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# $^{129}$Xe NMR Proof for the Distribution of Platinum Species during Pt/NaY Preparation by $H_2PtCl_6$ Impregnation and $Pt(NH_3)_4^{2+}$ Cation Exchange Methods

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$^{129}$Xe NMR spectroscopy was used to measure the distribution of platinum species during the preparation of Pt/NaY catalysts by the impregnation of $H_2PtCl_6$ or the cation exchange of $Pt(NH_3)_4^{2+}$ into a NaY zeolite. The location of platinum species during the impregnation was found to be affected by the impregnation time and the drying mode. More uniform distributions of platinum species in the impregnation were achieved by longer thermal treatments in a 100% relative humidity chamber before calcination. However, the cation exchange method gave uniform distribution of Pt species in the zeolite channel throughout the ion exchange, calcination, and reduction. This result was consistent with the rate of $H_2PtCl_6$ adsorption on the NaY zeolite in aqueous solution and the platinum metal dispersion of the Pt/NaY samples.

## INTRODUCTION

Impregnation of a desired active species onto a porous support with a solution is a common practice in the manufacture of catalysts. The impregnation method commonly involves contacting the support with the impregnating solution for a certain period of time, drying the support to remove the imbibed liquid, and activating the catalyst by calcination, reduction, or other appropriate treatment. Any of these steps can affect the particle size and the local concentration of the active species on the support. Since Maatman and Prater (*1, 2*) reported an attempt to predict and control the concentration profile of platinum species on alumina supports, many theoretical and experimental works on the prediction and the control of the impregnation profile have been published (*3–15*).

The distribution of an active component on the surface of the support pore can be measured by the electron probe microanalyzer (*3–10*), the scanning microscope (*11*), autoradiographic (*12*) or light transmission techniques (*10*), and staining methods (*1, 2, 13–15*). All these methods are suitable to probe a macroscopic distribution of the concentration profile on supports such as silica or alumina. However, it is difficult to detect a rather microscopic concentration distribution inside the NaY zeolite crystallite of normally 1 μm in diameter. Recently, Fraissard and coworkers (*16–18*) have found that $^{129}$Xe NMR of xenon gas adsorbed on zeolites is a very sensitive probe of local environment inside the zeolite channel (*16–19*). The adsorbed xenon atoms can be more or less polarized by rapid collisions or adsorption on the zeolite walls, other xenon atoms, and other species present inside the zeolite channel. The magnitude of the polarization is therefore signaled by the chemical shift of $^{129}$Xe NMR. The chemical shift of $^{129}$Xe

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TABLE 1

Preparation of Pt/NaY Samples

| | IMPt/NaY-D | IMPt/NaY-DT | IMPt/NaY-LDT | IEPt/NaY |
|---|---|---|---|---|
| Method | Impregnation | Impregnation | Impregnation | Ion exchange |
| Stirring time (h)[a] | 0 | 5 | 5 | 24[b] |
| Evaporation time (h) | 0.2 | 2 | 2 | — |
| Thermal treatment (h) | 0 | 12 | 48 | — |
| Calcination temp. (K) | 573 | 573 | 573 | 573 |
| Reduction temp. (K) | 673 | 673 | 673 | 673 |
| Pt content (wt%)[c] | 4 | 4 | 4 | 4 |

[a] The NaY slurry in CPA solution was stirred in rotary evaporator at 343 K except for the IEPt/NaY.

[b] NaY (10 g) was stirred in 1000 ml aqueous solution of $Pt(NH_3)_4Cl$ at 343 K by magnetic stirrer.

[c] Pt content after the final reduction of Pt/NaY.

NMR can thus become a useful probe to monitor the changes in the chemical state and the number of active species inside the supercage of Y zeolites. However, the species located inside the sodalite cage does not alter the chemical shift because a xenon atom of 0.43 nm size cannot enter through the cage window of 0.22 nm size. The change in the chemical shift caused by the active species adsorbed on the external surface of the zeolite crystal is also negligible since the amount of xenon adsorbed inside the crystal is much greater than that experiencing collisions or adsorption on the external surface. In this way, $^{129}Xe$ NMR provides useful information about the location of a metallic species within the zeolite channel. Ito *et al.* (*20*) reported that a $^{129}Xe$ NMR investigation of xenon adsorbed on coke-fouled zeolite provided quantitative information on the distribution of carbonaceous residues during coking and after decoking. Boudart *et al.* (*21*) also reported that the surface of platinum supported on alumina prepared by impregnation could be characterized by the $^{129}Xe$ NMR method.

In this work, the $^{129}Xe$ NMR method was used to measure the distribution of platinum species during the preparation of Pt/NaY catalysts by the initial impregnation of $H_2PtCl_6$ or the ion exchange of $Pt(NH_3)_4^{2+}$ into NaY zeolite and proper successive treatments.

## EXPERIMENTAL

A NaY zeolite of 0.7-$\mu$m-mean-diameter crystal supplied by Strem Chemical Co. was used as a support. A series of Pt/NaY samples was prepared in the following way. The first sample was prepared by quickly evaporating water at 343 K immediately after 5-g NaY was allowed to form a slurry in 100 ml of 0.01 *M* $H_2PtCl_6$ (CPA, Aldrich) solution. The evaporation, which was carried out in a rotary evaporator, took about 10 min. The second sample was prepared by stirring the same slurry of NaY in CPA solution for 5 h at 343 K and then by evaporating water at 343 K over 2 h. This sample was kept in 100% relative humidity chamber at 343 K for 12 h. This step was called thermal treatment. The third sample was prepared in the same way as the second except that the thermal treatment was performed four times longer. The last sample was prepared by an ion exchange treatment of the NaY zeolite with an aqueous solution of $Pt(NH_3)_4Cl^{2+}$ (Strem) via the procedure of Gallezot *et al.* (*22*). The samples thus prepared were designated as IMPt/NaY-D, -DT, and -LDT, and IEPt/NaY (Table 1), respectively.

About 0.5 g of sample was placed into an NMR tube which had specially designed vertical ground-glass stopcocks. It was evacuated at 313 K for 48 h until the pressure in vacuum manifold decreased to $1 \times 10^{-5}$ Torr. Xenon gas (Matheson, 99.995%) at various pressures was then equilibrated with the sample at 296 K to obtain $^{129}$Xe NMR spectra. Afterward, the sample was placed in a Pyrex U-tube flow reactor which was connected to the NMR tube. It was calcined by $O_2$ (99%, dried through molecular sieve 3A trap) flowing at 1000 ml g$^{-1}$ min$^{-1}$ while the temperature was raised from room temperature to 573 K over 12 h and kept there for 2 h. It was subsequently evacuated at 573 K for 2 h under $1 \times 10^{-5}$ Torr. The sample was transferred from the reactor to the NMR tube *in situ*. The NMR tube was then sealed off by a flame. Xenon gas was again equilibrated with the sample to obtain $^{129}$Xe NMR spectra.

Another 0.5-g aliquot of the impregnated or cation-exchanged sample was calcined and evacuated in the same way as described above. It was then reduced in $H_2$ (Matheson, 99.999%) flowing 150 ml$^{-1}$ at 673 K for 2 h. The NMR spectra were obtained *in situ* as described above after the sample was evacuated at 673 K for 2 h. Platinum content of all the samples was 4.0 wt% after the reduction.

The $^{129}$Xe NMR spectra was obtained at 296 K by a Bruker AM 300 instrument operating at 83.0 MHz for $^{129}$Xe. Each spectrum was taken after acquisition of 100 to 5000 pulse transients with a 0.5-s repetition time. The chemical shift value was referenced with respect to xenon gas extrapolated to zero pressure.

The adsorption isotherm of $H_2$ on the Pt/NaY sample was volumetrically obtained at 296 K after all the preadsorbed hydrogen was desorbed at 673 K and $1 \times 10^{-5}$ Torr for 1 h. The total number of hydrogen atoms chemisorbed per platinum atom ($H_{total}/Pt_{total}$) was determined by extrapolating the high-pressure linear part of the isotherm to zero pressure. Another adsorption isotherm was obtained after the preadsorbed hydrogen was desorbed at 296 K and $1 \times 10^{-5}$ Torr for 1 h. The difference between the two isotherms was a horizontal straight line and corresponded to the number of hydrogen atoms chemisorbed irreversibly ($H_{irrev.}/Pt_{total}$) at 296 K. The rate of CPA adsorption on NaY was determined from the decrease of the intensity of 295-nm UV absorbance of the impregnating solution.

## RESULTS AND DISCUSSION

In Fig. 1, the amount of adsorbed CPA is plotted as a function of impregnation time. The amount of CPA present initially in the solution corresponded to $2.1 \times 10^{-4}$ mole Pt/g-NaY. The adsorption of CPA was nearly saturated after 5 h, and 40% of the total platinum species was adsorbed on the NaY at this time. Fenelonov *et al.* (*23*) and Neimark *et al.* (*24*) classified catalyst according to $P$ value, the ratio of adsorbed solute to unadsorbed solute. They called the catalysts sorption catalysts if $P \gg 1$, impregnated catalysts if $P \ll 1$, and sorption-impregnated catalysts if $P = 0.2$ to 5.0. In our case, the $P$ value is 0.67 (from Fig. 1). Therefore, our impregnated Pt/NaY can be called a sorption-impregnated catalyst. Maatman and Prater (*2*) reported that the initial adsorption of CPA was negligible with silica supports, low but appreciable with silica–alumina, and relatively dominant with high surface-area alumina and carbon. Our $P$ value with a NaY zeolite support is much lower than that previously reported with

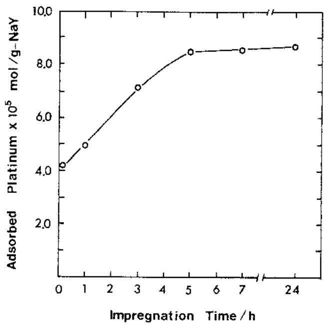

FIG. 1. The amount of $H_2PtCl_6$ adsorbed on NaY from the impregnating solution at 343 K.

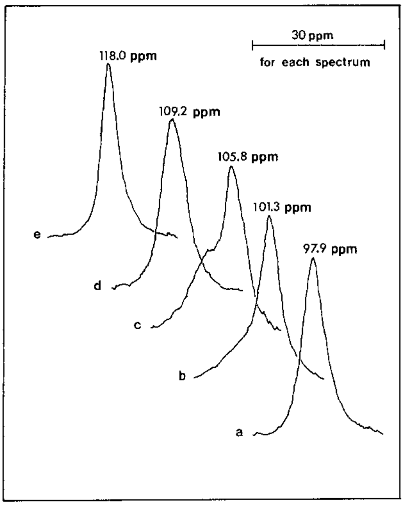

FIG. 2. $^{129}$Xe NMR spectra of (a) NaY, (b) IMPt/NaY-D, (c) IMPt/NaY-DT, (d) IMPt/NaY-LDT, and (e) IEPt/NaY after vacuum treatment at 313 K (400 Torr xenon at 296 K).

alumina, which indicates a strong sorption of CPA (*2, 6*), and thus the strength of the adsorption of chloroplatinic acid (CPA) on the NaY zeolite can be comparable to that of silica–alumina. For a good distribution of platinum metal on the NaY support, the secondary impregnation of CPA achieved on evaporation of the solvent is as important as the initial CPA-adsorption from the solution.

The $^{129}$Xe NMR spectra shown in Fig. 2 were obtained at 400 Torr and 296 K from the NaY zeolite and the Pt/NaY samples which were prepared with different treatments after the dried samples were evacuated under $1 \times 10^{-5}$ Torr at 313 K. According to de Ménorval *et al.* (*16*), the chemical shift of $^{129}$Xe NMR should increase linearly with respect to the number of targets with the xenon atom adsorbed in the zeolite channel interacts. Moreover, the amount of xenon adsorbed inside the zeolite supercages is much more than that adsorbed on the external surface or present in the gas phase. Therefore, the chemical shift increase from Fig. 2a to Fig. 2d can provide evidence that the thermal treatments applied to Pt/NaY-DT and Pt/NaY-LDT samples were very effective for the platinum species adsorbed on the external surface of NaY to diffuse into the NaY zeolite channels. This redistribution of platinum species during the thermal treatment can be explained as follows. When a sample filled with impregnating solution is subjected to heating, heat is transferred from the external surface to the interior of the sample, establishing a temperature gradient. Evaporation of water begins at the external surface, resulting in a receding gas–liquid interface. The impregnant in the solution increases its concentration at the menisci, and it begins to deposit on the pore wall when the concentration exceeds the saturation point. If the drying proceeds slowly enough, the impregnant diffuses into the remaining liquid. As a result, zeolite supports with uniform pores have a tendency to redistribute the impregnant toward vacant sites in the crystal. Our result is similar to that of Maatman and Prater (*2*). According to their results, chloroplatinic acid impregnation onto $\alpha$-alumina gives an eggshell profile if the pellets are dried immediately after the impregnation, while a virtually uniform Pt profile is obtained if they are kept wet in a closed container at 100% relative humidity for 3 h (*2*).

Ryoo *et al.* (*25*) recently reported that a complete intercrystalline diffusion of xenon atoms can take place at room temperature on the time scale of the difference between the inverse NMR frequences obtained from NaY and 2% Pt/NaY zeolites consisting of approximately 1-$\mu$m crystals. In this work, a 1 : 1 mixture of IEPt/NaY and NaY zeolite was ground in a mortar, rereduced in flowing $H_2$, and treated under vacuum at 673 K. Xenon gas of 400 Torr was equilibrated on this mixture at 296 K. Figure 3a, a $^{129}$Xe NMR spectrum obtained at 296 K from this sample, shows only one NMR peak. The NMR tube containing the mixture and the initially adsorbed xenon gas was then cooled in the NMR probehead to obtain low-temperature $^{129}$Xe NMR spectra (Figs. 3b and 3c). Similar to the result of Ryoo *et al.* (*25*),

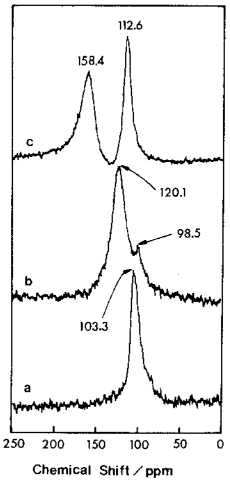

FIG. 3. $^{129}$Xe NMR spectra obtained from a 1 : 1 uniform mixture of IEPt/NaY and NaY at (a) 296 K, (b) 223 K, and (c) 163 K. Initially, the xenon pressure was 400 Torr and 296 K and the sample tube was cooled in the NMR probehead.

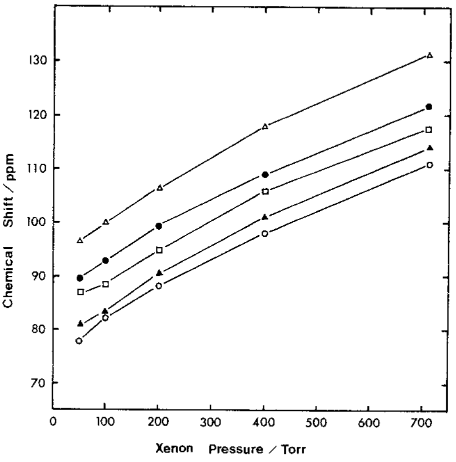

FIG. 5. Chemical shift versus xenon pressure for NaY (○), IMPt/NaY-D (▲), IMPt/NaY-DT (□), IMPt/NaY-LDT (●), and IEPt/NaY (△) after vacuum treatment at 313 K.

the $^{129}$Xe NMR spectrum shows two well-resolved peaks at 163 K. This result indicates that the exchange of xenon between the IEPt/NaY and the NaY crystals was normally fast enough to show only a $^{129}$Xe NMR signal averaged over the mixture at 296 K. Therefore, the xenon NMR experiment carried out at room temperature could not distinguish a difference between the regions inside the same crystallite but gives the information on the macroscopic heterogeneity averaged over many crystallites. According to this interpretation, the left shoulders of the NMR peaks obtained from Pt/NaY-D and Pt/NaY-DT came from the

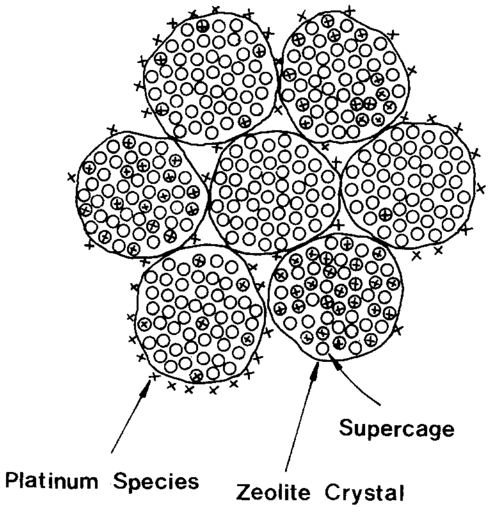

FIG. 4. A proposed model for the distribution in IMPt/NaY-DT sample.

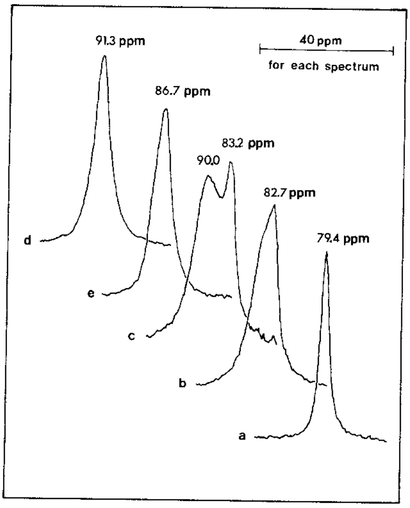

FIG. 6. $^{129}$Xe NMR spectra of (a) NaY, (b) IMPt/NaY-D, (c) IMPt/NaY-DT, (d) IMPt/NaY-LDT, and (e) IEPt/NaY after calcination at 573 K.

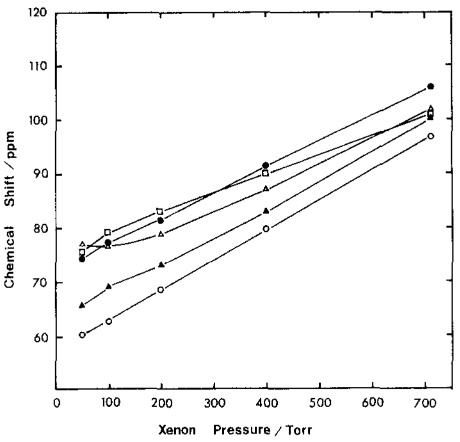

FIG. 7. Chemical shift versus xenon pressure for NaY (○), IMPt/NaY-D (▲), IMPt/NaY-DT (□), IMPt/NaY-LDT (●), and IEPt/NaY (△) after calcination at 573 K.

macroscopic heterogeneity of Pt species distribution in the samples. It may be safely stated that some parts of the samples contained more platinum species than the rest, as proposed in Fig. 4.

Figure 5 illustrates the effect of xenon pressure on the chemical shift for the samples dried at 313 K. The $^{129}Xe$ chemical shift increases with increasing xenon pressure for all the samples. The slope of the increase is very similar to the result obtained by Gedeon *et al.* (*26*) from partially hydrated NaY. It seems that the platinum species is surrounded by water of hydration and therefore does not exhibit a strong interaction with the adsorbed xenon atom.

Figure 6 shows the $^{129}Xe$ NMR spectra obtained at 400 Torr and 296 K after the Pt/NaY samples were calcined in flowing $O_2$ and subsequently treated under vacuum at 573 K. Compared with those in Fig. 2, they generally show narrower linewidths and smaller chemical shifts. The decreases in the chemical shift and linewidth could come from the removal of zeolite water from the supercage at higher temperatures (*27*). It should also be noticed that the shoulders of the NMR peaks observed from the IMPt/NaY-D and IMPt/NaY-DT samples increased after the calcination. The peak shoulders on the left came from the xenon gas adsorbed in a sample region containing more Pt species than other parts. The increase in shoulder after the calcination may be explained if the platinum species adsorbed at the external surface migrated into the zeolite crystal during the calcination treatment. Furthermore, Fig. 7 shows that the chemical shift of IMPt/NaY samples increased linearly to the xenon pressure whereas the chemical shift of IEPt/NaY catalysts has a minimum at about 100 Torr. This difference between the two calcined samples suggests the formation of different platinum species during the calcination step. When the impregnated Pt/NaY catalysts were calcined at 573 K, the platinum species could exist as a mixture of platinum(II) chloride and platinum oxide (*28*). Comparatively, when an ion-exchanged Pt/NaY catalyst was calcined at 573 K, the platinum species could be platinum oxide clusters (*29–31*). It seems that platinum(II) chloride existing in the calcined IMPt/NaY-LDT sample polarized xenon atoms more strongly than the platinum oxide(PtO) clusters existing in the IEPt/NaY did.

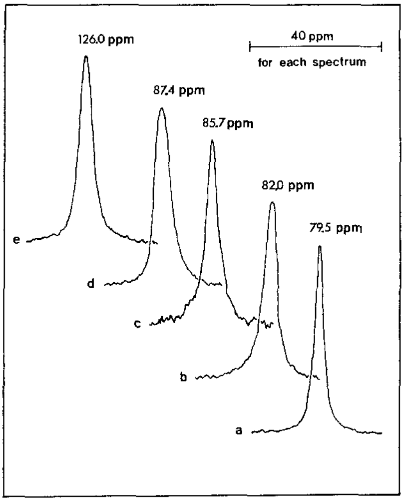

FIG. 8. $^{129}Xe$ NMR spectra of (a) NaY, (b) IMPt/NaY-D, (c) IMPt/NaY-DT, (d) IMPt/NaY-LDT, and (e) IEPt/NaY after reduction with $H_2$ at 673 K.

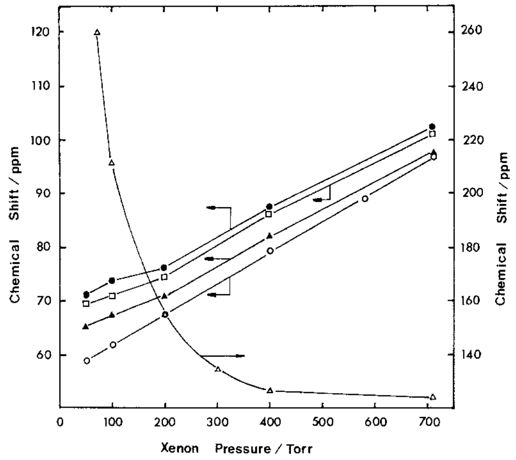

FIG. 9. Chemical shift versus xenon pressure for NaY (○), IMPt/NaY-D (▲), IMPt/NaY-DT (□), IMPt/NaY-LDT (●) and IEPt/NaY (△) after reduction with $H_2$ at 673 K.

The $^{129}$Xe NMR spectra shown in Fig. 8 were obtained at 400 Torr and 296 K from the Pt/NaY samples which were reduced by flowing $H_2$ at 673 K and subsequently evacuated at 673 K. At this step, the $^{129}$Xe NMR lineshapes were more similar to each other than at the previous treatments. It may be speculated that the migration of reduced platinum species could make the distribution of platinum clusters more uniform. Figure 9 shows the variation in the $^{129}$Xe NMR chemical shift obtained at different xenon pressures from the reduced Pt/NaY samples. The chemical shift increased with increasing xenon pressures for the impregnated samples. On the other hand, the chemical shift of the IEPt/NaY sample represented a minimum at about 200 Torr, similar to the results of others (*16, 32*). The heat of adsorption of xenon on platinum metal (*33*) is greater than that on the zeolite walls (*16*) and therefore relatively more xenon can be adsorbed on the platinum cluster at lower pressures than on the zeolite wall (*34*). This explains why the chemical shift obtained from the IEPt/NaY samples increased at low pressures. It is considered that the IMPt/NaY samples did not exhibit a sharp increase in the chemical shift at low pressures because the IMPt/NaY samples contained much fewer platinum clusters within the zeolite crystal. These results indicate that a smaller number of platinum clusters existed in the zeolite supercage of the impregnated samples than in the ion-exchanged samples. It is possible that Pt species in the IMPt/NaY samples have either moved to the external surface of the crystallite or moved into the sodalite cage during the reduction.

Hydrogen chemisorption data are given in Table 2. From the H/Pt values, the platinum dispersion was IMPt/NaY-D < IMPt/NaY-DT < IMPt/NaY-LDT < IEPt/NaY in increasing order. This result agrees with our previous interpretation that more platinum species can diffuse into the zeolite crystals by longer impregnations and thermal treatments. This result is also consistent with the chemical shift values of $^{129}$Xe NMR of reduced catalysts.

## CONCLUSIONS

Our measurement of CPA adsorption showed that about 40% of the chloroplatinic acid (CPA) present initially in the impregnation solution could be adsorbed on NaY zeolite at a saturation point which was reached in 5 h. The $^{129}$Xe NMR probe showed that a significant amount of the initially adsorbed platinum species, if not all, was located in the zeolite channel. The $^{129}$Xe NMR data indicated that the CPA remaining in the solution became impregnated on the external surface of the zeolite as the solution was quickly evaporated. It was also indicated

TABLE 2

Hydrogen Chemisorption Data on Pt/NaY

| | $H_{total}$/Pt | $H_{irrev.}$/Pt |
|---|---|---|
| IMPt/NaY-D | 0.40 | 0.28 |
| IMPt/NaY-DT | 0.58 | 0.38 |
| IMPt/NaY-LDT | 0.68 | 0.42 |
| IEPt/NaY | 1.20 | 0.75 |

that some of the platinum species impregnated on the external zeolite surface could then diffuse into the zeolite channel as the sample was subsequently heated in a humid chamber. Calcination treatment at 573 K also seemed to diffuse the platinum species into the zeolite crystal. In good agreement with the above explanation, a thermal treatment in a humid chamber resulted in the increase of hydrogen chemisorption of the prepared Pt/NaY sample.

The IEPt/NaY sample prepared by the ion exchange method indicated that the Pt species were uniformly distributed in the zeolite crystal during the cation exchange, calcination, and reduction treatment. In this way, the $^{129}$Xe NMR method was very useful in measuring the distribution of Pt species during the preparation of Pt/NaY catalyst according to the impregnation or the cation exchange method.

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