl/Pt=2.3; (▲) KCl/Pt=4.5; (▼) KCl/Pt=6.8.

It has been shown that the selectivity for benzene is dependent on the hexane conversion, and therefore that the product distribution over different catalysts should be compared at the same hexane conversion.[27] The selectivity ratio of benzene to MCP plus methylpentanes (MPs) plotted as a function of hexane conversion over the different Pt/KL catalysts is shown in Fig. 6. The benzene selectivity advantage for the IE-KCl catalyst is demonstrated at the same level of conversion. The formation of MCP and MPs as well as the hydrogenolysis was effectively retarded when KCl (KCl/Pt=4.5) was added into the IE sample.

Tauster and Steger[4] suggested that the terminal adsorption of the hexane molecule can be ascribed to a geometric effect imposed by the zeolite structure. We propose that the terminal adsorption of hexane resulting in the formation on the primary alkyl species is favorable for electron-rich Pt particles. It has been found that the metal electron density determines the primary/secondary ratio of coordinated alkyls; the electron-richness of metal gives rise to a greater carbanion character of the coordinated alkyls, favoring the primary type of alkyl species (Scheme 1).[28] It can thus be imagined that the primary alkyl species generated on Pt particles with high electron density, via 1,6-ring closure and dehydrogenation, selectively transfers into benzene. On the IE-KCl catalysts the presence of the electron-

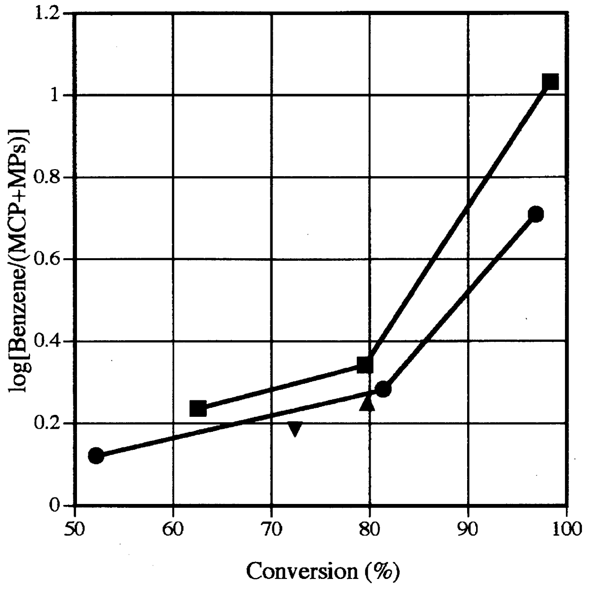
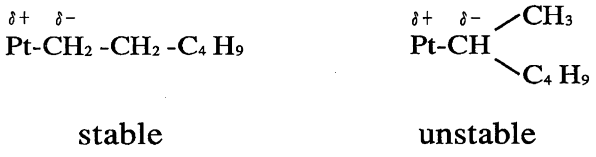


Fig. 6. Effect of hexane conversion on selectivity over the various Pt/KL catalysts. (●) IE; (■) IE-KCl; (▲) IWI; (▼) IWI-KCl.



Scheme 1.

rich site of the Pt metal should be advantageous to the terminal adsorption of hexane, leading to high activity and selectivity for benzene formation. If the alkyl species has a less anionic or radical character as a result of the less electron-rich character of the metal, secondary alkyl species could be more stable than the primary alkyl species. On the IWI series catalysts the selectivities for MCP and MPs were not sufficiently low, although they have no significant acidity so as to promote unwanted hydrogenolysis or isomerization reactions.

The authors wish to thank Dr. A. Muramatsu (Tohoku University) for obtaining the transmission electron micrographs.

References

1) J. R. Bernard, in "Proc. 5th Int. Conf. Zeolites," ed by L. V. C. Rees, Heyden, London (1980), p. 686.

2) T. R. Hughes, W. C. Buss, P. W. Tamm, and R. L. Jacobson, *Stud. Surf. Sci. Catal.*, **28**, 725 (1986).

3) S. J. Tauster and J. J. Steger, *Mater. Res. Soc. Symp. Proc.*, **111**, 419 (1988).

4) S. J. Tauster and J. J. Steger, *J. Catal.*, **125**, 387 (1990).

5) E. G. Derouane and D. J. Vanderveken, *Appl. Catal.*, **45**, L15 (1988).

6) C. Besoukhanova, J. Guidot, D. Barthomeuf, M. Breysse, and J. R. Bernard, *J. Chem. Soc., Faraday Trans. 1*, **77**, 1595 (1981).

7) G. Larsen, and G. L. Haller, *Catal. Lett.*, **3**, 103 (1989).

8) M. Sugimoto, H. Katsuno, and T. Murakawa, *Appl. Catal.*, **A96**, 201 (1993).

9) K. R. Poeppelmeier, T. D. Trowbridge, and J. L. Kao, U. S. Patent 4568656 (1986).

10) D. J. Ostgard, L. Kustov, K. R. Poeppelmeier, and W. M. H. Sachtler, *J. Catal.*, **133**, 342 (1992).

11) L. X. Dai, H. Sakashita, and T. Tatsumi, *Chem. Lett.*, **1993**, 387.

12) T. Ohsuna, O. Terasaki, L. X. Dai, and T. Tatsumi, to be published.

13) T. M. Tri, J. Massardier, P. Gallezot, and B. Imelik, *Stud. Surf. Sci. Catal.*, **11**, 141 (1982).

14) M. Sugimoto, H. Katsuna, T. Hayasaka, N. Ishikawa, and K. Hirasawa, *Appl. Catal.*, **A102**, 167 (1993).

15) G. B. McVicker, J. L. Kao, J. J. Ziemiak, W. E. Gates, J. L. Robbins, M. M. J. Treacy, S. B. Rice, T. H. Vanderspurt, V. R. Cross, and A. K. Ghosh, *J. Catal.*, **139**, 48 (1993).

16) A. de Mallmann, and D. Barthomeuf, *Stud. Surf. Sci. Catal.*, **46**, 429 (1989).

17) L. M. Kustov, D. Ostgard, and W. M. H. Sachtler, *Catal. Lett.*, **9**, 121 (1991).

18) G. S. Lane, J. T. Miller, F. S. Modica, and M. K. Barr, *J. Catal.*, **141**, 465 (1993).

19) W. J. Han, A. B. Kooh, and R. F. Hicks, *Catal. Lett.*, **18**, 193 (1993).

20) L. X. Dai, H. Sakashita, and T. Tatsumi, submitted for publication.

21) S. Boujana, D. Demri, J. Cressely, A. Kiennemann, and J. P. Hindermann, *Catal. Lett.*, **7**, 359 (1990).

22) H. Praliaud, M. Primet, and G. A. Martin, *Appl. Surf. Sci.*, **17**, 107 (1983).

23) P. A. J. M. Angevaare, H. A. C. M. Hendrickx, and V. Ponec, *J. Catal.*, **110**, 11 (1988).

24) P. A. J. M. Angevaare, H. A. C. M. Hendrickx, and V. Ponec, *J. Catal.*, **110**, 18 (1988).

25) A. Zecchina, S. Bordiga, E. E. Platero, and C. O. Arean, *J. Catal.*, **125**, 568 (1990).

26) R. J. Davis, and E. G. Derouane, *J. Catal.*, **132**, 269 (1991).

27) G. S. Lane, F. S. Modica, and J. T. Miller, *J. Catal.*, **129**, 145 (1991).

28) K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 9268 (1972).