

# Preparation of Highly Dispersed Platinum Particles in HZSM-5 Zeolite: A Study of the Pretreatment Process of $[\text{Pt}(\text{NH}_3)_4]^{2+}$

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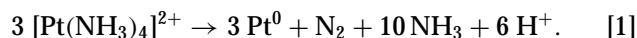
The pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , ion exchanged into zeolite HZSM-5, was studied using temperature-programmed techniques and diffuse-reflectance UV/VIS spectroscopy. The pretreatment is an important part of the preparation of bifunctional Pt/HZSM-5 catalysts, which are active in the hydroisomerization of alkanes. Pretreatment in a helium atmosphere leads to autoreduction and the conversion of part of the  $\text{NH}_3$  ligands into  $\text{H}_2$  and  $\text{N}_2$ . Pretreatment in an oxygen-containing atmosphere leads to the oxidation of the  $\text{NH}_3$  ligands into  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$ . Temperature-programmed pretreatment with oxygen gives rise to three reaction-rate maxima if the sample is not dried, and the conclusion is that  $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$  is formed as an intermediate in the first step. If temperature-programmed pretreatment with oxygen is carried out on a previously dried sample, oxidation of the ligands is a two-step process: three of the  $\text{NH}_3$  ligands are oxidized in one rapid step and the last ligand is oxidized at a higher temperature. Careful pretreatment in an oxygen-containing atmosphere of  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$  leads to the formation of the pale green PtHZSM-5 in which platinum is present as  $\text{Pt}^{2+}$  coordinated to the zeolite framework. Small platinum particles are formed by subsequent reduction of these platinum ions in flowing hydrogen. © 1997 Academic Press

## 1. INTRODUCTION

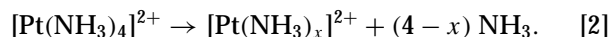
The preparation of platinum particles in zeolites is a task which must be carried out with care; this fact has been recognized since the early days of Pt-zeolite catalysis (1-3). The preparation can be divided into three steps: introduction of the platinum, pretreatment (or calcination, when conducted in an oxygen-containing atmosphere), and reduction.

The preferred way of introducing platinum into a zeolite is to exchange  $\text{Na}^+$  or  $\text{H}^+$  ions for positively charged platinum complexes (mostly  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ) (4). Much research was done to establish the best conditions for this ion exchange (temperature, with or without competition of  $\text{NH}_4^+$ , concentrations, etc.); it was found that a low concentration of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  at room temperature is a good condition for the exchange (5).

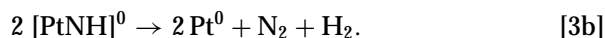
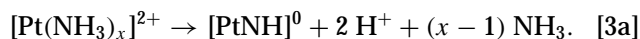
The processes that occur during pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  or  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolites were examined in many studies, because they can be of great influence on the location and size of the metal particles formed in the subsequent reduction. The studies in which both Pt and Pd were examined showed that both metals behave similarly in the pretreatment process (2, 5, 6). The differences between the metals that were reported are the greater tendency to autoreduction of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in zeolites (5) and the lower stability of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolite X (6). Therefore, also studies are discussed here that concern  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  exchanged in zeolites; these studies (7-9) are more detailed about the pretreatment process than the studies concerning  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  exchanged in zeolites (1, 3, 4, 10-12). Reagan *et al.* (2) studied the pretreatment of both  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  and  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolite NaY using thermogravimetric analysis (TGA). They concluded that the overall reaction in helium or air is



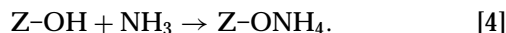
In Eq. [1] the platinum ions are reduced by the  $\text{NH}_3$  ligands; processes like this are called autoreduction (5, 13). Only minor differences were observed in pretreatment behavior between platinum and palladium. Exner *et al.* (6) studied the pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  and  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolite NaX using temperature-programmed evolved gas analysis by mass spectrometry (TPMS), differential thermal analysis (DTA), and differential thermogravimetry (DTG). They concluded that, during the temperature program, several reactions take place in a vacuum. At temperatures below 200°C, some ligands are expelled:



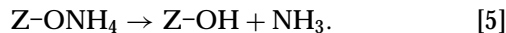
At temperatures above 200°C, an autoreduction reaction takes place:



The reactions in Eqs. [3a] and [3b] occur simultaneously. Brønsted acid sites (Z is zeolite, Z-OH is a Brønsted acid site) react with the liberated ammonia:



At temperatures above 300°C, the reaction in Eq. [4] is reversed:



At temperatures above 450°C, the platinum particles decompose the liberated  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$ . In this atmosphere (containing  $\text{H}_2$  and  $\text{NH}_3$ ), mobile neutral complexes such as  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2)]^0$  (1) can be formed; these complexes can diffuse rapidly in the zeolite, forming large platinum particles (2). The products of the pretreatment in oxygen were  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{N}_2$ ; nitrogen oxides were not found in the study of Exner *et al.* (6). Homeyer and Sachtler (7) studied the pretreatment of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolite NaY using TPMS. In this study it was concluded that the pretreatment of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  is a stepwise process: two of the  $\text{NH}_3$  ligands are oxidized at 270°C, another  $\text{NH}_3$  is oxidized rapidly at 340°C, and the last  $\text{NH}_3$  ligand is oxidized at 400°C. The oxidation of the first two  $\text{NH}_3$  ligands yields  $[\text{Pd}(\text{NH}_3)_2]^{2+}$  coordinated to the zeolite lattice in the supercage. The rapid oxidation of the third  $\text{NH}_3$  ligand is evidence for the migration of  $[\text{Pd}(\text{NH}_3)]^{2+}$  into a sodalite cage. The oxidation of the last  $\text{NH}_3$  ligand occurs in the sodalite cage forming  $\text{Pd}^{2+}$  coordinated to the sodalite cage oxygen atoms. Oxidation of the  $\text{NH}_3$  ligands was found to yield  $\text{N}_2$  and  $\text{H}_2\text{O}$ . A complementary study (9) using diffuse-reflectance (DR) UV/VIS spectroscopy confirmed these conclusions and furthermore it was concluded that the final  $\text{Pd}^{2+}$  ion is coordinated to four oxygen atoms in square planar symmetry. Sauvage *et al.* (8) recently studied the pretreatment and reduction of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolites Y and X using TPMS, TPO, and DR-UV/VIS/NIR spectroscopy. In this study it was concluded that in the stepwise pretreatment some  $\text{NH}_3$  ligands are desorbed as  $\text{NH}_3$  gas, while others are oxidized to  $\text{N}_2$  and  $\text{N}_2\text{O}$ ; the ratio of oxidized to desorbed ligands depended on the zeolite and the zeolite counterion. Another conclusion was that, before the final product  $\text{Pd}^{2+}$  coordinated to the zeolite lattice is formed, partly deaminated complexes are formed with general formula  $[\text{Pd}(\text{NH}_3)_x(\text{A})_y]^{2+}$  coordinated to the zeolite framework, where A is either  $\text{H}_2\text{O}$  or OH. Sauvage *et al.* (8) comment that no conclusion about the symmetry of the final  $\text{Pd}^{2+}$  coordination could be made from the UV/VIS spectrum: both  $\text{C}_{3v}$  (14) and  $\text{D}_{4h}$  (9) symmetry were proposed in the literature. Several studies report that bare  $\text{Pt}^{2+}$  ions are the final product of the pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , if carried out in a fast stream of air or oxygen with a very slow heating rate ( $<1^\circ\text{C}/\text{min.}$ ) (4, 10–12); however,  $\text{PtO}$  is also reported as the final product of the pretreatment (15).

Reduction of the platinum ions is necessary to gain an active catalyst. The reduction of  $\text{Pt}^{2+}$  (or  $\text{Pd}^{2+}$ ) leads to the formation of two protons which participate in the metal-zeolite interaction (10, 16), stabilizing small metal particles.

In the literature cited above samples have been examined which contain a high metal loading (from 5 wt% (8) up to 80 wt% (6)) and are based on the sodium form of the zeolite. However, the bifunctional catalyst that is normally used in the hydroisomerization of alkanes contains much less active metal (0.5–1 wt%) and is based on the acid form of the zeolite. In this study, therefore, samples were examined that are suitable as bifunctional catalysts. The pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5 was studied using TPMS, temperature-programmed oxidation (TPO), and diffuse-reflectance UV/VIS spectroscopy. The results may provide a basis for the empirical procedures for the pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in zeolites and may make improved pretreatment procedures possible. Hydrogen chemisorption measurements were used to determine the number of platinum surface atoms present, formed after pretreatment and reduction, and hence from the known amount of platinum present, to estimate the particle size.

## 2. METHODS

### 2.1. Sample Preparation

A batch of 10 g of NaZSM-5 (Exxon, AT281/78962, Si/Al  $\approx$  40) was calcined up to a temperature of 550°C in order to remove the template. HZSM-5 was prepared from the calcined NaZSM-5 by triple exchange with 1 M  $\text{NH}_4\text{NO}_3$  followed by calcination in dry air up to 500°C.  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$  was prepared by ion exchange, following literature methods (7). A dilute solution of  $[\text{Pt}(\text{NH}_3)_4](\text{OH})_2$  (Strem Chemicals, Lot 132413-S4) was added dropwise to a stirred HZSM-5 slurry (200 ml doubly deionized water per gram of zeolite); after 24 h of stirring at room temperature, the slurry was filtered and washed twice with 100 ml doubly deionized water. During the exchange, the pH of the solution was found to be 7. UV/VIS measurements of the filtrate showed that the ion exchange was complete. The platinum loading of the sample was 0.50 wt%.

### 2.2. TPMS Procedure

The TPMS data were obtained in a fixed-bed flow reactor system, containing approximately 0.5 g of catalyst. Up to 15 mass numbers could be measured using a computer-interfaced quadrupole mass spectrometer (Balzers QMG 420) downstream of the catalyst. The TPMS data were measured in a He or a  $\text{O}_2/\text{He}$  flow (2.4%  $\text{O}_2$  or 4%  $\text{O}_2$ ) of 20 ml/min, while the temperature was increased from 28 to 600°C with a heating rate of 5°C/min.

### 2.3. TPO Procedure

The TPO data were obtained in a fixed-bed flow apparatus similar to that typically used for temperature-programmed reduction, containing approximately 0.3 g of catalyst; the oxygen consumption was measured by a TCD device. TPO experiments were measured in a 4%  $\text{O}_2/\text{He}$  flow of 5 ml/min; the temperature was increased from 20 to 500°C with various heating rates.

### 2.4. Diffuse-Reflectance UV/VIS

The diffuse reflectance UV/VIS spectra were obtained in a Hitachi 150-20 double-beam spectrophotometer equipped with a 60-mm-diameter integrating sphere device coated with  $\text{BaSO}_4$ . The reflectance was measured with  $\text{Ca}(\text{OH})_2$  in a quartz cuvette as a reference. The reflectance of HZSM-5 was also measured as a blank sample. Because zeolites are known to show absorption below 400 nm (17, 18) it is necessary to correct for this influence. Therefore, the Kubelka–Munk function (9, 19) was calculated from the measured reflectance of which the reflectance of the blank material was subtracted. A sample of approximately 2 g of the  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  exchanged HZSM-5 was placed in a small reactor; thereafter, the temperature was ramped with a heating rate of 0.5°C/min to a specified temperature in a  $\text{O}_2/\text{N}_2$  (20/80) flow and held at that temperature for 2 h. After cooling in a nitrogen atmosphere the sample was transferred under nitrogen into a quartz cuvette, after which the UV/VIS spectrum was measured. Thereafter the sample was transferred back into the reactor and the pretreatment was started again to the next temperature. After the final pretreatment to 450°C, the sample was contacted with moist air and spectra were measured after several times of exposure.

### 2.5. Pretreatment and Reduction

A sample of 3 g of the  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  exchanged HZSM-5 was pretreated and reduced in a separate apparatus. Pretreatment was carried out under a  $\text{O}_2/\text{N}_2$  (20/80) flow of 120 ml/min/g, while the temperature was ramped from room temperature to 450°C with a rate of 0.5°C/min. After 2 h at 450°C, the sample was cooled in a flow of nitrogen. Subsequently, the sample was reduced in a  $\text{H}_2$  flow of 90 ml/min/g, while the temperature was ramped from room temperature to 400°C with a rate of 5°C/min.

### 2.6. Hydrogen Chemisorption Measurements

Hydrogen chemisorption was measured at 25°C using a conventional glass apparatus, following the procedure of Kip *et al.* (20). Before measuring hydrogen chemisorption the pretreated and reduced catalyst was rereduced in a flow of hydrogen at 250°C for 1 h and subsequently evacuated ( $10^{-2}$  Pa) for 1 h at the same temperature in order to remove chemisorbed hydrogen. Thereafter a mea-

sured amount of hydrogen ( $P = 100$  kPa at room temperature) was admitted to the sample which was kept at 250°C. Hydrogen chemisorption equilibrium was reached quickly (<5 min), because of the elevated temperature. After adsorption, the sample was allowed to cool to room temperature and to stabilize for at least 1 h. The hydrogen desorption isotherm was measured by lowering the pressure stepwise and determining the amount of hydrogen that was desorbed from the sample for each step. The H/Pt ratio was determined by extrapolation of the linear high pressure part (20 kPa <  $P$  < 80 kPa) of the isotherm to zero pressure. As a blank experiment hydrogen chemisorption was measured on a sample of HZSM-5 pretreated in the same way as the catalyst.

## 3. RESULTS

### 3.1. TPMS

In the first experiment, a  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$  sample was heated in a helium flow. The signals for water were significant over a temperature range from room temperature up to 450°C. Figure 1 is a response versus temperature plot, showing the results for  $\text{H}_2$  (mass 2),  $\text{N}_2$  (mass 28), and  $\text{NH}_2$  (mass 16), the latter from fragmentation of  $\text{NH}_3$ . The plot reveals that there is a sharp peak in the  $\text{N}_2$  signal at a temperature of 330°C and a broad peak in the  $\text{N}_2$  signal from 330 up to 450°C, whereas only a small signal for  $\text{H}_2$  is observed in this temperature region. Another feature that can be observed is that the release of  $\text{NH}_3$  ligands from the platinum complex occurs at high temperature (>450°C); part of the released  $\text{NH}_3$  is converted to  $\text{N}_2$  and  $\text{H}_2$ .

In the second experiment, a  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$  sample was heated in a flow of 2.4%  $\text{O}_2$  in He. The signals for  $\text{N}_2$  (mass 28) and  $\text{N}_2\text{O}$  (mass 44) were almost equal over the entire temperature range. No  $\text{NH}_3$ , no  $\text{NO}_2$ , and only a very small amount of  $\text{NO}$  was measured. Figure 2 is a response versus temperature plot, showing the results for  $\text{O}_2$  (mass 32),  $\text{N}_2$  (mass 28), and  $\text{H}_2\text{O}$  (mass 18). In the plot

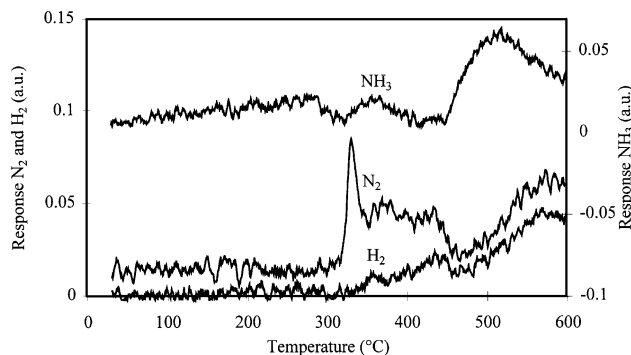


FIG. 1. TPMS of 0.5 wt%  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5 in a helium atmosphere.  $\text{NH}_3$  ( $\text{NH}_2$  (mass 16) was used as a marker for  $\text{NH}_3$ ),  $\text{N}_2$  (mass 28), and  $\text{H}_2$  (mass 2) are shown.

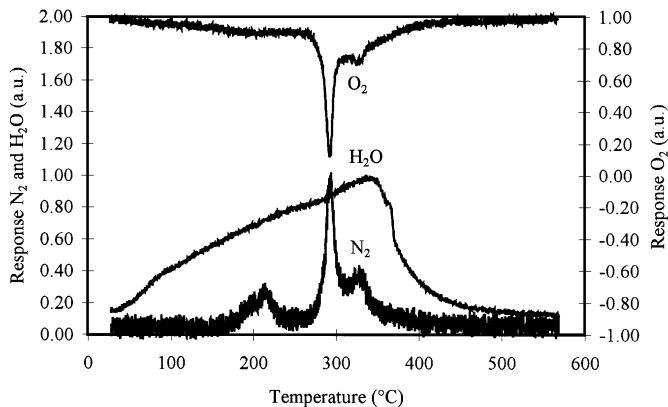


FIG. 2. TPMS of 0.5 wt%  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5 in a 2.4%  $\text{O}_2/\text{He}$  atmosphere.  $\text{O}_2$  (mass 32),  $\text{N}_2$  (mass 28), and  $\text{H}_2\text{O}$  (mass 18) are shown.

it can be clearly seen that the consumption of oxygen is mirrored in the production of  $\text{N}_2$ , although it is evident that the  $\text{O}_2$  baseline is influenced by the large amount of water in the mass spectrometer. There are three peaks in the signal for  $\text{N}_2$  at 215, 295, and 325°C. The oxygen concentration decreases to very low values in the sharp peak at 295°C. Quantitative analysis of the  $\text{N}_2$  signal reveals that the area of the sharp peak at 295°C is twice the area of the peak at 215°C. Also evident is the large release of water from the zeolite up to high temperatures.

In the third experiment, a  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$  sample was dried by flowing dry helium over the sample overnight at room temperature, after which the sample was heated in a flow of 4.0%  $\text{O}_2$  in He. A higher concentration of oxygen was used in this experiment to avoid the concentration falling to the extremely low level of the second experiment. The signals of  $\text{N}_2$  (mass 28) and  $\text{N}_2\text{O}$  (mass 44) were almost equal over the entire temperature range and no  $\text{NO}_2$ , no  $\text{NH}_3$ , and only a very small amount of  $\text{NO}$  was measured, similar to the results of the second experiment. Figure 3 is a response versus temperature plot, giving the results for  $\text{O}_2$  (mass 32),  $\text{N}_2$  (mass 28), and  $\text{H}_2\text{O}$  (mass 18). The consump-

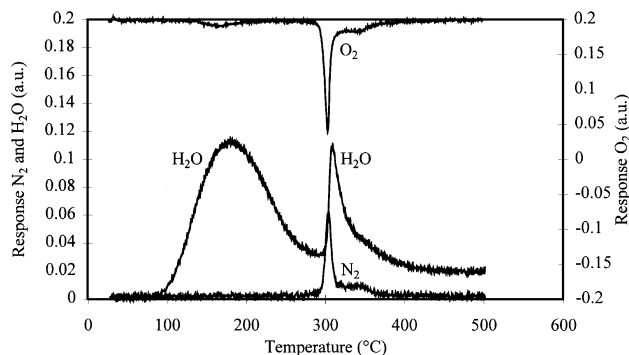


FIG. 3. TPMS of dried 0.5 wt%  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5 in a 4%  $\text{O}_2/\text{He}$  atmosphere.  $\text{O}_2$  (mass 32),  $\text{N}_2$  (mass 28), and  $\text{H}_2\text{O}$  (mass 18) are shown.

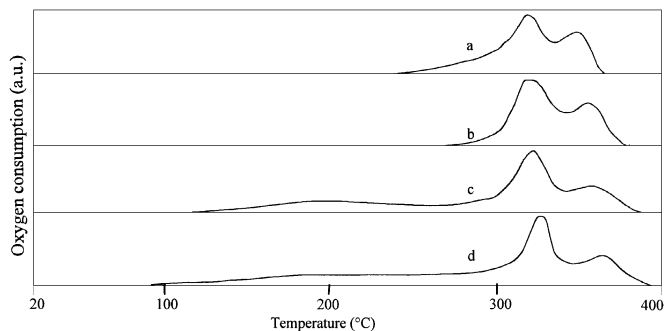


FIG. 4. TPO of 0.5 wt%  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5 with various heating rates: (a) 1°C/min; (b) 2°C/min; (c) 4°C/min; and (d) 5°C/min.

tion of oxygen is mirrored in the production of  $\text{N}_2$ , as in the second experiment, although also in this experiment it is evident that the  $\text{O}_2$  baseline is influenced by the amount of water in the mass spectrometer. Only two peaks can be seen in the signal for  $\text{N}_2$ , at 305 and 340°C. The release of water by the zeolite is much smaller than in the second experiment; the water concentration in the flow is low at a much lower temperature. Water is formed in the reaction of  $\text{O}_2$  with  $\text{NH}_3$ , besides  $\text{N}_2$  and  $\text{N}_2\text{O}$ : this is evidenced by the second peak in the water signal. This peak occurs at a slightly higher temperature than the peak of the formation of  $\text{N}_2$  and  $\text{N}_2\text{O}$ ; this is due to a strong adsorption of water in the zeolite.

### 3.2. TPO

A series of four TPO experiments was made, with various heating rates (5, 4, 2, and 1°C/min). Figure 4 shows oxygen concentration versus temperature for each heating rate. Since the samples are not dried before the experiment, these results should be comparable with the results of the second TPMS experiment. However, only two peaks were measured in the two experiments with the lowest heating rate; three peaks are found in the other two experiments. The low temperature peak is too small and too broad to be detected in the former case. As can be seen in Fig. 4, the peak position in the TPO depends on the heating rate applied: the peaks shift to a lower temperature with decreasing heating rate. Quantitative analysis shows that the area under the large peak is in all cases approximately twice the area under the high temperature peak.

### 3.3. Diffuse-Reflectance UV/VIS

The results of a series of UV/VIS experiments made after pretreatment at a successively higher temperature are shown in Figure 5. Only the start of one large peak with a maximum below 200 nm could be detected after pretreatment to 20°C. A similar spectrum was measured after pretreatment to a temperature of 120°C. After pretreatment to a temperature of 250°C (Fig. 5b) the large band appears

to have shifted to lower wavelength and a small band can be observed at a wavelength of 250 nm; this small band was also observed after pretreatment to higher temperatures. Starting after pretreatment to a temperature of 275°C a band at 640 nm was detected (Figs. 5c–5f). The intensity of this peak increases with increasing pretreatment temperature; furthermore, the band becomes less broad after pretreatment to a temperature of 450°C. Starting after a pretreatment to a temperature of 300°C, a band at 440 nm was detected (Figs. 5d–5f), also increasing in intensity with increasing pretreatment temperature. The large peak with a maximum below 200 nm also appears to increase in intensity with increasing pretreatment temperature. Because of the absorption in the visible region, the sample acquired a light green color after pretreatment at 450°C. The same color change was reported before in literature for  $\text{Pt}^{2+}$  in zeolite Y (11).

The green color fades after prolonged exposure to ambient air; this has been examined by measuring UV/VIS spectra of a sample of the  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ , pretreated to 450°C, after exposure to air for a certain time (Fig. 6). After exposure to moist air the intensities of the peaks at 250, 440, and 640 nm decrease with time (Figs. 6b–6e). Eventually, all three peaks disappear from the spectrum (Fig. 6e); only the start of a large band with a maximum below 200 nm can still be observed in the DR-UV/VIS spectrum.

### 3.4. Pretreatment and Hydrogen Chemisorption

During careful pretreatment, pale green PtHZSM-5 is formed from white ion-exchanged  $[\text{Pt}(\text{NH}_3)_4]\text{HZSM-5}$ . During reduction the color changes from green to gray. Hydrogen chemisorption experiments on the reduced Pt/HZSM-5 sample show that small platinum particles are present: the H/Pt ratio measured is 2.0 ( $\pm 0.1$ ). The val-

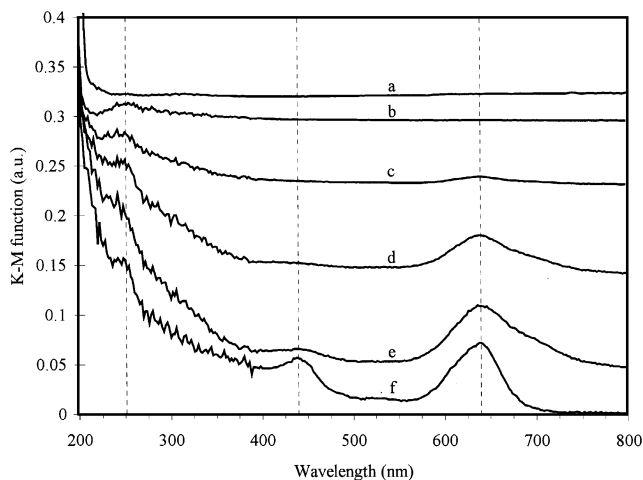


FIG. 5. UV/VIS spectra of 0.5 wt%  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5, after pretreatment at a temperature of: (a) 20°C, (b) 250°C, (c) 275°C, (d) 300°C, (e) 350°C, and (f) 450°C.

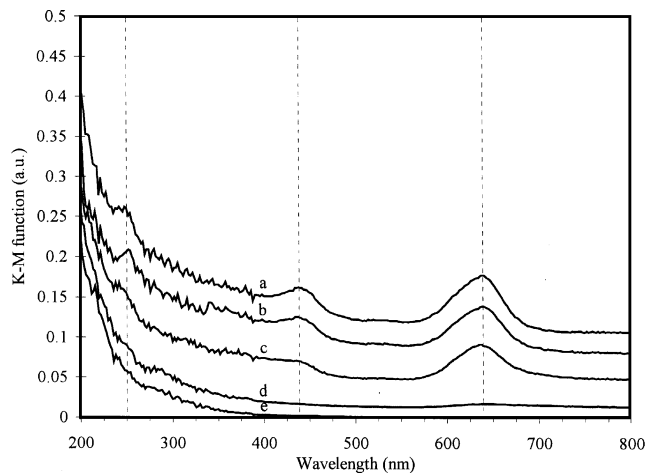


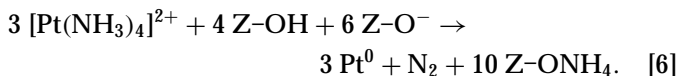
FIG. 6. UV/VIS spectra of 0.5 wt%  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in HZSM-5, after (a) pretreatment to 450°C and (b–e) subsequent exposure to ambient air for: (b) 1 h, (c) 3 h, (d) 21 h, and (e) 4 days.

ues measured with this hydrogen chemisorption method are usually slightly higher than those obtained by hydrogen chemisorption at room temperature (20). The HZSM-5 sample was found to chemisorb no detectable amount of hydrogen within experimental error. From the calibration made by Kip *et al.* (20) and extended by Vaarkamp *et al.* (21) it can be determined that a H/Pt value of 2.0 indicates a particle size of 2.5 to 5 Å.

## 4. DISCUSSION

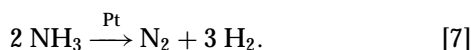
### 4.1. Pretreatment in Helium

Pretreatment in a helium atmosphere leads to autoreduction, as can be derived from the TPMS results shown in Fig. 1. At temperatures between 300 and 450°C the  $\text{N}_2$  signal is much larger than the  $\text{H}_2$  signal, whereas at temperatures higher than 450°C the  $\text{N}_2$  and  $\text{H}_2$  are almost equal. The result obtained between 300 and 450°C contradicts the results of Exner *et al.* (6), where  $\text{N}_2$  and  $\text{H}_2$  are observed simultaneously (Eq. [3b]). However, the theory of Reagan *et al.* (2) (Eq. [1]) can describe our results, if we consider that in HZSM-5 all  $\text{NH}_3$  will be adsorbed on the Brønsted acid sites (Eq. [4]). Therefore, the total reaction will be



In Eq. [6] the only gaseous product that would be observed is  $\text{N}_2$ , as was measured in the experiment at temperatures between 300 and 450°C. Therefore, we can conclude that autoreduction takes place in a helium atmosphere. At temperatures above 450°C,  $\text{NH}_3$  will desorb from the Brønsted acid sites (Eq. [5]): this desorption is observed in the experiments, as can be seen in Fig. 1. At these temperatures part of the released  $\text{NH}_3$  is converted into  $\text{N}_2$  and  $\text{H}_2$ ; this

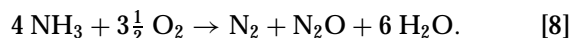
reaction is catalyzed by the autoreduced platinum particles:



The occurrence of this reaction is evidenced by the results of the first experiment (Fig. 1). From the data presented in this study, no conclusions regarding the occurrence of neutral complexes such as  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2)]^0$  can be made.

#### 4.2. Pretreatment in Oxygen/Helium

The oxidation of the  $\text{NH}_3$  ligands produces  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$ . In all TPMS experiments, no response was observed for  $\text{NO}_2$  and only a very small signal was observed for  $\text{NO}$ . Therefore, the reaction stoichiometry for the oxidation of  $\text{NH}_3$  ligands in this system must be



This result differs from the results in the literature (6, 7) on the pretreatment of Pt or Pd tetrammines: in these studies no nitrogen oxides were reported. However, it must be noted that only  $\text{NO}$  and  $\text{NO}_2$  were followed by Homeyer and Sachtler (7), whereas it is not clear which masses were followed by Exner *et al.* (6). Only in the study of Sauvage *et al.* (8) was  $\text{N}_2\text{O}$  reported as a product of the oxidation of  $\text{NH}_3$  ligands. Another difference with the previously published studies (2, 6, 8) is that these show a desorption of  $\text{NH}_3$  in the pretreatment of Pt or Pd tetrammines, even in an oxygen-containing atmosphere. In our study no desorption of  $\text{NH}_3$  could be measured when there was oxygen present. This is probably caused by the much lower metal loading used in this study (0.5 wt% Pt) as opposed to the metal loading used in the above-mentioned work (from 5 wt% Pd (8) up to more than 10 wt% Pd or Pt (2, 6)). Because of the higher metal loading a (local) shortage of  $\text{O}_2$  can arise, which suppresses the oxidation of  $\text{NH}_3$ , whereas in this study the metal loading is so low that similar shortages of oxygen cannot occur. That shortages of oxygen do not occur in our experiments is evidenced by the results of the second TPMS experiment, in which the oxygen concentration decreases to a very low value in the sharp peak at 295°C. Therefore, a shortage of oxygen could be expected in the zeolite channels. This lack of oxygen would lead to the autoreduction mechanism. If autoreduction takes place, more  $\text{N}_2$  than  $\text{N}_2\text{O}$  should be formed, according to Eqs. [6] and [8]. However, the  $\text{N}_2$  and  $\text{N}_2\text{O}$  signals are also equal in this part of the TPMS plot; therefore, there is no indication that this mechanism is occurring. Apparently, there is no shortage of oxygen in the zeolite channels during pretreatment.

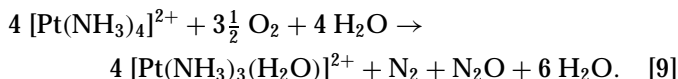
The UV/VIS spectra presented in Fig. 5 provide information about the pretreatment process. From the literature (22) it is known that the spectrum of the square planar complex  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in solution has a strong absorption maximum at 198 nm with a small shoulder at 218 nm, both

of which are caused by  $5d \rightarrow 6p_z$  transitions; this large peak is accompanied by two other small shoulders, caused by ligand field ( $d-d$ ) transitions at 233 and 288 nm. The start of the large peak that can be seen in Fig. 5a is therefore probably the start of the large  $5d \rightarrow 6p_z$  transition of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ; the shoulders are apparently too weak to be detected. In the literature there are reports that these small shoulders were detected on the strong absorption in the spectrum of samples of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  adsorbed on silica (23), alumina (24), and zeolite X (25). The fact that the metal loading in our experiment was much lower (0.5 wt%) than the ones used in the previously published studies (2.5 to 3.0 wt%) must be the explanation for the absence of the shoulders in our study. Therefore, we conclude that  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  has not changed upon exchange into the zeolite. The shift of the large peak and the appearance of the band at 250 nm after pretreatment to 250°C can be attributed to a small distortion of square planar symmetry caused by a stronger ionic interaction of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  with the zeolite negative charge; the increased interaction is caused by the loss of the solvating effect of water as the zeolite becomes drier. The two peaks at a wavelength of 440 and 640 nm are interpreted as the  $d-d$  transitions shifted and increased in intensity from 233 and 288 nm in  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ; the exchange of the  $\text{NH}_3$  ligands with the oxygen atoms of the zeolite can explain this shift, because the oxygen atoms of the zeolite are known to be much weaker ligands than  $\text{NH}_3$  (9). Because of the shift to longer wavelength, the interference of the zeolite signal becomes less important and the peak can be detected more easily. We assume that the symmetry of the complex remains square planar, because this is the most common symmetry for Pt(II)  $L_4$  complexes; the spectrum measured after pretreatment to 450°C is in agreement with this assumption. Before the final coordination of  $\text{Pt}^{2+}$  to the zeolite lattice is established, apparently another species exists as made evident by the broad nature of the peak at 640 nm after pretreatment to a temperature of 300 to 350°C. This species could be a partly deamminated complex with the general formula  $[\text{Pt}(\text{NH}_3)_x(\text{A})_y]^{2+}$  (with A either  $\text{H}_2\text{O}$  or OH), similar to the one proposed for palladium (8). This species has disappeared after pretreatment to a temperature of 450°C: the peak at 640 nm has become narrower. The visual result of the shift is the light green color of the sample. A similar shift and increase in intensity was reported to occur in the pretreatment of  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  in zeolite X or Y (8, 9, 14). The shift in the case of platinum (approx.  $19,500 \text{ cm}^{-1}$ ) is larger than the shift in the case of palladium (approx.  $12,700 \text{ cm}^{-1}$ ), which can be expected for a third row transition metal as opposed to a second row transition metal (26). Even though the assumption of square planar symmetry ( $D_{4h}$ ) holds, the possibility of coordination with three zeolite oxygen atoms in a  $C_{3v}$  symmetry cannot be excluded from our DR-UV/VIS results; this is similar to the case of  $\text{Pd}^{2+}$  in zeolite X or Y (8). Also in the case of

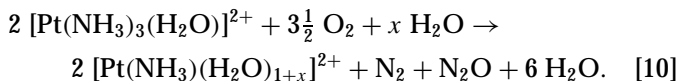
palladium in zeolites NaY and H-mordenite (7, 27) a color change was observed (from white to pink).

The disappearance of the bands at 250, 440, and 640 nm after exposure of Pt<sup>2+</sup> in zeolite HZSM-5 to moist air (Fig. 6) can be attributed to the formation of [Pt(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> solvated in the pores of the zeolite; the spectrum of [Pt(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> in solution shows a high intensity peak at wavelengths shorter than 210 nm and three small bands at wavelengths of 273, 319, and 389 nm (28). Similarly to the spectrum of [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> in zeolite HZSM-5 (Fig. 5a) these small bands are not likely to be detected, because of the low platinum loading used in this study. The same reaction was reported to occur on Pd<sup>2+</sup> in zeolites Y and 5A, forming [Pd(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> in the zeolite pores (29).

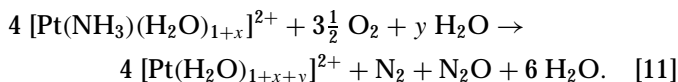
There is a remarkable difference in the TPMS results for the dried and the nondried sample. The nondried sample gives rise to three N<sub>2</sub>/N<sub>2</sub>O peaks with a mutual ratio of 1:2:1 (combining the ratios found in the TPMS and TPO experiments). The dried sample gives rise to only two N<sub>2</sub>/N<sub>2</sub>O peaks: the peak at 215°C disappeared. Therefore, it can be concluded that the existence of this peak is caused by the presence of water. We propose that, in the nondried case, a NH<sub>3</sub> ligand is exchanged for a water ligand, which is a normal reaction for platinum tetrammine complexes (26); the released NH<sub>3</sub> ligand is oxidized:



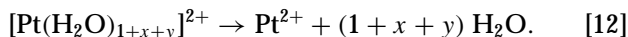
By contrast, in the dried case this reaction will occur to a much lower extent, because there is much less water present. In the nondried case, the next step in the pretreatment is that two of the three NH<sub>3</sub> ligands are oxidized rapidly and possibly more water ligands are added (due to the oxidation of NH<sub>3</sub> water is formed):



This reaction takes place at a temperature of 295°C. The last NH<sub>3</sub> ligand is lost and, again, possibly more water is added:

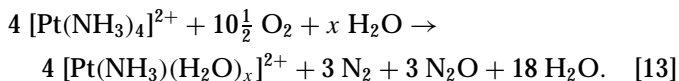


This reaction takes place at a temperature of 325°C. From the results of the DR-UV/VIS measurements it was concluded that after pretreatment to 450°C bare Pt<sup>2+</sup> ions are formed; therefore, the water ligands must be lost finally:

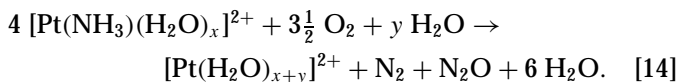


In the dried case, the first reaction step is that three NH<sub>3</sub> ligands are oxidized in one rapid step. Since the NH<sub>3</sub> oxidation gives rise to a high water concentration (see Fig. 3),

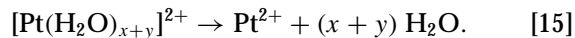
this can lead to the addition of some water ligands:



This reaction takes place at a temperature of 305°C. From the DR-UV/VIS results no conclusions could be made regarding the presence of water ligands; however, it is clear that ligands are present up to a pretreatment temperature of 350°C. When the last NH<sub>3</sub> ligand is lost a high concentration of water is still present, so again water ligands can be added to the complex



This reaction takes place at a temperature of 340°C. From the DR-UV/VIS spectra it can be concluded that ligands are present up to a pretreatment temperature of 350°C; however, after pretreatment to 450°C all ligands are lost and bare Pt<sup>2+</sup> is formed:



The observed influence of water might afford a new interpretation of the results of Homeyer and Sachtler (7). In that study a pattern was observed in the N<sub>2</sub> signal which is similar to the pattern observed in the nondried case of this study. Furthermore, the authors reported that a large amount of water was released by the zeolite. Therefore, it can be concluded that the intermediate observed by Homeyer and Sachtler is [Pd(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> and not [Pd(NH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> coordinated to the zeolite lattice. This conclusion is supported by the knowledge that palladium complexes are, like platinum complexes, capable of ligand exchange with water (26). Another comment concerns the sharp peak observed in both studies. Our data cannot be explained in terms of this sharp peak being evidence for the migration of [Pd(NH<sub>3</sub>)]<sup>2+</sup> into the sodalite cage, because no such cages are present in HZSM-5. Instead, a different, more general, interaction must be responsible for the sharpness of this peak: apparently the [Pt(NH<sub>3</sub>)(H<sub>2</sub>O)<sub>x</sub>]<sup>2+</sup> or [Pd(NH<sub>3</sub>)(H<sub>2</sub>O)<sub>x</sub>]<sup>2+</sup> species are stabilized well by any zeolite framework.

Our results support the empirical knowledge that has been developed during the past 20 years for the pretreatment of [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> in zeolites in the formation of Pt/zeolite catalysts: a high oxygen-containing flow and a low heating rate are necessary to gain small platinum particles in zeolites. The oxygen is necessary to prevent autoreduction, while the high flow rate and the low heating rate provide for the removal of water.

#### 4.3. Pretreatment and Hydrogen Chemisorption

As was discussed above, the green color of pretreated Pt(NH<sub>3</sub>)<sub>4</sub>HZSM-5 is an indication for the presence of Pt<sup>2+</sup>

coordinated to the zeolite lattice. This is in contrast to studies on  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  in zeolite Y, in which PtO was found after pretreatment (15), leading to a gray/black color. This can be attributed to the high metal loading used in those studies and also to the use of zeolite Y. Apparently, autoredox of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  is much more difficult to avoid with these conditions: this gives rise to the formation of Pt metal particles, which are oxidized to PtO or  $\text{PtO}_2$  particles (5). Some studies report a green/gray color (11): this is probably caused by the presence of a mixture of  $\text{Pt}^{2+}$  and PtO. The green color changes to gray during reduction of the  $\text{Pt}^{2+}$  ions, indicating the formation of metallic platinum. Very small platinum particles (2.5–5 Å) are formed during this process, according to hydrogen chemisorption measurements.

## 5. CONCLUSIONS

Pretreatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  ion exchanged into zeolite HZSM-5 in a helium atmosphere leads to autoredox; part of the  $\text{NH}_3$  ligands are converted into  $\text{N}_2$  and  $\text{H}_2$ . Pretreatment in an oxygen-containing atmosphere causes the  $\text{NH}_3$  ligands to be oxidized into  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$ . If the sample is not dried, temperature-programmed oxidation of the ligands occurs in three steps. In this case  $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$  is formed as an intermediate in the first step. If the sample is dried, temperature-programmed oxidation of the ligands occurs in two steps;  $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$  cannot be formed, because not enough water is present. The reaction forming  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})_x]^{2+}$  is fast, in both cases. In the last step  $\text{Pt}[(\text{H}_2\text{O})_x]^{2+}$  is formed, which is dehydrated to bare  $\text{Pt}^{2+}$  at higher temperatures. If pretreatment is carried out in a high flow of an oxygen-containing atmosphere with a low heating rate,  $\text{Pt}^{2+}$  coordinated to oxygen atoms of the zeolite is formed; these platinum ions can be recognized by the characteristic green color. Reduction of these platinum ions leads to the formation of very small platinum particles.

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