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

I. Catalyst Preparation by the Vapor Phase Impregnation Method

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A vapor phase impregnation method with $Pt(acac)_2$ has been developed and used to load Pt into aluminosilicate (KL, BaKL, NaY, CsNaY, cubic and hexagonal polytypes of faujasite, ZSM-12, and SSZ-24) and aluminophosphate ($AlPO_4$-5 and VPI-5) molecular sieves. Pt-containing molecular sieves are characterized by XRD, TPD, elemental analysis, ^{13}C MAS NMR, TEM, and H_2 chemisorption. ^{13}C MAS, NMR, TEM, and H_2 chemisorption measurements reveal that Pt can be loaded into the micropores of molecular sieves with both charged and neutral frameworks. Pt impregnated into zeolites and aluminophosphates by this method does not migrate to the exterior surface of the molecular sieve catalysts at *n*-hexane aromatization reaction conditions of atmospheric pressure and temperatures between 460 and 510°C.

INTRODUCTION

Catalytic reforming of hydrocarbons is an important process for increasing the aromatic content and octane rating of hydrocarbon streams in the gasoline boiling range. $PtRe/Al_2O_3$–Cl, one of the conventional reforming catalysts, is known to be very effective for increasing the aromatic content and octane rating of C_9 or higher hydrocarbons. However, it is not a good catalyst in promoting the aromatization of C_6 and C_7 hydrocarbons, especially *n*-hexane and *n*-heptane. This may be due to the selectivity limit intrinsic to the conventional bifunctional reforming catalysts that contain acidic halided-alumina supports. Pt supported on the Ba,K-exchanged form of zeolite L (Pt/BaKL) is of current interest since it shows exceptional selectivity for the aromatization of *n*-hexane (*1–3*). It is speculated that the Ba and K cations play a role in neutralizing the zeolite L framework. Thus, this catalyst can be regarded as monofunctional rather than as bifunctional. That is, only the Pt centers act as active sites.

Derouane and Vanderveken (*4*) suggest that the high aromatization selectivity of the Pt/BaKL catalyst be attributed to the zeolite L pore system which confines reactants within its pores in such a manner as to assist the organization of *n*-hexane into a "pseudocycle." Zeolite L contains a unidimensional pore system consisting of ellipsoidal polyhedra (cages) connected via 12-membered ring windows of 7.4 Å (*5*) and it is this geometry that is stated to be necessary for the "pseudocycle" formation (*4*). However, Tauster and Steger (*6, 7*) claim that the high aromatization selectivity of the catalyst comes from the ability of the zeolite to collimate *n*-hexane molecules and produce terminal adsorption. Tauster and Steger imply that terminal cracking (C_5/C_4 ca. above 1.5) and high aromatization are linked. Also, they report that a dealuminated faujasite with SiO_2/Al_2O_3 of about 40 (*8*) has the same high selectivity for *n*-hexane aromatization as Pt/BaKL. Thus, in contrast to Derouane and Vanderveken (*4*), Tauster and Steger

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(*7*) claim that zeolite L is not unique and it is only the presence of a zeolite that is necessary for high aromatization selectivity. Tennison *et al.* (*9*) show that *n*-hexane can form benzene at selectivities near those reported from Pt/BaKL using Pt/carbon catalysts. We speculate that this carbon is in fact microporous due to the high Pt dispersion. Thus, the presence of a zeolite may not be necessary. However, microporosity may play a significant role in achieving high aromatization selectivities. Very recently, Davis and Derouane (*10*) reported that the *n*-hexane aromatization selectivity from Pt/Mg(Al)O is similar to that of Pt/KL. These authors rule out any effects of microporosity and instead speculate on metal–support interactions between Pt clusters and a high surface area basic support. These studies taken in total do not lead to a consistent picture of the true role of the catalyst in obtaining high *n*-hexane aromatization selectivities.

Recently, our group has been involved in two investigations which have lead to new catalytic materials that should be useful in helping to understand the essential physicochemical properties necessary for high *n*-hexane aromatization selectivities. First, VPI-5 (*11*) is an aluminophosphate molecular sieve with unidimensional pores of 12–13 Å diameter. Since $AlPO_4$'s are neutral, VPI-5 provides a neutral unidimensional pore system larger than zeolite L to explore pore sizes above 7–8 Å. Second, Hathaway and Davis (*12, 13*) have shown how to prepare zeolite Y (CsNaY) which is as basic as MgO. Thus, zeolite Y can be synthesized in an acidic, neutral, and basic form.

The purpose of our work is to elucidate the physicochemical properties of catalytic materials which are essential to produce high aromatization selectivities from normal alkanes. We report results from a broad spectrum of catalytic materials which show variations in acidity/basicity, microporosity, chemical composition, and structure. In this paper, we describe the materials preparation and physicochemical properties. Our accompanying reports (*14, 15*) describe further the details of the catalytic results.

EXPERIMENTAL

Materials

NaY (SiO_2/Al_2O_3 = 4.86) and KL (SiO_2/Al_2O_3 = 6.0) were obtained from Strem and Union Carbide, respectively. $Pt(NH_3)_4(NO_3)_2$ and $Pt(acac)_2$ were purchased from Strem. $AlPO_4$-5 was synthesized in accordance with the Union Carbide procedure (*16*). As-synthesized $AlPO_4$-5 was then calcined in air at 600°C for 6 h to remove the organic template prior to Pt loading. $AlPO_4$-5 is an aluminophosphate molecular sieve which contains a unidimensional cylindrical pore system consisting of 12-membered rings that have a molecular diameter of 7.3 Å (*16*). VPI-5 was synthesized and activated according to the procedures that are given elsewhere (*17*). FAU(C) and hex with the bulk SiO_2/Al_2O_3 ratio of 6.8 were prepared according to the procedures developed by Delprato *et al.* (*18*) and our group (*19*). We denote FAU(C) and hex as the cubic and hexagonal faujasites which are synthesized using crown ethers as structure-directing agents (*18, 19*). As-synthesized FAU(C) and hex samples were calcined in air at 500°C for 1 h in order to remove the crown ethers occluded in the cages of the zeolites. ZSM-12 with SiO_2/Al_2O_3 of 140 was synthesized using triethylmethylammonium bromide as a structure directing agent following the procedure of Weitkamp and co-workers (*20*). SSZ-24, which is the pure silica form of $AlPO_4$-5 was prepared by a modification of examples, 1, 3 and 10 in the Chevron patent (*21*).

Exchange Procedure

All the molecular sieves were exchanged at 0.02 g/ml. The NaY and KL were refluxed twice in 1.0 *M* $NaNO_3$ and 1.0 *M* KNO_3 solutions for 4 h, respectively, in order to ensure the complete corresponding cation forms. BaKL was prepared by ion exchange of KL three times with 0.3 M $Ba(NO_3)_2$ solutions followed by drying at 110°C and calcination in air at 600°C for 16 h. The Na forms of FAU(C), hex, and ZSM-12 were prepared by refluxing twice in 1.0 M $NaNO_3$ solutions for 4 h. CsNaY was prepared by the procedure given elsewhere (*12, 13*).

Platinum Loading Procedures

Pt was loaded onto the support materials by ion exchange, liquid phase impregnation, and vapor phase impregnation. $Pt(NH_3)_4(NO_3)_2$ and $Pt(acac)_2$ were used in ion exchange and in liquid and vapor phase impregnation methods, respectively.

Ion exchange. 40.9 mg of $Pt(NH_3)_4(NO_3)_2$ dissolved in 20 ml of H_2O was added dropwise to a slurry of the solid support (2 g) in 50 ml of H_2O. After being stirred for 6 h, the powder was carefully filtered, washed with H_2O, and then dried in air at room temperature. The color of the $Pt(NH_3)_4^{2+}$-exchanged material was white.

Liquid phase impregnation. 41.6 mg of $Pt(acac)_2$ was first dissolved in 20 ml of acetone and then 2 g of dehydrated (heated to 350°C under vacuum for 4 h) molecular sieve were added with vigorous stirring. The sample was evacuated to dryness after slurrying at room temperature for 1 h.

Vapor phase impregnation. The amounts of $Pt(acac)_2$ and the dehydrated molecular sieve used for the vapor phase impregnation are the same as those used in the liquid phase impregnation. $Pt(acac)_2$ was physically mixed with the dehydrated molecular sieve inside a tube with volume of 15 ml. The mixture was kept under a vacuum of better than 10^{-4} Torr and sealed. The sample (in the sealed tube) was slowly heated to 145°C and then stored at this temperature for 16–24 h. When $Pt(acac)_2$ began to sublime, the color of the sample changed (was dependent on the type of molecular sieve). After heat treatment, the sample was slowly cooled to room temperature (20°C/h). Regardless of the Pt loading method, the content of Pt added in each loading step was fixed to approximately 1 wt% or less of the corresponding molecular sieve weight.

Pt/BaKL was prepared by the three methods described above in order to investigate the influence of different loading methods on the physicochemical properties of the catalysts. Pt loadings into other zeolites (KL, NaY, CsNaY, FAU(C), hex, ZSM-12, and SSZ-24) were carried out by vapor phase impregnation only. Both liquid phase and vapor phase impregnation methods were used in preparing Pt-containing $AlPO_4$-5 and VPI-5. Table 1 summarizes the types of catalysts prepared and the Pt loading methods used.

TABLE 1

Detailed Information on Pt-Containing Molecular Sieves

Sample	Material	Method of Pt loading[a]	Wt% Pt	Total H/Pt
A	BaKL	VI	0.79	1.43
B	BaKL	EX	0.21	2.06
C	KL	VI	0.75	1.56
D	NaY	VI	0.51	0.82
E	CsNaY	VI	0.65	0.63
F	hex	VI	0.63	1.10
G	Na-hex	VI	0.75	1.72
H	FAU(C)	VI	0.82	1.44
I	Na-FAU(C)	VI	0.74	1.89
J	Na-ZSM-12	VI	0.18	1.75
K	SSZ-24	VI	0.70	0.72
L	$AlPO_4$-5	VI	0.80	0.77
M	VPI-5	VI	0.68	0.69

[a] VI, vapor phase impregnation; EX, ion exchange.

The $Pt(acac)_2$ content of the catalysts for the ^{13}C MAS NMR measurements was adjusted to 6 wt% (3 wt% Pt) in both liquid and vapor phase impregnation methods in order to increase the ^{13}C content. Prior to ^{13}C NMR measurements, the samples prepared by the liquid phase impregnation method were evacuated at room temperature under vacuum overnight in order to ensure the complete removal of the solvent acetone.

Analytical Methods

The X-ray powder diffraction patterns of all materials were recorded on a Siemens I2 X-ray diffractometer.

Transmission electron micrographs (TEMs) were recorded on a Philips 420-T scanning and transmission electron microscope with an acceleration voltage of 100 kV.

The Pt contents of the catalysts were obtained using a Jerrell–Ash Atomscan 2400 inductively coupled plasma (ICP) spectrometer.

The hydrogen chemisorption measurements were carried out at ambient temperature in a Coulter, Omnisorp-100 CX Analyzer. Prior to the chemisorption experiment, the samples were outgassed at a temperature of 400°C in vacuum and then reduced in a flowing stream of hydrogen at 400°C for 8 h. After reduction, the samples were outgassed at 400°C for 1 h, cooled to room temperature in vacuum, and then the isotherms were recorded. This procedure gives the total amount of adsorbed hydrogen. Thus, the data given in Table 1 are listed as total H/Pt.

Magic angle spinning ^{13}C NMR spectra were measured on a Bruker MSL 300 spectrometer. The ^{13}C NMR spectra were taken at a frequency of 75.47 MHz with sample spinning rates of about 4 kHz. Typically, 20,000 scans were accumulated and chemical shifts are reported relative to TMS.

RESULTS AND DISCUSSION

Platinum Loading Method

Since $AlPO_4$-5 and VPI-5 have virtually no cation exchange capacity, it is not possible to load Pt into the neutral pores of $AlPO_4$-5 and VPI-5 by conventional methods such as ion exchange. Thus, liquid and vapor phase impregnation methods using an organoplatinum compound were attempted to load Pt into the neutral pores of $AlPO_4$-5 and VPI-5. The choice of a suitable Pt precursor compound is important for the vapor phase impregnation method because the Pt precursor should be as volatile and small as possible. $Pt(acac)_2$ is one of the smallest organoplatinum compounds and it is reported to be sublimed at 82°C under a pressure of 1 Torr without decomposition (*22*). Thus, $Pt(acac)_2$ was chosen as the Pt precursor compound for both liquid and vapor phase impregnation methods in this study.

The Pt/$AlPO_4$-5 and Pt/VPI-5 catalysts prepared by liquid phase impregnation are yellow like that of $Pt(acac)_2$. The Pt/BaKL catalyst prepared by the same method is also yellow. However, the samples prepared by vapor phase impregnation method show colors which are dependent on the type of the molecular sieve. The $Pt(acac)_2$-containing $AlPO_4$-5 and VPI-5 are brown, while $Pt(acac)_2$-containing zeolites are light gray. These color variations may be due to the differences in the interaction of $Pt(acac)_2$ with the internal and/or outer surface of the molecular sieves. However, the precise reason for this behavior remains unknown to us. The color of the catalysts prepared by both liquid and vapor phase impregnation methods is generally more intense with increasing $Pt(acac)_2$ content, and in both cases changes to dark gray after the reduction step. When the reaction mixture of $Pt(acac)_2$ and molecular sieve is exposed to temperatures higher than 170°C, the color of the sample changes from yellow to black and is due to the decomposition of $Pt(acac)_2$. Also, the color of the reaction mixture remains almost unchanged when the heating temperature is below 110°C, indicating that most of the $Pt(acac)_2$ is not sublimed. The optimum temperature obtained in this study is approximately 145°C. The heating time affects the dispersion of $Pt(acac)_2$ in the molecular sieve. For the case of the mixture of $Pt(acac)_2$ with $AlPO_4$-5, about 16 h heating at the optimum temperature is required to make the color of the mixture homogeneous. The smaller the pores of the molecular sieve, the longer the heating time that is needed. When the pressure inside the tube is on the order of 10^{-2} Torr, the color of the reaction mixture heated at 145°C changes to black, indicating that $Pt(acac)_2$ is not sublimed but rather decomposed. This result demonstrates the importance of maintaining the pressure inside the sealed tube as low as possible in order to sublime $Pt(acac)_2$ without decomposition.

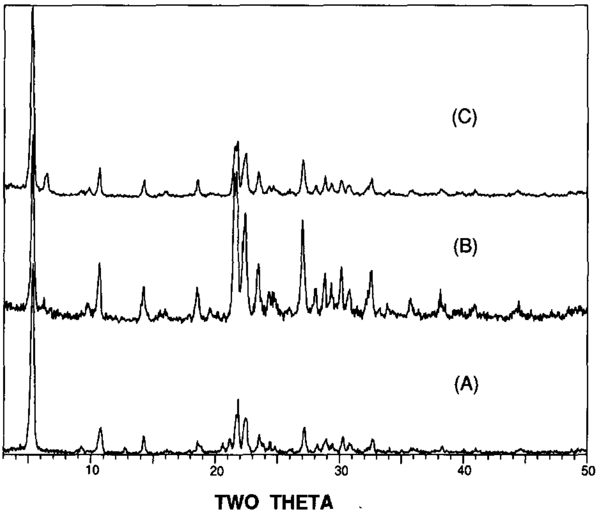

FIG. 1. X-ray powder diffraction patterns of Pt-containing VPI-5: as – synthesized (A), after reduction (B), and after *n*-hexane aromatization (C).

X-Ray Powder Diffraction

X-ray diffraction patterns of the Pt-containing molecular sieves show that the structures of all the molecular sieves remain intact during the Pt loading, reduction, and *n*-hexane aromatization, regardless of the Pt loading method. Since there is some controversy concerning the stability of VPI-5, we illustrate all results involving these samples. Figure 1 gives the X-ray diffraction patterns of the Pt/VPI-5 samples prepared by the vapor phase impregnation method after the various treatment steps. All the characteristic peaks of VPI-5 remained intact during the Pt loading and reduction steps. However, a small amount of $AlPO_4$-8 (small peak at $2\Theta = 6.5°$ in Fig. 1C) is observed in the Pt-containing VPI-5 catalyst after *n*-hexane aromatization. $AlPO_4$-8 has a unidimensional 14-ring channel system with pore dimensions of 7.8 × 8.7 Å between oxygen atoms (*23*). Also, there are no X-ray peaks from Pt particles, indicating that the particle size is small. Further evidence to support this claim is provided below.

^{13}C MAS NMR Measurements

Table 2 shows the ^{13}C NMR chemical shift values of $Pt(acac)_2$ supported on the molecular sieves by various preparation methods. There are three types of C atoms in $Pt(acac)_2$: methyl, methylene, and carbonyl.

TABLE 2

^{13}C NMR Chemical Shift Values of $Pt(acac)_2$-Containing Molecular Sieves

Sample	Material	Preparation method[a,b]	Shift (ppm) of ^{13}C atoms in $Pt(acac)_2$		
			$—CH_3$	$—CH_2—$	C=O
I	$Pt(acac)_2$	—	25.9, 26.9	104.8	185.5
II	BaKL	PM	25.9, 26.9	104.8	185.5
III	BaKL	VI	26.3, 30.3	103.4	189.7
IV	BaKL	LI	25.9, 26.9	105.0	185.2
V	$AlPO_4$-5	PM	25.9, 26.8	104.8	185.5
VI	$AlPO_4$-5	VI	24.0, 30.2	102.0	188.2
VII	$AlPO_4$-5	LI	26.0, 26.9	104.8	185.5
VIII	VPI-5	VI	24.7, 30.0	103.7	188.2
IX	VPI-5	LI	26.0, 27.0	104.8	185.1

[a] The content of $Pt(acac)_2$ added in the Pt loading step is 6 wt% of the molecular sieve.

[b] PM, physical mixture; VI, vapor phase impregnation; LI, liquid phase impregnation.

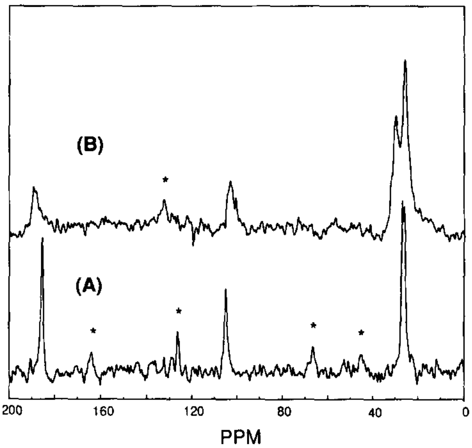

FIG. 2. ^{13}C NMR spectra of $Pt(acac)_2$ (A) and $Pt(acac)_2$-containing BaKL prepared by the vapor phase impregnation method (B). Peaks marked by * are spinning side bands.

The ^{13}C MAS NMR spectra of $Pt(acac)_2$ and the sample III in Table 2 are given in Fig. 2. The ^{13}C NMR spectrum of $Pt(acac)_2$ shows two peaks at 25.9 and 26.9 ppm which are attributed to methyl C atoms in the acac ligand. This indicates that all the methyl groups in $Pt(acac)_2$ are not in the same chemical environment. The peaks at 104.8 and 185.5 ppm can be assigned to the methylene and carbonyl C atoms in the acac ligand, respectively. The $Pt(acac)_2$ in sample III, which is prepared by the vapor phase impregnation method, shows considerably different chemical shift values from those of $Pt(acac)_2$ itself. The peaks due to the methyl C atoms in the acac ligand are observed at 26.9 and 30.3 ppm. The half-band width (about 200 Hz) of the peak at 26.9 ppm is more than three times larger than that of $Pt(acac)_2$ at 25.9 or 26.9 ppm (about 60 Hz). Furthermore, the peak from the carbonyl C atom in the acac ligand is observed at 189.7 ppm, which shifts 4.2 ppm from the corresponding peak of $Pt(acac)_2$ at 185.5 ppm. Such changes in the chemical shift values may be due to the interaction of $Pt(acac)_2$ with the BaKL pore walls. The $Pt(acac)_2$ in the samples VI and VIII, which is supported on $AlPO_4$-5 and VPI-5, respectively, also shows similar chemical shift values to those of sample III. These data are consistent with the loading of the Pt precursor compound into the micropores of molecular sieves with neutral as well as charged frameworks via the vapor phase impregnation method.

The samples prepared by liquid phase impregnation (samples VI, VII, and IX) show the same ^{13}C NMR chemical shift values as those of $Pt(acac)_2$ or a physical mixture of $Pt(acac)_2$ with the molecular sieve (II and V). There is also no difference in the half-band width of the peaks between these samples and $Pt(acac)_2$. This suggests that the chemical environment of $Pt(acac)_2$ is not affected by the presence of the molecular sieve. That is, most of the $Pt(acac)_2$ in the BaKL, $AlPO_4$-5 and VPI-5 prepared by liquid phase impregnation does not exist inside the pores but on the outer surface. It is expected that a complex of $Pt(acac)_2$ with acetone, which is much larger than $Pt(acac)_2$ alone, is formed when the $Pt(acac)_2$ molecule is solvated by acetone. Hence, the solvated complex may be too large to enter the pores of BaKL, $AlPO_4$-5 and VPI-5. Furthermore, the loading of Pt into micropores by liquid phase impregnation may be more difficult if the interaction of $Pt(acac)_2$ with solvent molecules is much stronger than that with the pore walls. Therefore, it is concluded that the loading of $Pt(acac)_2$ into the micropores of molecular sieves via vapor phase impregnation is possible while loading by liquid phase impregnation is not. Further evidence to support this conclusion is given below. Persaud *et al.* (*24*) deposited $Pt(acac)_2$ exclusively into the channels of zeolite L using a liquid phase impregnation method. However, the maximum Pt loading by this method was less than 0.01 wt%. Here we are approximately two orders of magnitude higher in Pt concentration. If we have in fact loaded a very small amount of intrazeolitic Pt like Persaud *et al.* via our liquid phase impregnation method, it would not be detectable in the presence of the large abundance of extracrystalline $Pt(acac)_2$.

Hydrogen Chemisorption Measurements

All Pt-loaded molecular sieves were characterized by hydrogen chemisorption. Since hydrogen chemisorption onto Pt can be performed in different ways and yield different results (*25*), chemisorption results obtained in this work are shown as the ratio of the total number of chemisorbed hydrogen atoms over the total number of platinum atoms (H/Pt) (Table 1). Hydrogen chemisorption did not occur on the molecular sieves in the absence of Pt.

The H/Pt ratio from ion exchanged Pt/BaKL (sample B) is 2. H/Pt values above 1 have been reported for highly dispersed Pt on nonzeolitic (*25*) and zeolitic supports (*25*, *26*). In fact, Boudart *et al.*(*27*) report H/Pt = 2 for small Pt clusters located within the supercages of zeolite Y. Note that the H/Pt from the Pt/BaKL sample prepared by vapor phase impregnation also gives a very high value and is similar to the value (1.3) reported by Vaarkamp *et al.* (*26*). Thus, the Pt in sample A must be intrazeolitic. Samples A and C-M of Table 1 are listed to show the broad range of molecular sieves for which we have exploited the use of the vapor phase impregnation technique to create Pt clusters within microporous environments. For most samples, the H/Pt ratios are high indicating good dispersion.

Transmission Electron Microscopic (TEM) Measurements

Figure 3 shows TEM pictures of the Pt/BaKL catalyst prepared by the vapor phase impregnation method before and after use in the *n*-hexane aromatization reaction (see accompanying reports for reaction conditions (*14*, *15*)). In general, the Pt particles cannot be observed in the as-synthesized Pt/BaKL catalyst, indicating that they are well-dispersed over the BaKL crystal. As seen in Figure 3A, rarely there is an observable Pt particle which exists between the lattice planes of zeolite L. The Pt/BaKL catalyst prepared by ion exchange shows also TEMs similar to those given in Figure 3A. The average Pt particle size of the BaKL catalyst after *n*-hexane reaction must be close to that of the Pt/BaKL before reaction since no large Pt particles are observed after exposure to reaction conditions (Fig. 3B). This indicates that Pt particles in BaKL do not migrate to the surface of the catalysts at reaction conditions (510°C) in a time period of approximately 10–20 h. However, it cannot be ruled out that the sintering of small Pt particles (<10 Å) that remain within the micropores may occur during the reaction.

The TEM (not shown) of the Pt/$AlPO_4$-5 catalyst prepared by the liquid phase impregnation method shows that the average particle size is larger than 200 Å and that the morphology of Pt particles is irregular. The micrograph indicates that most of the Pt particles are located on the outer $AlPO_4$-5 surface rather than inside the $AlPO_4$-5 pores. However, the sample prepared by the vapor phase impregnation method shows that Pt particles with diameters of 20–30 Å are well-dispersed over the $AlPO_4$-5 crystal and that the particle size distribution is narrow. No Pt particles are observed on the outer $AlPO_4$-5 surface, unlike the sample prepared by the liquid phase impregnation method. Figure 4 shows TEM pictures of the Pt/VPI-5 catalyst which are prepared by the vapor phase impregnation method before and after use in the *n*-hexane aromatization reaction.

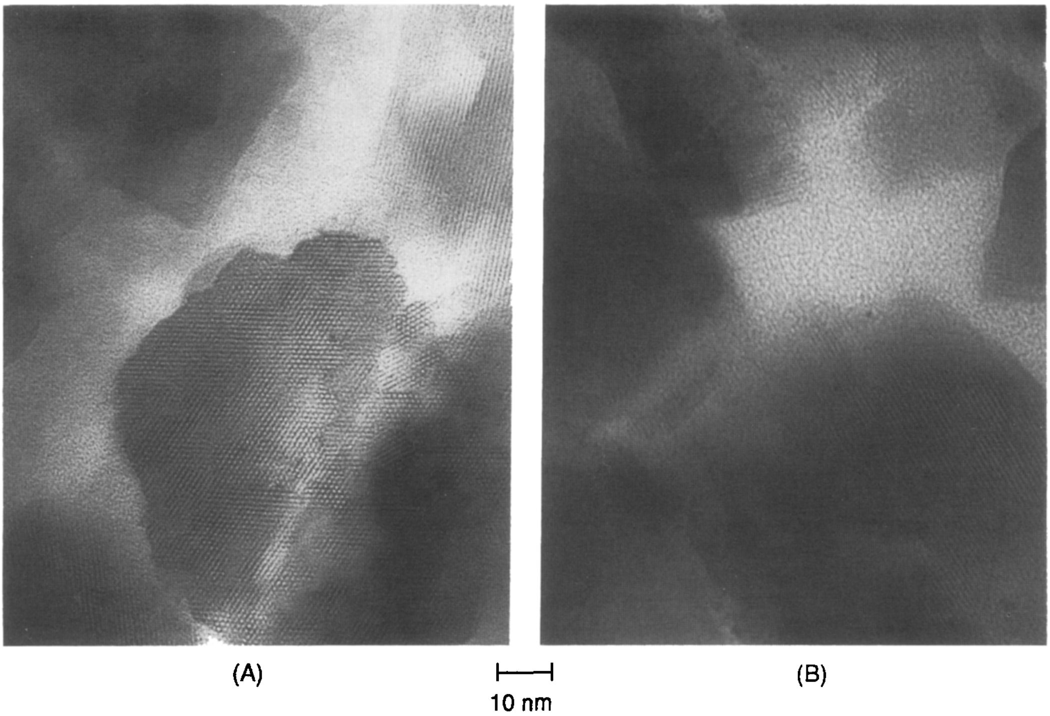

FIG. 3. TEM pictures of Pt/BaKL catalysts before (A) and after (B) *n*-hexane aromatization.

The Pt particles are well-dispersed over the VPI-5 crystals. The average particle size is similar to that of Pt/$AlPO_4$-5. Large Pt particles are not observed on the outer crystal surfaces of the $AlPO_4$-5 and VPI-5 catalysts after *n*-hexane reaction. The average Pt particle size of the sample after reaction is similar to that of the sample before reaction.

The average Pt particle size observed in Fig. 4 is still larger than the pore size of the molecular sieve. Rice *et al.* (*28*) have discussed the difficulties in imaging Pt clusters of fewer than 20 atoms in zeolites and Pan *et al.* (*29*) recently reported that the particle size distribution of highly dispersed Pt particles in zeolite Y determined by TEM is very sensitive to experimental conditions. This is because the zeolites are easily damaged when the incident beam is sufficiently strong (200 kV). They report that the incident electron beam causes the extremely small Pt particles (<10 Å) to sinter. This process is promoted by the local structure destruction. In this study all TEM pictures were recorded at 100 kV. Lattice fringes of $AlPO_4$-5 and VPI-5 completely disappear within 10 s in the electron beam and continued exposure creates large holes (100–1000 Å) within the crystals. Therefore, the TEMs shown in Fig. 4 certainly do not indicate the state of Pt prior to contact with the electron beam. The points illustrated by our TEM results are (i) the vapor phase impregnation method can produce intracrystalline Pt and (ii) the Pt does not migrate to the outer surface of the molecular sieve crystals during reaction. We do not believe that the observed particle sizes are really representative of the size of the Pt particles exposed to reaction conditions. We believe that they are smaller than those illustrated by TEM (see hydrogen chemisorption results).

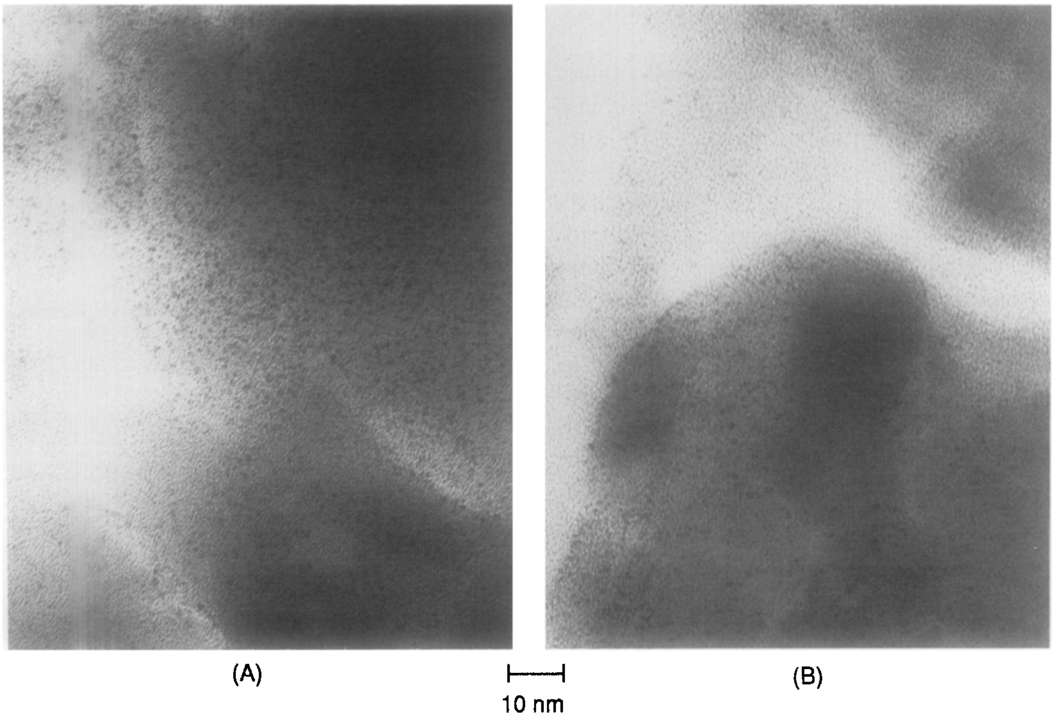

FIG. 4. TEM pictures of the Pt/VPI-5 catalysts before (A) and after (B) *n*-hexane aromatization.

Summary of the Vapor Phase Impregnation Method

It is well known that the physicochemical properties of the metal loaded catalysts can be significantly modified according to the loading method of metal. Metal loading by the vapor phase impregnation method has two advantages. First, it is possible to load metal into the molecular sieves with neutral frameworks as well as charged frameworks. Second, metal loading by this method should not change the acid/base properties of the molecular sieve. Metal loading by ion exchange can alter the acidic properties of the molecular sieve since metal cations added in the ion exchange step can be exchanged not only with H^+ but also with other cations neutralizing the acidic sites of the molecular sieve. Furthermore, the reduction step can produce H^+. Metal loading into aluminosilicate molecular sieves is generally carried out by ion exchange since they have cation exchange capacities. The Pt loadings into aluminosilicate molecular sieves in this study were attempted mainly by the vapor phase impregnation method in order to compare their catalytic properties with those of Pt/$AlPO_4$-5 and Pt/VPI-5 prepared by the same method. Our ^{13}C NMR and TEM results show that microporous Pt loadings into the molecular sieves with neutral frameworks as well as charged frameworks via vapor phase impregnation are successful (vide supra).

It is observed that Pt loading by the vapor phase impregnation method may be influenced by the factors (i) heating temperature, (ii) heating time, and (iii) the pressure inside the sealed tube containing the reaction mixture. We have found that it is necessary that $Pt(acac)_2$ and the molecular sieves be fully dehydrated and kept in a vacuum of better than 10^{-4} Torr for the successful sublimation of $Pt(acac)_2$.

Berg and Hartlage showed that most acetylacetonate (acac) forms of divalent and trivalent metal cations can be easily sublimed below their decomposition temperature under low pressure (*22*). This suggests that a broad spectrum of metal acetylacetonate complexes can be used as metal sources in the vapor phase impregnation method. Hence, we believe that the vapor phase impregnation method can be used to load other metals such as Ni or Co into the micropores of the molecular sieves with charged as well as neutral frameworks. In addition, calcination of microporous acetylacetonate complexes in O_2 or air can lead to microporous metal oxide particles.

Finally, Schweizer (*30*) very recently disclosed the use of $Pt(acac)_2$ and/or $Pd(acac)_2$ in creating noble metal-containing zeolites which possess an "egg-shell" of noble metal. His method is significantly different from the vapor phase impregnation method shown here in that it is purposefully designed not to disperse intact $Pt(acac)_2$ thoughout the zeolite.

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