

Initial Steps of the Alumina-Supported Platinum Catalyst Preparation: A Molecular Study by ¹⁹⁵Pt NMR, UV–Visible, EXAFS, and Raman Spectroscopy

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The compositions of Pt complexes adsorbed on γ -alumina from acidic H_2PtCl_6 solutions and their transformations upon drying, rewetting, and calcination were studied using ¹⁹⁵Pt NMR, UV–Vis diffuse reflectance, EXAFS, and Raman spectroscopy. Two acidic H_2PtCl_6 solutions (at pH 1.15 and 2.8) were used to impregnate unmodified and HCl treated Al_2O_3 . On the basis of ¹⁹⁵Pt NMR measurements, platinum is found to be adsorbed on alumina as $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$, the latter species being produced by deprotonation of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ present in the initial solutions. Depending on the pH of the impregnating H_2PtCl_6 solutions and alumina pretreatment, the ¹⁹⁵Pt chemical shift (δ_{Pt}) varies from -6.5 to 0.1 ppm for $[\text{PtCl}_6]^{2-}$ and from 638 to 660 ppm for $[\text{PtCl}_5(\text{OH})]^{2-}$ ($\delta_{\text{Pt}}[\text{PtCl}_6]^{2-} = 0$ ppm in the H_2PtCl_6 solution at pH 1.15). The $[\text{PtCl}_6]^{2-}/[\text{PtCl}_5(\text{OH})]^{2-}$ ratio depends on the pH of the impregnating solutions, the alumina pretreatment, and the impregnation time. The adsorbed Pt anion complexes are held on the surface by electrostatic interaction with positively charged protonated hydroxyls. No marked grafting of the adsorbed Pt species occurs upon impregnating the unmodified or HCl treated aluminas with the H_2PtCl_6 solution at pH 1.15, whereas a certain part of these species becomes grafted when unmodified alumina is brought into contact with the H_2PtCl_6 solution at pH 2.8. After removal of physisorbed water by drying at 20°C , the NMR signals are no longer observed. The UV–Vis, Raman, and EXAFS data evidence a modification of the Pt coordination sphere upon drying at 20°C which can be explained in terms of a Cl^- ligand exchange with neighboring alumina hydroxyls, i.e., grafting. The ligand exchange can be reversed by hydration of the dried solids accompanied by the reappearance of the initial NMR signals. Upon drying $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ at 90 or 150°C , the number of Cl and O atoms in the Pt coordination sphere does not change markedly, but the adsorbed Pt species become irreversibly grafted to the surface. No ligand exchange and no grafting of $[\text{PtCl}_6]^{2-}$ adsorbed on the HCl treated alumina was found to occur upon drying at temperatures up to 150°C . © 1999 Academic Press

Key Words: alumina; impregnation; platinum; catalyst preparation; Pt NMR, UV–Vis diffuse reflectance; EXAFS; Raman spectroscopy; reforming.

INTRODUCTION

The interaction of a platinum metal precursor with an alumina support is an important step in the preparation of Pt/ Al_2O_3 catalysts which have found various important applications, in particular as reforming catalysts in the oil-refining industry (1).

The initial steps of the Pt/ Al_2O_3 preparation procedure routinely consist of alumina impregnation with an acidic H_2PtCl_6 solution followed by drying and calcination of the resulting solids in air. These steps may significantly influence the Pt metal dispersion in the final reduced catalysts and, consequently, their performance.

Different spectroscopic techniques, such as UV–Vis diffuse reflectance spectroscopy (2–4), laser Raman spectroscopy (2, 5, 6), and EXAFS (7, 8), have been used to identify Pt complexes adsorbed on the alumina surface from H_2PtCl_6 solutions and to follow their evolution upon subsequent thermal treatments. We will refer later in this paper to these studies while discussing the results obtained in this work. In addition to these spectroscopic techniques, some information concerning the behavior of Pt adsorbed on γ -alumina during reduction with hydrogen was obtained in temperature-programmed reduction experiments (9–15).

Recently, we have applied static ¹⁹⁵Pt NMR spectroscopy to follow the Pt complex speciation at the γ -alumina– H_2PtCl_6 solutions interface and succeeded in observing NMR signals of adsorbed $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ (16, 17). On the basis of their NMR parameters (Pt chemical shifts and line widths), it was concluded that, upon adsorption, the coordination sphere of the Pt anion complexes experiences only a slight perturbation from the alumina surface and that they are held near positively charged protonated hydroxyls ($\sim\text{Al}-\text{OH}_2^+$) by electrostatic

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interaction. After removal of physisorbed water from alumina powder by evacuation at room temperature, the $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$ signals disappear. It was suggested that this phenomenon is associated with an increase in chemical shift anisotropy for the adsorbed Pt species when they approach the positively charged surface of the dry solid. The initial NMR signals can be restored upon rewetting the solids dried at 20°C. However, after heating the $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ system at 90°C, no Pt NMR signal is observed for dried or rewetted solids, probably due to the formation of lower-symmetry ligand-exchanged Pt complexes which escape NMR detection.

Thus, it appears that further progress in studying the evolution of adsorbed Pt complexes upon various thermal treatments of $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ requires the use of other techniques. In the present paper, we report on the results of an investigation employing a combination of ^{195}Pt NMR with UV-Vis, laser Raman spectroscopy, and EXAFS to follow in more detail the initial steps of the preparation of Pt/ Al_2O_3 catalysts.

EXPERIMENTAL

Materials and procedures. Spherical beads of γ -alumina (cubic) were provided by Procatalse. The specific surface area was 195 m^2/g , and the total pore volume was 0.6 cm^3/g . Prior to adsorption experiments, alumina beads were crushed in a mortar, and the fraction of the resulting powder with particle sizes ranging from 180 to 250 μm was separated using calibrated sieves. This material is hereafter referred to as $\text{Al}_2\text{O}_3(\text{un})$.

In some experiments, *HCl treated* alumina was used as a support. *Singly HCl treated* alumina, hereafter referred to as $\text{Al}_2\text{O}_3(\text{st})$, was prepared by the following procedure. $\text{Al}_2\text{O}_3(\text{un})$ (10 g) was added to 150 ml of 0.1 M HCl at pH 1.4, and the suspension was stirred for 3 h until pH 4.0 was reached. The alumina was then separated from the HCl solution by decantation, 120 ml of distilled H_2O was added, and the mixture was stirred for 0.5 h. No marked change in pH was found to occur during this operation. The alumina powder was then filtered and placed in a vacuum dessicator over P_2O_5 for drying for 2 days. *Doubly HCl treated* alumina, referred to as $\text{Al}_2\text{O}_3(\text{dt})$, was prepared as follows. Al_2O_3 (15 g) was added to 250 ml of 0.1 M HCl at pH 1.4, and the mixture was stirred for 4 h until pH 4.0 was reached. The excess HCl was then removed, and 200 ml of 0.1 M HCl was added followed by stirring for 3 h until pH 1.7 was attained, decanting, filtering the powder, and drying it at 90°C overnight.

A stock (6.6×10^{-2} M) H_2PtCl_6 solution at pH 1.15 was used for alumina impregnation; it was prepared by diluting a 8 wt% aqueous solution of H_2PtCl_6 (Aldrich) with water. The pH values were measured using a Tacussel PHN-850 digital pH meter. No change in pH was found to occur for

the aged stock solution. A less acidic H_2PtCl_6 solution at pH 2.83 also used for alumina impregnation was prepared by adding 1 or 0.1 M NaOH to the stock H_2PtCl_6 solution. This solution was aged for at least 2 days before alumina impregnation.

$\text{H}_2\text{PtCl}_6/\gamma\text{-Al}_2\text{O}_3$ samples were prepared by adding the H_2PtCl_6 solution to alumina upon continuous stirring at 20°C. The volume of the impregnating solution was typically twice greater than the alumina pore volume. After impregnation, the samples were first dried in a dessicator over P_2O_5 under vacuum and then in air at 90 and/or 150°C and finally calcined at a higher temperature. The Pt content in the impregnated alumina samples was 1.5 wt%.

^{195}Pt NMR measurements. The 86-MHz ^{195}Pt NMR spectra were recorded at room temperature with a Bruker MSL-400 spectrometer equipped with a multinuclear probe for liquid-state NMR. A simple one-pulse sequence was employed; the pulse width was 5 μs , dead time before acquisition was 20 μs , and equilibration time between two pulses was 0.5 s. In MAS NMR experiments with the same pulse sequence, the spinning rate of the sample was 5 kHz. Line broadening factors of 25 Hz were introduced to improve the signal-to-noise ratio during the Fourier transforms. The ^{195}Pt chemical shifts (δ_{Pt}) were referenced to the $[\text{PtCl}_6]^{2-}$ signal ($\delta_{\text{Pt}} = 0$ ppm) in the stock H_2PtCl_6 solution at pH 1.15.

In some experiments, the spectrometer was operated in the deuterium lock mode to eliminate the effect of the magnetic-field drift. H_2PtCl_6 solutions containing about 10 vol% of D_2O were used in these experiments.

In NMR runs, the impregnation of alumina was carried out by slowly adding 1.5 g of Al_2O_3 to 1.8 ml of a H_2PtCl_6 solution placed in an NMR sample tube ($\phi = 10$ mm) followed by stirring the resulting mixture with a glass stick.

UV-visible and laser Raman spectroscopy measurements. Diffuse reflectance UV-Vis spectra of $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ samples were recorded with a Cary-5 instrument using a BaSO_4 pellet as a reference sample. The scan range was from 500 to 190 nm with a 1.0-nm interval, and the averaging time at each point was 1.0 s.

Laser Raman spectra were taken with a Jobin-Yvon U-1000 instrument using a Spectra Physics Ar laser ($\lambda = 514.5$ nm) operating at 100–200 mW. The scan range was from 100 to 650 cm^{-1} with a 0.5 cm^{-1} step and the counting time 1 s/point. The samples powders were pressed into a stainless-steel sample holder which was mounted onto the axis of a small motor directed at $\sim 45^\circ$ to the exciting laser beam. The sample holder was rotated at approximately 1500 rpm to avoid excessive heating of the sample. All measurements were performed at room temperature in air.

EXAFS measurements. EXAFS experiments were carried out at the LURE synchrotron radiation facilities at the

D44 beam line (Orsay, France) using synchrotron radiation from the DCI storage ring (positron energy 1.85 GeV; mean ring current 200 mA). The spectra were recorded at room temperature in the transmission mode using two Ar-filled ionization chambers and a single-crystal Si(111) monochromator at the L_{III} edge of platinum (11,563 eV). The energies were scanned with a 2-eV step in the 11450- to 12450-eV range. The counting time was 1 s/point.

The data analyses were performed using the “EXAFS pour le Mac” package (18). A linear fit for the preedge region and a k^3 -weighted Fourier transform with Kaiser-Bessel windows beyond the edge were applied. To improve the signal-to-noise ratio, three experimental spectra were averaged. The amplitude and phase shift parameters associated with the backscattering process were extracted from reference compounds (K₂PtCl₆ and PtO₂). The fitting of experimental and calculated EXAFS was carried out with a simplex algorithm (18).

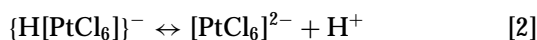
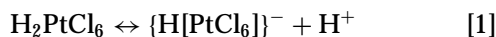
RESULTS AND DISCUSSION

¹⁹⁵Pt NMR

In our previous publication [17], we reported the parameters of the ¹⁹⁵Pt NMR spectra of platinum anions ([PtCl₆]²⁻ and [PtCl₅(OH)]²⁻) at the alumina–aqueous H₂PtCl₆ solution interface. The platinum chemical shifts (δ_{Pt}) were found to be dependent on the pH of the starting H₂PtCl₆ solutions used for alumina impregnation. The effect was more pronounced for [PtCl₅(OH)]²⁻ and less evident for [PtCl₆]²⁻ due to the inaccuracy in measuring small differences in δ_{Pt} for the latter complex. In this work, the NMR spectrometer was operated in the deuterium lock mode to eliminate the effect of magnetic-field drift during NMR acquisitions. Therefore, the δ_{Pt} values for hexachloroplatinates were determined more accurately, and, thus, more information about the structure of adsorbed platinum complexes could be gained. The relevant data are summarized in Table 1 which also includes δ_{Pt} values for the impregnating H₂PtCl₆ solutions.

Chemical Shift in the ¹⁹⁵Pt NMR Spectra of H₂PtCl₆ Solutions

As seen from Table 1, δ_{Pt} of hexachloroplatinates increases from –2.00 ppm for the most acidic solution at pH < 0.1 to 0.84 ppm for the least acidic solution at pH 2.8. This variation can be best accounted for by assuming that the equilibria



shift to the right with decreasing proton concentration. Since protonation–deprotonation reactions [1] and [2] are

TABLE 1

Chemical Shift (δ_{Pt}) of the PtCl₆ and PtCl₅X Lines in ¹⁹⁵Pt NMR Spectra of H₂PtCl₆ Solutions and of the H₂PtCl₆/Al₂O₃ System

System	δ_{Pt} (ppm)	
	PtCl ₆	PtCl ₅ X ^a
6.6 × 10 ⁻² M H ₂ PtCl ₆ solution + HNO ₃ at pH < 0.1	–2.00	500.8
2 × 10 ⁻¹ M H ₂ PtCl ₆ solution at pH 0.24	0.74	502.0
6.6 × 10 ⁻² M H ₂ PtCl ₆ solution at pH 1.15 ^b	0.00 ^c	502.6
Above solution + Al ₂ O ₃ (un) ^{d,e,f}	–6.2	642
Above solution + Al ₂ O ₃ (cal) ^{e,g}	–6.2	643
Above solution + Al ₂ O ₃ (dt) ^{e,h}	–6.5	No signal
	–1.4	
6.6 × 10 ⁻² M H ₂ PtCl ₆ solution at pH 2.8	0.84	518.9
Above solution + Al ₂ O ₃ (un) ^{d,e}	0.1	660

^a X = H₂O or OH⁻.

^b Figs. 1a and 2a.

^c Reference line.

^d Al₂O₃(un), untreated alumina.

^e NMR acquisitions for impregnation time within 20–40 min.

^f Fig. 1b.

^g Al₂O₃(cal), alumina calcined in an air flow at 500°C for 1 h.

^h Al₂O₃(dt), alumina doubly treated with HCl solution treatment (see Experiment).

fast on the NMR time scale, only one averaged signal for the hexachloroplatinates is expected to be observed, with a chemical shift that is the concentration-weighted average of the δ_{Pt} values for H₂PtCl₆, {H[PtCl₆]}⁻, and [PtCl₆]²⁻. Thus, deprotonation of H₂PtCl₆ to {H[PtCl₆]}⁻ and finally to [PtCl₆]²⁻ results in a continuous increase of δ_{Pt} .

In the least acidic 6.6 × 10⁻² M H₂PtCl₆ solution at pH 2.8, equilibria [1] and [2] are profoundly shifted to the right because of the low proton concentration and, thus, [PtCl₆]²⁻ is the most abundant species in this solution. Correspondingly, $\delta_{\text{Pt}} = 0.84$ ppm should be rather close to δ_{Pt} ([PtCl₆]²⁻).

On the other hand, in the 6.6 × 10⁻² M H₂PtCl₆ solution at pH 1.15 with $\delta_{\text{Pt}} = 0.00$ ppm, part of the hexachloroplatinate species must be protonated, as proved by a simple calculation of the charge balance. If no protonated species (H₂PtCl₆ and {H[PtCl₆]}⁻) were present, one could write the following equation on concentrations:

$$[\text{H}^+] = 2 [\text{PtCl}_6]^{2-} + [\text{PtCl}_5(\text{H}_2\text{O})^-] + [\text{Cl}^-], \quad [3]$$

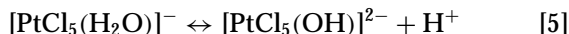
where [PtCl₅(H₂O)]⁻ is the concentration of monoqua complex arising from the hydrolysis of [PtCl₆]²⁻,



According to the ¹⁹⁵Pt NMR spectrum, the ratio [PtCl₆]²⁻/[PtCl₅(H₂O)]⁻ is 1.69, and we can thus calculate that 2[PtCl₆]²⁻ + [PtCl₅(H₂O)]⁻ equals 10.7 × 10⁻² M. At pH

1.15, $[H^+] = 9.3 \times 10^{-2}$ M (taking into account the activity coefficient for protons); that is, we cannot equal the left-hand side of Eq. [3] with its right-hand side under the above hypothesis. Hence, we can conclude that a certain part of hexachloroplatinates is present in the solution as uncharged H_2PtCl_6 molecules or $\{H[PtCl_6]\}^-$.

In accord with our earlier data (17), the displacement of the pentachloroplatinate signal in solutions from $\delta_{Pt} = 502.6$ ppm at pH 1.15 to $\delta_{Pt} = 518.9$ at pH 2.8 (Table 1) is due to the shift of the equilibrium



to the right at higher pH, $\delta_{Pt} = 503$ ppm being characteristic of the $[PtCl_5(H_2O)]^-$ complex.

Chemical Shift in the ^{195}Pt NMR Spectra of Platinum Complexes Adsorbed on Alumina (Table 1)

As a preliminary note to this section, we should state that all the observed ^{195}Pt NMR peaks discussed here were apparently due to adsorbed species, as witnessed, e.g., by the absence of the $[PtCl_5(H_2O)]^-$ signal which is predominant in solution. In other words, the low amount of Pt species remaining in the free solution may be neglected in first approximation: adsorption equilibria are strongly shifted to the right.

Adsorbed hexachloroplatinates. A significant decrease of δ_{Pt} to -6.2 or -6.5 ppm is characteristic of alumina impregnated with H_2PtCl_6 solution at pH 1.15 with $\delta_{Pt} = 0$ ppm (Figs. 1 and 2). In addition, a second line at $\delta_{Pt} = -1.4$ ppm appears in the spectrum of *doubly HCl treated* alumina, $Al_2O_3(dt)$. The presence of two lines means that the corresponding hexachloroplatinate species are not in a fast exchange. Note that precalcination of alumina at $500^\circ C$ in an air flow has no effect on the peak position. A smaller decrease of δ_{Pt} from 0.84 to 0.1 ppm is also found for hexachloroplatinates adsorbed on $Al_2O_3(un)$ from the less acidic solution at pH 2.8. Thus, on the basis of the ^{195}Pt NMR data, one can discriminate three types of adsorbed hexachloroplatinates resonating at $\delta_{Pt} -6.2$ to -6.5 , -1.4 , and 0.1 ppm.

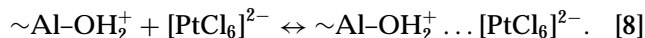
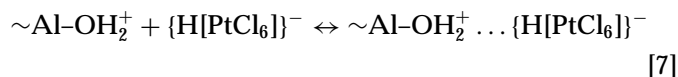
To rationalize these findings, let us consider possible mechanisms of hexachloroplatinate adsorption on the alumina surface. It is known (1, 2) that the surface hydroxyl groups of alumina are protonated in an acidic aqueous medium at $pH \leq 8$,



and the surface is positively charged to an extent that depends on the $[H^+]/Al_2O_3$ ratio.

As a result of the surface charging, electrostatic adsorption of negatively charged hexachloroplatinates on the pro-

tonated hydroxyl groups can occur:



The electrostatic adsorption is probably accompanied by a more specific, although rather weak, interaction of adsorbed Pt species, which are supposed to be held in the Stern layer, with the surface sites (specific adsorption or outer-sphere complex formation).

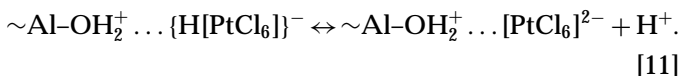
It is reasonable to assume that, in addition to reaction [6], a certain part of alumina hydroxyls can be protonated by interaction with H_2PtCl_6 or $\{H[PtCl_6]\}^-$:



As follows from Eqs. [7]–[10], two different types of adsorbed hexachloroplatinates may exist on the alumina surface in a ratio that depends, among other factors, on the pH of the impregnating solution.

When the most acidic H_2PtCl_6 solution at pH 1.15 is used for alumina impregnation, reactions [7] and [9] appear to be more probable than reactions [8] and [10] because of higher initial concentrations of $\sim Al-OH_2^+$, H_2PtCl_6 , and $\{H[PtCl_6]\}^-$. Therefore, the $\delta_{Pt} = -6.2$ ppm NMR line may be assigned to the $\sim Al-OH_2^+ \dots \{H[PtCl_6]\}^-$ ion pair which represents the most protonated hexachloroplatinic species adsorbed on the surface. This assignment is in line with the general trend of the δ_{Pt} decrease upon protonation of hexachloroplatinates in H_2PtCl_6 solutions (see above).

On the other hand, in the case of alumina impregnation with the least acidic solution at pH 2.8, reactions [8] and [10], which result in the formation of $\sim Al-OH_2^+ \dots [PtCl_6]^{2-}$, become more important because of a much lower concentration of the protonated hydroxyls and a higher $[PtCl_6]^{2-}$ fraction in the solution. Moreover, in a weakly acidic medium, reaction [7], if it occurs, can be followed by fast deprotonation of the $\{H[PtCl_6]\}^-$ moiety to yield the same ion pair:

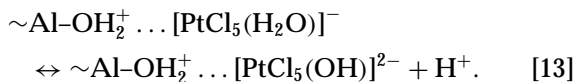
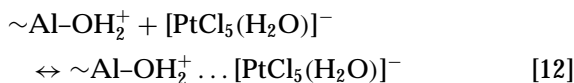


Thus, on these grounds, we may assign the $\delta_{Pt} = 0.1$ ppm NMR line to the $\sim Al-OH_2^+ \dots [PtCl_6]^{2-}$ ion pair which represents the least protonated adsorbed hexachloroplatinic species characterized by the highest δ_{Pt} value.

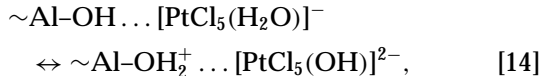
The simultaneous presence of two lines in the hexachloroplatinic region in the case of $Al_2O_3(dt)$ impregnated with H_2PtCl_6 solution at pH 1.15 (Table 1) requires some comments. A characteristic feature of $Al_2O_3(dt)$ is that it initially contains a large number of protonated hydroxyls produced by the pretreatment with an HCl solution

(see Experimental). The formation of an ion pair $\sim\text{Al}-\text{OH}_2^+ \dots [\text{PtCl}_6]^{2-} \dots + \text{H}_2\text{O}-\text{Al}\sim$ on paired protonated hydroxyls may provide a reasonable explanation for the appearance of the $\delta_{\text{Pt}} = -1.4$ ppm line in the spectra. The degree of protonation of the hexachloroplatinic moiety in the above structure and its δ_{Pt} value would be intermediate between those of $\sim\text{Al}-\text{OH}_2^+ \dots \{\text{H}[\text{PtCl}_6]\}^-$ and $\sim\text{Al}-\text{OH}_2^+ \dots [\text{PtCl}_6]^{2-}$.

Adsorbed pentachloroplatinates. Two mechanisms for the fixation of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ on the alumina surface were proposed earlier (17), which, in fact, are very similar to those of $[\text{PtCl}_6]^{2-}$ adsorption. One of them suggests electrostatic interaction of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ with positively charged protonated hydroxyls followed by fast deprotonation of the water molecule ligand of the pentachloroplatinic moiety:



Another mechanism involves direct deprotonation of the water molecule ligand of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ by surface basic hydroxyls,



followed by fast protonation of the resulting hydroxy species via reversed reaction [13].

According to the above equations, the Pt chemical shift of the resulting ion pairs should be dependent on the concentration of free protons at the alumina-solution interface. In the case of the least acidic system studied (H_2PtCl_6 solution at pH 2.8 + $\text{Al}_2\text{O}_3(\text{un})$), $\delta_{\text{Pt}} = 660$ ppm (Table 1) is very close to $\delta_{\text{Pt}}[\text{PtCl}_5(\text{OH})]^{2-} = 662$ ppm in H_2PtCl_6 solutions (17); i.e., the hydroxy pentachloroplatinate is largely predominant on the surface.

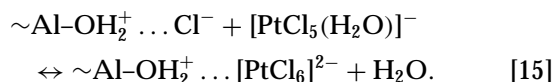
Contrary to this, in the case of a more acidic system (H_2PtCl_6 solution at pH 1.15 + $\text{Al}_2\text{O}_3(\text{un})$), $\delta_{\text{Pt}}[\text{PtCl}_5\text{X}] = 642$ ppm indicates that some part of the adsorbed pentachloroplatinate is in the form of the mono aqua complex. Taking $\delta_{\text{Pt}}[\text{PtCl}_5(\text{H}_2\text{O})]^- = 503$ ppm and $\delta_{\text{Pt}}[\text{PtCl}_5(\text{OH})]^{2-} = 662$ ppm (Table 1 and (17)), one may calculate that 88% of the pentachloroplatinates are adsorbed as $[\text{PtCl}_5(\text{OH})]^{2-}$ and 12% as $[\text{PtCl}_5(\text{H}_2\text{O})]^-$.

Using the values for $\delta_{\text{Pt}}[\text{PtCl}_5(\text{H}_2\text{O})]^- = 503$ ppm, $\delta_{\text{Pt}}[\text{PtCl}_5(\text{OH})]^{2-} = 662$ ppm, and $\delta_{\text{Pt}} = 642$ ppm for the adsorbed pentachloroplatinate, the pH value at the alumina-solution interface was calculated using (19)

$$\delta_{\text{Pt}} = (\delta_{\text{Pt}}[\text{PtCl}_5(\text{H}_2\text{O})]^- \cdot [\text{H}^+] + \delta_{\text{Pt}}[\text{PtCl}_5(\text{OH})]^{2-} \cdot K_a) / ([\text{H}^+] + K_a),$$

where K_a is the equilibrium constant of the protonation-deprotonation equilibrium. By putting $K_a = 1.58 \times 10^{-4}$ ($\text{p}K_a = 3.8$) (20) into this equation, we obtain a value of 4.64 for the final pH which evidences significant proton consumption by the alumina support from the impregnating solution at initial pH 1.15. The pH increase was reported in a number of earlier publications (2, 5, 21) in which pH values of H_2PtCl_6 solutions-alumina suspensions were directly measured in the bulk of the H_2PtCl_6 solution with a pH meter. It should be underlined here that the local pH value at the alumina-solution interface estimated from our NMR data may be somewhat higher than that in the bulk solution in accordance with the double-layer model (22), which predicts a deficiency of protons near the positively charged surface.

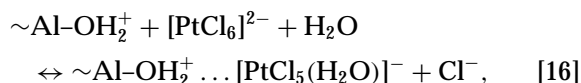
The absence of an NMR signal in the pentachloroplatinate region for $\text{Al}_2\text{O}_3(\text{dt})$ impregnated with H_2PtCl_6 solution at pH 1.15 (Table 1) is rather surprising taking into account that the fractions of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_6]^{2-}$ are comparable in the impregnating solution. Possibly, this effect can be explained by a fast transformation of the aqua complex to hexachloroplatinate due to a high local Cl^- content on the surface of $\text{Al}_2\text{O}_3(\text{dt})$:



It should be noted, however, that the replacement of a water molecule ligand by Cl^- in the Pt coordination sphere is relatively slow in H_2PtCl_6 solutions at room temperature.

Evolution of the NMR Spectra of Adsorbed Platinum Complexes with Adsorption Time

Figure 1 gives the evolution of ^{195}Pt NMR spectra of platinum complexes adsorbed on alumina $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 1.15 vs adsorption time. As seen from Figs. 1b-1d, the ratio $\alpha = I(\text{PtCl}_6)/I(\text{PtCl}_5\text{OH})$, where I stands for integral intensities of the corresponding NMR signals, decreases significantly with adsorption time. For instance, $\alpha = 1.07$ for adsorption time 7-45 min (Fig. 1b), whereas α falls down to 0.15 after adsorption overnight (Fig. 1d). Most likely, this effect is associated with a slow hydrolysis of the adsorbed hexachloroplatinate,



followed by deprotonation of the resulting aqua complex by reaction [13] to give rise to $\sim\text{Al}-\text{OH}_2^+ \dots [\text{PtCl}_5(\text{OH})]^{2-}$.

In contrast to the above experiment, when the singly HCl treated alumina ($\text{Al}_2\text{O}_3(\text{st})$, see Experimental) is used as a support and impregnated with H_2PtCl_6 solution at pH 1.15 (Fig. 2), the ratio $\alpha = I(\text{PtCl}_6)/I(\text{PtCl}_5\text{OH})$ is considerably

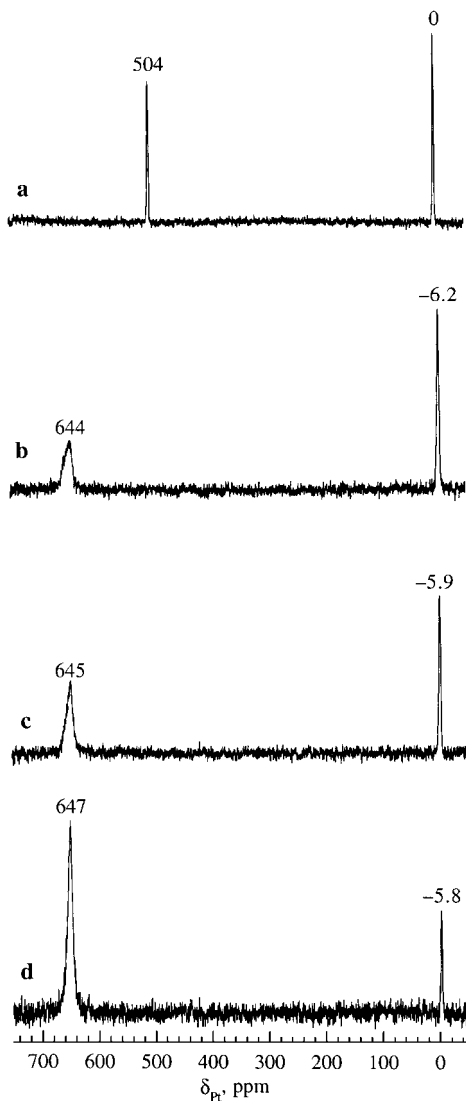


FIG. 1. ^{195}Pt NMR spectra of: (a) H_2PtCl_6 solution at pH 1.15; (b) $\text{Al}_2\text{O}_3(\text{un})$ impregnated with the above solution for 7–45 min; (c) impregnation for 4–4.5 h; (d) impregnation overnight.

higher for a short adsorption time ($\alpha = 2.0$ after 15–40 min, Fig. 2b) and decreases to a much lesser extent for a long adsorption time ($\alpha = 1.0$ after adsorption overnight, Fig. 2d). This effect can be accounted for by a higher Cl^- concentration on the surface of the acidified alumina $\text{Al}_2\text{O}_3(\text{st})$ which prevents equilibrium [16] from shifting to the right.

Thus the composition of adsorbed platinum complexes is strongly dependent on the pH of the impregnating solution, the acidity of the alumina support, and the adsorption time. The two extreme cases are well illustrated by the spectra of Fig. 3. For the most acidic system and short adsorption time, ^{195}Pt NMR reveals the presence of only $[\text{PtCl}_6]^{2-}$ species at $\delta_{\text{Pt}} = -5.8$ ppm (Fig. 3a), while for the least acidic system and long adsorption time, only $[\text{PtCl}_5(\text{OH})]^{2-}$ species at $\delta_{\text{Pt}} = 660$ ppm can be detected (Fig. 3b).

Integral Intensities of the NMR Signals of Adsorbed Platinum Complexes versus Adsorption Time

Figure 4(I) enables one to compare the integral intensities of the Pt NMR signals in the initial impregnating solution at pH 1.15 and those of the Pt complexes adsorbed on $\text{Al}_2\text{O}_3(\text{un})$. The following conclusions emerge from the analysis of Fig. 4(I):

(i) The sum of the integral intensities of the NMR signals of Pt species for the impregnated alumina is approximately constant and similar to the integrated intensity for the starting H_2PtCl_6 solution (taking into account the inaccuracy in measuring the spectra of the solution and the solid, the filling factor, etc.). Thus, virtually *all* adsorbed platinum complexes can be detected by NMR or, in other words,

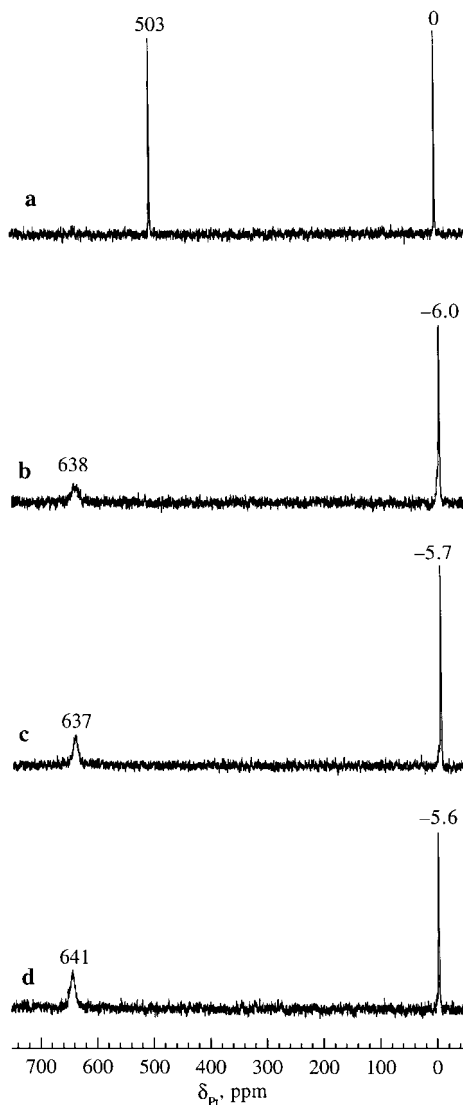


FIG. 2. ^{195}Pt NMR spectra of: (a) H_2PtCl_6 solution at pH 1.15; (b) $\text{Al}_2\text{O}_3(\text{st})$ impregnated with the above solution for 15–40 min; (c) impregnation for 7 h; (d) impregnation overnight.

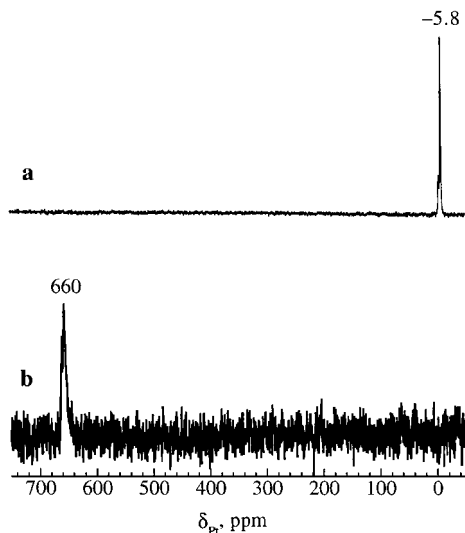


FIG. 3. ^{195}Pt NMR spectra of: (a) $\text{Al}_2\text{O}_3(\text{dt})$ impregnated with H_2PtCl_6 solution at pH 1.15 for 0.8–2 h; (b) $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 2.8 for 44 h.

there is no marked grafting of the Pt species to the surface at this stage of the catalyst preparation.

(ii) The sum of the integral intensities of the NMR signals of the adsorbed Pt species remain constant in the course of alumina impregnation with the H_2PtCl_6 solution.

(iii) When alumina is brought into contact with the H_2PtCl_6 solution, $[\text{PtCl}_6]^{2-}$ giving rise to the NMR signal at $\delta_{\text{Pt}} = -6.2$ ppm is electrostatically fixed on protonated hydroxyls, whereas the 504 ppm signal of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ species in the solution almost quantitatively transforms to the 645 ppm signal of $[\text{PtCl}_5(\text{OH})]^{2-}$ fixed on protonated hydroxyls.

Contrary to the system described above, when the same alumina $\text{Al}_2\text{O}_3(\text{un})$ is brought into contact with the less acidic H_2PtCl_6 solution at pH 2.8, the overall integral intensity of the NMR signals diminishes by about 20%, as indicated by the arrows in Fig. 4(2). This probably means that a part of adsorbed Pt complexes becomes grafted via ligand exchange to the surface hydroxyls and thus escapes NMR detection (see below). A greater extent of ligand exchange with the surface hydroxyls at higher initial pH values of the impregnating solutions agrees with the data by Mang *et al.* (2). At longer adsorption times (17 and 44 h), the overall integral intensity considerably decreases, indicating further transformation of the adsorbed Pt complexes.

Effect of Drying, Rewetting, and Posttreatment with HCl of Impregnated Alumina on the NMR Spectra of Adsorbed Platinum Complexes

The relevant data are summarized in Table 2.

Dried solids. No Pt NMR signal (neither static nor MAS NMR) was detected for *untreated* alumina impregnated

with H_2PtCl_6 solutions after the removal of water by drying the samples under mild conditions (i.e., in a vacuum desiccator over P_2O_5 at 20°C overnight) or in an oven at 90°C overnight (samples 1 and 2). As assumed earlier (17), the absence of Pt NMR signal can be accounted for by an increase in chemical shift anisotropy due to a strong perturbation of the platinum atom coordination sphere. For dried solids, the chemical shift anisotropy may increase to such an extent that the signals of adsorbed platinum complexes become unobservable because of heavy line broadening.

On the other hand, for $\text{Al}_2\text{O}_3(\text{dt})$ impregnated with H_2PtCl_6 solution at pH 1.15 and then dried at 20°C (Table 2, sample 4), a Pt MAS NMR signal was detected as shown in Fig. 5a. It consists of a single peak of $[\text{PtCl}_6]^{2-}(\text{ads})$

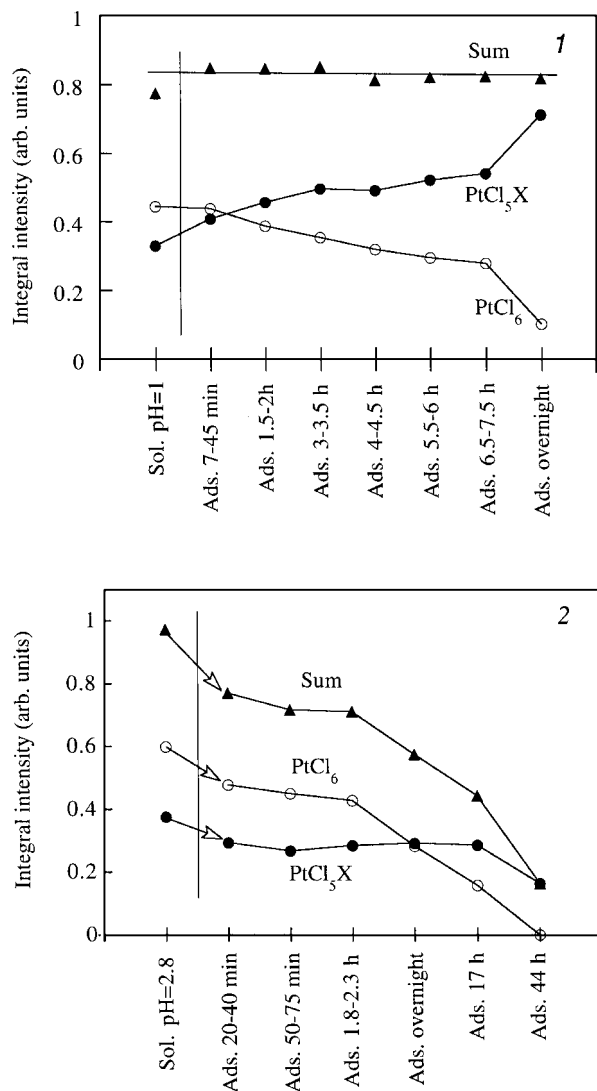


FIG. 4. Integral intensities of PtCl_6 and PtCl_5X ^{195}Pt NMR signals and their sum as a function of impregnation time. (1) $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 1.15. (2) $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 2.8. PtCl_5X stands for $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ or $[\text{PtCl}_5(\text{OH})]^{2-}$ signals.

TABLE 2
Effect of Drying, Rewetting, and Posttreatment with HCl on the ^{195}Pt NMR Spectra of the $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ System

Sample No.	System	Sample treatment after impregnation with H_2PtCl_6 solution	NMR signal
1	H_2PtCl_6 solution at pH 1.15 + $\text{Al}_2\text{O}_3(\text{un})$	Drying at 20°C ^a	No
		Rewetting with water	Yes
		Drying at 90°C overnight, rewetting with water	No (after 4000 scans)
		Drying at 90°C , treatment with 0.1 M HCl for 3 h at 20°C	Yes (Fig. 6a)
2	H_2PtCl_6 solution at pH 2.7 + $\text{Al}_2\text{O}_3(\text{un})$	Drying at 90°C overnight	No
		Rewetting with water	No (after 100,000 scans)
		Drying at 20°C ^a , treatment with 0.1 M HCl for 3 h at 20°C	Yes (Fig. 6b)
3	H_2PtCl_6 solution at pH 1.15 + $\text{Al}_2\text{O}_3(\text{st})$	Drying at 20°C ^a , rewetting with water	Yes (Fig. 7a)
		Drying at 90°C overnight, rewetting with water	Yes
		Drying at 150°C for 3 h, rewetting with water	Yes (Fig. 7b)
4	H_2PtCl_6 solution at pH 1.15 + $\text{Al}_2\text{O}_3(\text{dt})$	Drying at 20°C ^a	Yes ^b (Fig. 5a)
		Drying at 90°C for 3 h	Yes ^b (Fig. 5b)
		Drying at 90°C for 40 h, rewetting with water	Yes

^a In a vacuum desiccator over P_2O_5 , overnight.

^b ^{195}Pt MAS NMR.

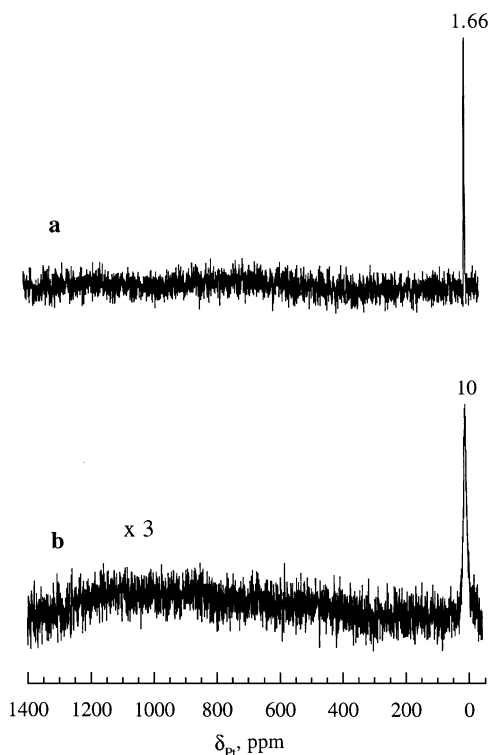


FIG. 5. ^{195}Pt MAS NMR spectra of: (a) $\text{Al}_2\text{O}_3(\text{dt})$ impregnated with H_2PtCl_6 solution at pH 1.15 and dried at 20°C overnight; (b) sample (a) dried at 90°C for 3 h. The Y-axis scale of spectrum (b) is enlarged by a factor of 3.

at 1.66 ppm similar to what was observed for the wet sample (Fig. 3a). After drying sample 4 at 90°C for 3 h, the $[\text{PtCl}_6]^{2-}$ line in the MAS NMR spectrum broadens and shifts downfield to 10 ppm (Fig. 5b). Integration of the $[\text{PtCl}_6]^{2-}$ peaks reveals that the intensities on the NMR signals in Figs. 5a and 5b are comparable: the difference is about 30% and may be due to the experimental uncertainty. Thus, the $[\text{PtCl}_6]^{2-}$ complex adsorbed on the acidified alumina retains its integrity after removal of water, although its coordination sphere becomes somewhat perturbed as evidenced by the change in δ_{Pt} values and line broadening. The possible reasons for the different behavior of Pt complexes adsorbed on $\text{Al}_2\text{O}_3(\text{un})$ and $\text{Al}_2\text{O}_3(\text{dt})$ will be discussed below.

Rewetted solids. For all samples studied, rewetting of $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ dried at 20°C overnight with water results in the reappearance of Pt NMR signals which are very similar to those of the original impregnated wet solids.

In contrast to this, after drying at 90°C overnight, no NMR signal reappears for the rewetted samples 1 and 2 (Table 2), indicating further irreversible transformations of the adsorbed platinum complexes which make impossible the backtransformation to an NMR detectable form. Most likely, a grafting reaction occurs which will be discussed below.

However, the NMR signals can be partly restored by treating the dried solids with aqueous HCl at 20°C . A $[\text{PtCl}_6]^{2-}$ line at -4.3 ppm appears after such treatment together with a much less intense peak of $[\text{PtCl}_5(\text{OH})]^{2-}$ at about 640 ppm for sample 1 precalcined at 90°C (Table 2

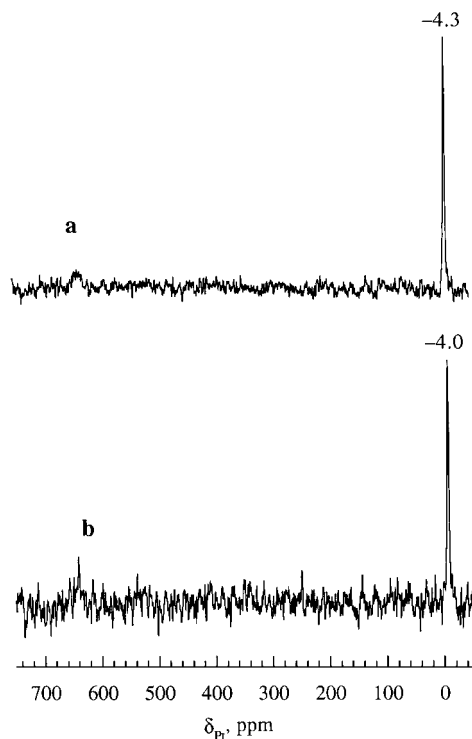


FIG. 6. ^{195}Pt NMR spectra of $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at (a) pH 1.15 or (b) pH 2.8, dried at 90°C overnight, and then treated with 0.1 M HCl for 3 h at 20°C .

and Fig. 6a). Similar results were obtained with sample 2 also precalcined at 90°C (Table 2 and Fig. 6b). Hence, the grafted platinum complexes (non detectable by NMR) can be transformed to an NMR detectable form by treatment with HCl.

When the HCl treated aluminas were used for impregnation, adsorbed Pt species exhibit much higher thermal stability. For instance, NMR signals of Pt complexes adsorbed on $\text{Al}_2\text{O}_3(\text{st})$ and $\text{Al}_2\text{O}_3(\text{dt})$ after heating the solids at 90 or 150°C (Table 2, samples 3 and 4) can be restored by rewetting the solids with water as illustrated by Fig. 7.

Thus, the grafting (ligand exchange) of adsorbed Pt complexes to the alumina surface upon heating is strongly inhibited in the case of the HCl treated aluminas. Presumably, this is due to much smaller concentrations of unprotonated hydroxyl groups (see discussion below).

UV-Visible Spectroscopy

Literature Data on UV-Vis Spectra of H_2PtCl_6 Solutions and the $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ System

The relevant literature data summarized in Tables 3 and 4. Aqueous solutions of H_2PtCl_6 exhibit two intense ligand-to-metal charge-transfer (CT) absorption bands at 201 and 261–262 nm which were assigned to $[\text{PtCl}_6]^{2-}$ (Table 3). They correspond to an $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1u}$ transition (25). The

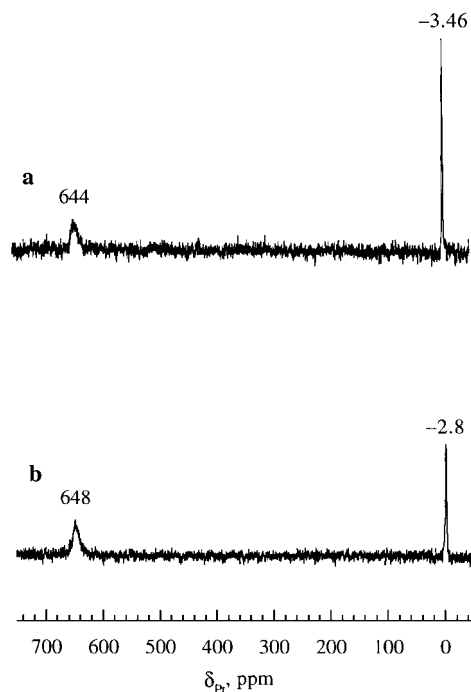


FIG. 7. ^{195}Pt NMR spectra of: (a) $\text{Al}_2\text{O}_3(\text{st})$ impregnated with H_2PtCl_6 solution at pH 1.15, dried at 20°C overnight, and rewetted with water; (b) sample (a) dried at 150°C for 2 h and rewetted with water. Both spectra are plotted at the same Y-axis scale.

261-nm band is due to transitions involving orbitals with Cl ligand π -character, whereas the 201-nm band is due to transitions from orbitals with ligand σ -character (27). In the visible-light region, two less intense $d-d$ transition bands of Pt(IV) are observed at 353 and 452 nm (23, 24). In Ref. [25], several other $d-d$ transition bands were reported for $[\text{PtCl}_6]^{2-}$ which, however, were not found in other studies.

After impregnation of γ -alumina with an H_2PtCl_6 solution, the positions of the $d-d$ bands for adsorbed Pt species do not change appreciably; i.e., the octahedral symmetry

TABLE 3

Literature Data on UV-Vis Spectra of H_2PtCl_6 in Aqueous Solutions and Its Hydrolysis Products

Pt complex	Band position (nm)		Ref.
	Ligand-to-metal CT bands	$d-d$ transition bands	
$[\text{PtCl}_6]^{2- a}$	262 ^b	353, 452	23, 24
$[\text{PtCl}_6]^{2- c}$	201, 261	473, 497, 527, 561	25
$[\text{PtCl}_5(\text{H}_2\text{O})]^-$	260 ^c	355, 452	23
<i>trans</i> - $[\text{PtCl}_4(\text{H}_2\text{O})_2]$	211, ~260	353, 458	26
<i>trans</i> - $[\text{PtCl}_4(\text{OH})_2]^{2-}$	222, 275	375, 495	26

^a H_2PtCl_6 in 1 M HCl solution.

^b The second CT band at lower wavelengths is not reported, since it lies beyond the limit of spectrometer detection.

^c In H_2PtCl_6 aqueous solution.

TABLE 4
Literature Data on UV-Vis Diffuse Reflectance Spectra of the $\text{H}_2\text{PtCl}_6/\gamma\text{-Al}_2\text{O}_3$ System

Sample	Band position (nm)		Assignment	Ref.
	CT	<i>d-d</i>		
Alumina impregnated with H_2PtCl_6 + HCl solution and dried at 120°C	275	353, 450	$[\text{PtCl}_6]^{2-}$	3
Alumina impregnated with H_2PtCl_6 solution and dried at 80°C	218	354, 452	$[\text{PtCl}_5(\text{OH})]^{2-}$	4
Adsorption of H_2PtCl_6 on alumina by liquid imbibition	248	^a	$[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$	2
Adsorption from H_2PtCl_6 solutions under equilibrium conditions				2
Final pH 1.13	263	^a	$[\text{PtCl}_6]^{2-}$	
Final pH 4.02	240	^a	$[\text{PtCl}_5(\text{OH})]^{2-}$	

^a *d-d* transitions not reported.

of the initial platinum complexes is preserved (Table 4). It should be noted, however, that small shifts in the positions of these bands are difficult to evidence, because the *d-d* bands appear in the spectra as more or less distinct shoulders rather than as well resolved bands.

In contrast to the *d-d* transitions, a considerable shift of the CT band maxima relative to their position in solutions was found to occur in the UV-Vis diffuse reflectance (DR) spectra of H_2PtCl_6 adsorbed on $\gamma\text{-Al}_2\text{O}_3$, which is strongly indicative of a metal precursor-alumina support interaction. However, as seen from Table 4, the reported maxima for the CT bands differ appreciably even for samples prepared by very similar procedures. Moreover, because of instrumental limitations, in most cases, UV-Vis DR spectra could not be recorded at wavelengths lower than ~ 230 nm, so that the 201-nm CT band of $[\text{PtCl}_6]^{2-}$ was beyond the limit of detection. In some studies, a single CT band at 275 nm (3) or at 248 nm (2) was observed for alumina impregnated with H_2PtCl_6 solutions, whereas Jackson *et al.* (4) reported the disappearance of the 260 nm CT band for $[\text{PtCl}_6]^{2-}$ adsorbed on alumina and a shift of the 201 nm band to 218 nm. The observed CT bands were ascribed to adsorbed $[\text{PtCl}_6]^{2-}$ or $[\text{PtCl}_5(\text{OH})]^{2-}$ which were supposed to be the major species. However, there is no agreement in the publications cited above on the assignment of one or several bands at precise positions to a specific Pt complex. A marked shift of the absorption maxima from 263 to 240 nm was noticed when the adsorption was carried out from acidic H_2PtCl_6 solutions at different pH values under equilibrium conditions (2).

Thus, it appears that the observed CT bands cannot be assigned unambiguously to a specific adsorbed Pt species on the sole basis of UV-Vis spectra. However, in combination

with ^{195}Pt NMR, UV-Vis spectroscopy can provide useful complementary information.

Evolution of UV-Vis Spectra of the $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ System upon Aging and Subsequent Treatments: Correlation with ^{195}Pt NMR Data

Figure 8(1) gives the UV-Vis DR spectrum of *untreated* alumina impregnated with H_2PtCl_6 solution at pH 1.15.

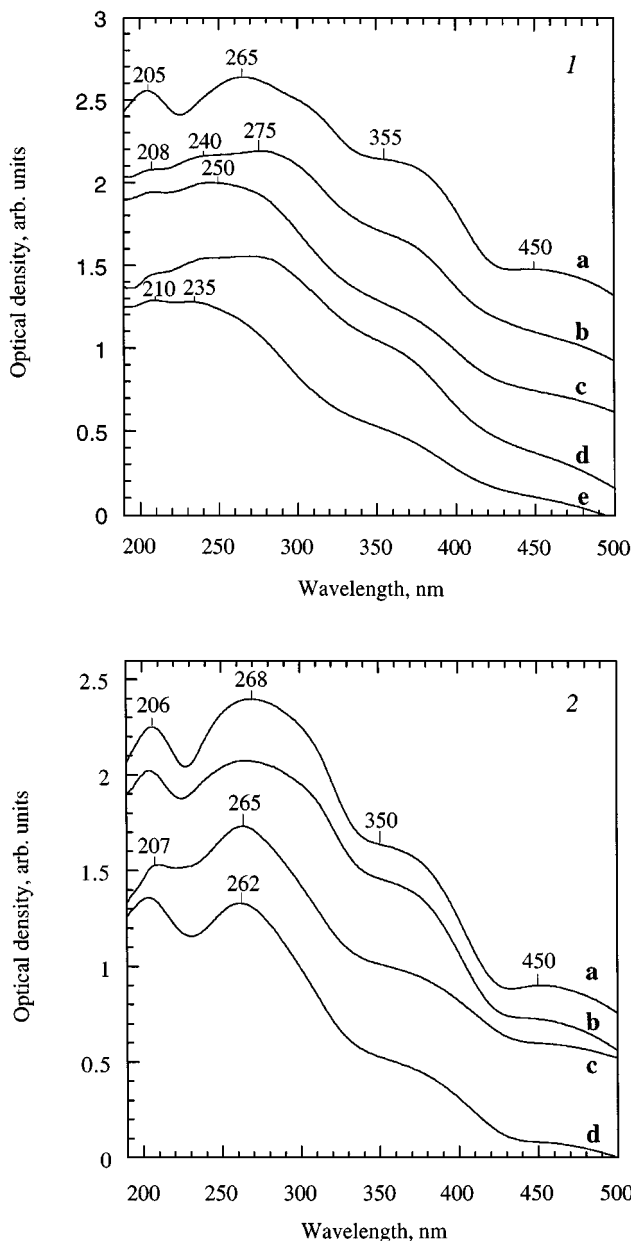


FIG. 8. (1) UV-Vis DR spectra of $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 1.15: (a) after impregnation for 1 h, (b) after impregnation overnight, (c) after drying at 20°C for 10 days, (d) after rewetting with water, (e) after drying at 90°C for 3 h. (2) UV-Vis DR spectra of $\text{Al}_2\text{O}_3(\text{st})$ impregnated with H_2PtCl_6 solution at pH 1.15: (a) after impregnation for 1 h, (b) after impregnation overnight, (c) after drying at 20°C for 4 days, (d) after drying at 90°C overnight.

Here, we do not discuss the *d-d* transition bands of adsorbed Pt complexes (i.e., those at 355 and 450 nm), since no marked change in their positions was found to occur upon adsorption and subsequent treatments. It is therefore likely that octahedral symmetry of the initial platinum complexes is preserved in the adsorbed state.

In the CT region, two absorption bands at 265 and 205 nm are clearly seen in the spectrum of Fig. 8(1a) for the freshly prepared sample which can be assigned to $[\text{PtCl}_6]^{2-}(\text{ads})$. The broadness of the 265-nm band points to the presence of another absorption band in this region which appears in the spectrum as a shoulder at 275–280 nm. The latter may be tentatively attributed to $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})$. No reliable data are available for the latter complex, but the closely related *trans*- $[\text{PtCl}_4(\text{OH})_2]^{2-}$, which also has Pt–Cl and Pt–OH bonds, has a band at 275 nm (26) (Table 3). In addition, according to the ^{195}Pt NMR results (Fig. 4(1)), $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})$ is present on the alumina surface approximately in the same amount as that of $[\text{PtCl}_6]^{2-}(\text{ads})$. In Fig. 8(1a), the 265-nm band of $[\text{PtCl}_6]^{2-}(\text{ads})$ is more intense than the 275-nm band of $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})$, probably because of a difference in the extinction coefficients (ϵ) for the CT bands: $\epsilon = 24500 \text{ M}^{-1} \text{ cm}^{-1}$ for the 262-nm band of $[\text{PtCl}_6]^{2-}$ (23), whereas $\epsilon \approx 6000 \text{ M}^{-1} \text{ cm}^{-1}$ for the 275-nm band of *trans*- $[\text{PtCl}_4(\text{OH})_2]^{2-}$ (26).

It is worth noting here that the replacement of one or two Cl ligands in $[\text{PtCl}_6]^{2-}$ with one or two H_2O molecules does not result in a marked shift of the 261-nm CT band (Table 3).

After impregnation of the sample overnight, its spectrum has changed considerably (Fig. 8(1b)). The maximum at 265 nm disappears, the 275-nm band becomes quite distinct, and the 205-nm band shifts to 208 nm. Such a modification of the spectrum is in accord with NMR data which evidence the predominance of $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})$ after impregnation overnight (Fig. 4(1)). The small shift of the 205-nm band is also consistent with the above assignment, since, as seen from Table 3, the substitution of a Cl ligand by OH causes the 201-nm band to shift to slightly higher wavelengths. In addition to the 275- and 208-nm bands, a band centered at ~ 240 nm is seen in the spectrum of Fig. 8(1b). The latter becomes more pronounced and shifts to 250 nm after drying the sample at 20°C , whereas the 275-nm band disappears (Fig. 8(1c)). In fact, this modification of the UV–Vis spectrum correlates with the disappearance of ^{195}Pt NMR signals, and we will later attribute both observations to ligand exchange in the Pt coordination sphere with the surface hydroxyls resulting in the formation of $\sim\text{Al-O-PtCl}_5$ and $(\sim\text{Al-O})_2\text{-PtCl}_4$ grafted species (see below).

Rewetting the sample with water restores the spectrum characteristic of the nondried impregnated alumina (cf. Figs. 8(1b) and 8(1d)). Hence, at this stage of the catalyst preparation, the changes in the UV–Vis spectra upon drying at 20°C and rewetting are *reversible*. This fact is in agreement with the Pt NMR data.

After drying at 90°C , the spectrum becomes rather featureless, but two bands at 235 and 210 nm are still observed (Fig. 8(1e)), indicating further transformations of adsorbed Pt complexes.

Figure 8(2) shows the evolution of the UV–Vis DR spectra of HCl treated alumina $\text{Al}_2\text{O}_3(\text{st})$ impregnated with H_2PtCl_6 solution at pH 1.15. The spectra of the “fresh” and “aged” for 24 h sample are very similar (Figs. 8(2a) and 8(2b)): the 268- and 206-nm bands (although rather broad) can be assigned to $[\text{PtCl}_6]^{2-}$ which is the major adsorbed species. Thus, the transformation of $[\text{PtCl}_6]^{2-}$ adsorbed on $\text{Al}_2\text{O}_3(\text{st})$ to other complexes is much slower than that on $\text{Al}_2\text{O}_3(\text{un})$. This also agrees with the Pt NMR data.

The spectra of the same sample dried at 20°C and then at 90°C are shown in Figs. 8(2c) and 8(2d), respectively. The 265- and 207-nm bands of $[\text{PtCl}_6]^{2-}$ are quite distinct in both spectra, indicating a much higher stability of the Pt coordination sphere of this species on the surface of HCl treated alumina in comparison with $\text{Al}_2\text{O}_3(\text{un})$. This fact is also in good accord with the Pt NMR data.

The UV–Vis spectra of different alumina samples impregnated with H_2PtCl_6 solutions and then dried in a vacuum desiccator at 20°C for 2 days are presented in Figs. 9(1) and 9(2). After rewetting these samples with water, the ^{195}Pt NMR spectra shown in Fig. 10 were obtained. A good correlation between UV–Vis and NMR data is evident.

As follows from the NMR spectrum of Fig. 10a, $[\text{PtCl}_6]^{2-}(\text{ads})$ is the major species for HCl treated alumina impregnated with an H_2PtCl_6 solution at pH 1.15. Correspondingly, two bands at 261 and 203 nm observed in Fig. 9a can be assigned to $[\text{PtCl}_6]^{2-}$ as indicated above.

On the other hand, when $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})$ is dominant in the NMR spectrum (untreated alumina impregnated with an H_2PtCl_6 solution at pH 1.15, Fig. 10c), the UV–Vis spectrum of the dried sample displays the 250-nm band which is

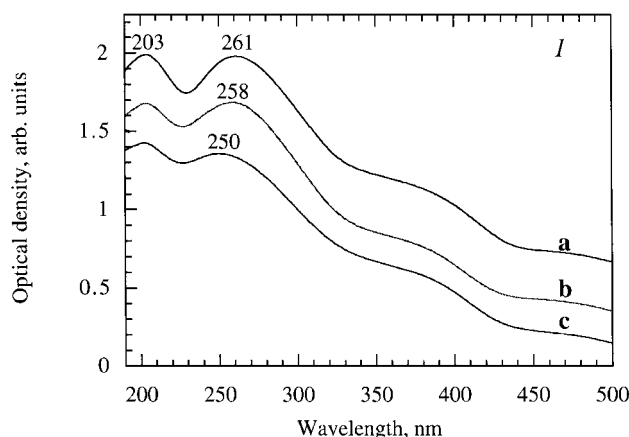


FIG. 9. UV–Vis DR spectra of: (a) $\text{Al}_2\text{O}_3(\text{st})$ impregnated with H_2PtCl_6 solution at pH 1.15; (b) $\text{Al}_2\text{O}_3(\text{st})$ impregnated with H_2PtCl_6 solution at pH 2.8; (c) $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 1.15. All samples were dried at 20°C for 2 days.

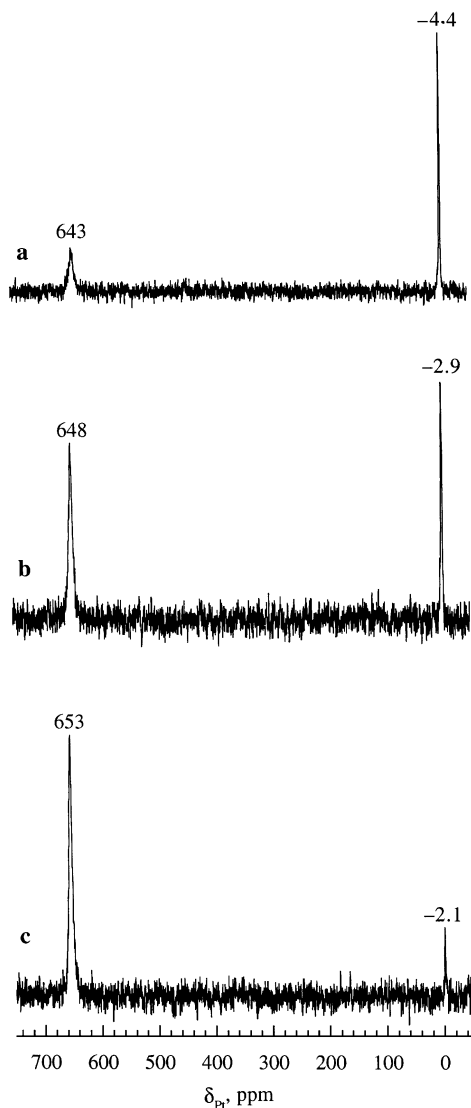


FIG. 10. ^{195}Pt NMR spectra of samples (a), (b), and (c) of Fig. 9 after rewetting with water.

characteristic of the grafted ligand-exchanged Pt complexes.

At intermediate situation (HCl treated alumina impregnated with the less acidic H_2PtCl_6 solution at pH 2.8), when both $[\text{PtCl}_6]^{2-}(\text{ads})$ and $[\text{PtCl}_5(\text{OH})]^{2-}(\text{ads})$ are detected by Pt NMR (Fig. 10b), a CT band appears at an intermediate position (at 258 nm) in the UV-Vis spectrum (Fig. 9b).

Raman Spectroscopy

Figure 11 gives the Raman spectra of K_2PtCl_6 (a reference compound) and of alumina impregnated with H_2PtCl_6 solutions.

In accordance with the literature data (28), three vibration bands at 175, 320, and 350 cm^{-1} are observed for

K_2PtCl_6 (Fig. 11a) which are typical of Pt-Cl bond vibrations of the $[\text{PtCl}_6]^{2-}$ unit.

For $\text{Al}_2\text{O}_3(\text{dt})$ impregnated with an H_2PtCl_6 solution at pH 1.15 and then dried at 20°C, the bands are observed at nearly the same positions, but markedly broadened, thus confirming the predominance of $[\text{PtCl}_6]^{2-}$ complexes on the surface of the doubly HCl treated alumina (Fig. 11b).

Figure 11c shows the spectrum of untreated alumina impregnated with the same H_2PtCl_6 solution and then dried at 20°C. All bands characteristic of the Pt-Cl bond vibrations are present, but those at 320 and 350 cm^{-1} are not well resolved. More importantly, an additional broader band centered at 570 cm^{-1} appears in the spectrum of Fig. 11c which, most likely, can be attributed to a Pt-O bond vibration in adsorbed PtCl_xO_y or $\text{PtCl}_x(\text{OH})_y$ species. Such an assignment agrees with the Raman data of Cox and Peters (26) who observed the following bands for a related *trans*- $\text{PtCl}_4(\text{OH})_2$ complex: at 182, 317, and 338 cm^{-1} for Pt-Cl bond vibrations and at 548 cm^{-1} for a Pt-O bond vibration. It should

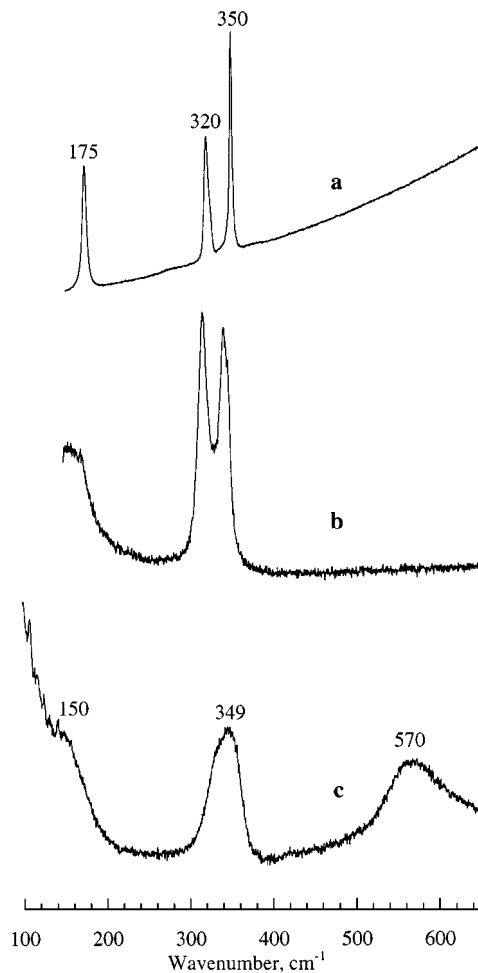


FIG. 11. Laser Raman spectra of: (a) K_2PtCl_6 , (b) $\text{Al}_2\text{O}_3(\text{dt})$, and (c) $\text{Al}_2\text{O}_3(\text{un})$ impregnated with H_2PtCl_6 solution at pH 1.15 and then dried at 20°C.

be noted in this context that the presence of a weak band at 580 cm^{-1} , which lies in the Pt–O bond vibration region, was earlier reported in Ref. (6) for $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ dried at 110°C , but no definite assignment of this band has been proposed.

Spectra similar to those of Fig. 11c were obtained for untreated alumina impregnated with a less acidic H_2PtCl_6 solution at pH 2.8 and then dried at 20°C (not shown).

No marked change in the Raman spectra of the $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ samples was found to occur upon drying in air up to 150°C .

EXAFS

The fitted structural parameters for three series of $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ samples as determined by EXAFS data processing for the subsequent treatments of the samples are given in Table 5, where $N(\text{Cl})$ and $N(\text{O})$ stand for the number of chlorine and oxygen atoms in the first coordination sphere of Pt complexes, respectively; $R(\text{Pt–Cl})$ and $R(\text{Pt–O})$ are Pt–Cl and Pt–O distances. The last column refers to the quality of spectra simulation.

Figure 12 depicts moduli of Fourier transforms (k^3 , Kaiser window) for the three series of samples. Figure 13 compares the fit of the experimental and calculated $k\chi(k)$ functions (filter of the first shell) for several selected samples. The fit was of similar quality for all samples studied (Table 5).

The following conclusions can be drawn from the EXAFS data processing:

For HCl treated alumina $\text{Al}_2\text{O}_3(\text{dt})$ impregnated with an H_2PtCl_6 solution at pH 1.15 (Table 5, samples 1–5), the first coordination sphere of adsorbed Pt complexes consists of about six chlorine atoms at a Pt–Cl distance of $R = 2.32\text{ \AA}$ which is characteristic of this bond in the reference sample K_2PtCl_6 . Although the determination of the Pt coordination numbers by EXAFS is not very accurate, we may conclude that adsorbed Pt is present on the alumina surface mainly as $[\text{PtCl}_6]^{2-}$ species. The coordination numbers remain unchanged upon heating the solids up to 150°C and slightly decrease (to 5.6 ± 0.1) after calcination at 350°C in air (sample 5).

In the case of untreated alumina impregnated with an H_2PtCl_6 solution at pH 1.15 (samples 6–10), the first coordination sphere of Pt consists of about four Cl atoms and two oxygen atoms at the following distances: $R(\text{Pt–Cl}) = 2.32\text{ \AA}$ as in K_2PtCl_6 and $R(\text{Pt–O}) = 2.01\text{--}2.04\text{ \AA}$. The latter value is close to the Pt–O bond length in PtO_2 (2.04 \AA) (7). Thus, the EXAFS data evidence the presence of $[\text{PtCl}_4\text{O}_2]$ complexes as the major surface species. This conclusion agrees with the EXAFS data obtained by Berdala *et al.* (8) for $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts at Pt loading of 0.3–1.5% prepared by competitive impregnation with H_2PtCl_6 and HCl and then dried at 110°C . No marked change in the coordination number is found to occur upon drying and calcination in air up to 270°C (sample 10).

For untreated alumina impregnated with an H_2PtCl_6 solution at pH 2.8 (samples 11–14), the EXAFS data seem to indicate that the first coordination sphere contains about three Cl atoms and three oxygen atoms at the distances

TABLE 5

Structural Parameters Determined from EXAFS Analysis of the $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ System at the L_{III} Edge of Pt

No.	Treatment ^a	$N(\text{Cl})$	$R(\text{Pt–Cl})$ (Å)	$N(\text{O})$	$R(\text{Pt–O})$ (Å)	Fit ($\times 10^3$)
$\text{H}_2\text{PtCl}_6(\text{pH } 1.15) + \text{Al}_2\text{O}_3(\text{dt})$						
1	Drying at 20°C for 2 days ^b	5.5 ± 0.6	2.31 ± 0.09			6.6
2	Drying at 90°C 3 h	6.3 ± 0.3	2.32 ± 0.12			1.4
3	Drying at 90°C for 20 h	6.0 ± 0.3	2.33 ± 0.11			7.4
4	Drying at 150°C for 3 h	5.8 ± 1.5	2.31 ± 0.41			5.9
5	Calcination at 350°C for 2 h	5.6 ± 0.1	2.29 ± 0.09			2.4
$\text{H}_2\text{PtCl}_6(\text{pH } 1.15) + \text{Al}_2\text{O}_3(\text{un})$						
6	Drying at 20°C for 1 day ^b	3.7 ± 0.5	2.31 ± 0.29	2.4 ± 0.2	2.01 ± 0.04	4.0
7	Drying at 90°C for 3 h	4.3 ± 1.9	2.30 ± 0.19	1.9 ± 1.2	2.01 ± 0.0	2.1
8	Drying at 90°C for 20 h	4.3 ± 0.3	2.30 ± 0.13	1.6 ± 0.3	2.01 ± 0.2	4.6
9	Drying at 150°C for 3 h	3.5 ± 0.04	2.31 ± 0.00	2.7 ± 1.5	2.04 ± 0.0	4.0
10	Calcination at 270°C for 2 h	3.5 ± 0.7	2.32 ± 0.09	2.5 ± 0.01	2.06 ± 0.22	4.9
$\text{H}_2\text{PtCl}_6(\text{pH } 2.8) + \text{Al}_2\text{O}_3(\text{un})$						
11	Drying at 20°C for 1 day ^b	3.0 ± 1.7	2.32 ± 0.08	3.1 ± 0.5	2.02 ± 0.07	2.5
12	Drying at 90°C for 17 h	3.0 ± 0.3	2.32 ± 0.15	3.1 ± 0.3	2.02 ± 0.14	2.6
13	Drying at 150°C for 3 h	3.1 ± 2.1	2.31 ± 0.01	3.9 ± 4.4	2.04 ± 0.21	4.7
14	Calcination at 270°C for 2 h	2.8 ± 2.4	2.31 ± 0.00	3.8 ± 0.4	2.04 ± 0.00	1.8

^a The sequence of sample treatments after impregnation of Al_2O_3 with an H_2PtCl_6 solution.

^b In a vacuum desiccator over P_2O_5 .

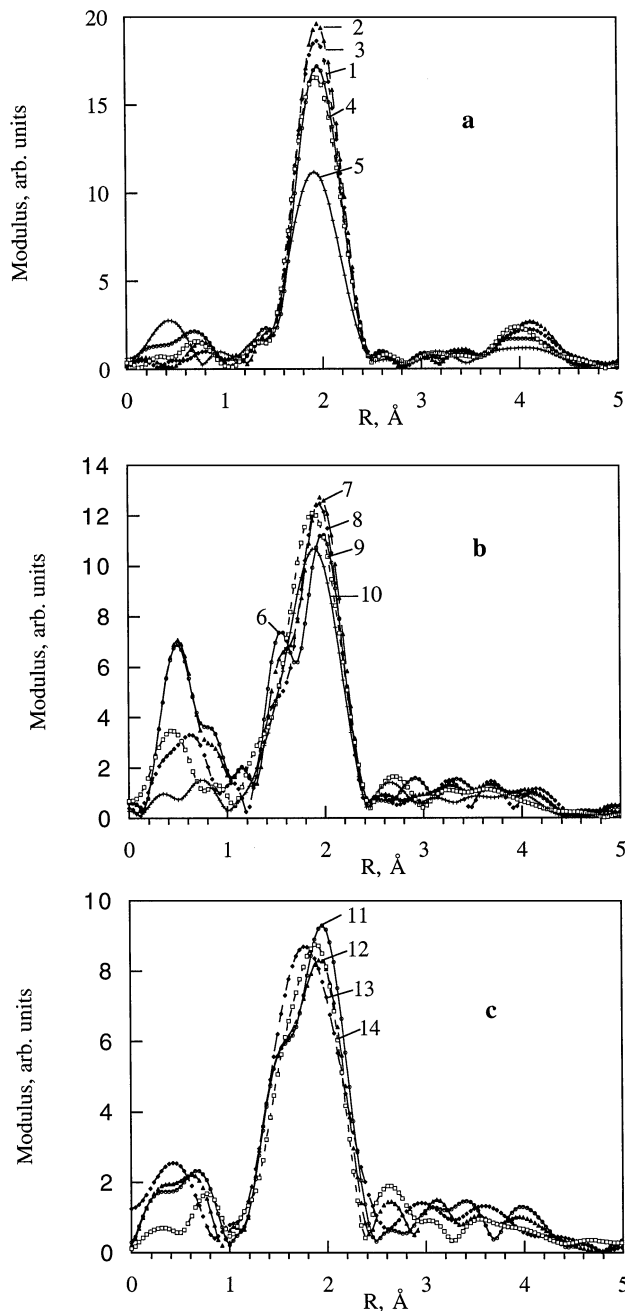


FIG. 12. Moduli of Fourier transforms for three series of $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3$ samples. The numbers on the curves correspond to sample numbers in Table 5.

characteristic of these bonds. However, this conclusion is not obvious in view of the large uncertainty in determining $N(\text{Cl})$ and $N(\text{O})$. The coordination number remains unchanged after heating the solids up to 270°C .

Transformations of Adsorbed Platinum Complexes during the Initial Steps of the Pt/ Al_2O_3 Catalyst Preparation

Table 6 summarizes the data obtained by different techniques employed in this study.

For wet impregnated samples (step A), the most important information concerning the interaction of Pt complexes from H_2PtCl_6 solutions with alumina was gained from ^{195}Pt NMR, and the corresponding data as already discussed above (see section ^{195}Pt NMR) agree well with those of UV-Vis spectroscopy.

In brief, the interaction of Pt complexes from the more acidic H_2PtCl_6 solution at pH 1.15 with untreated and HCl

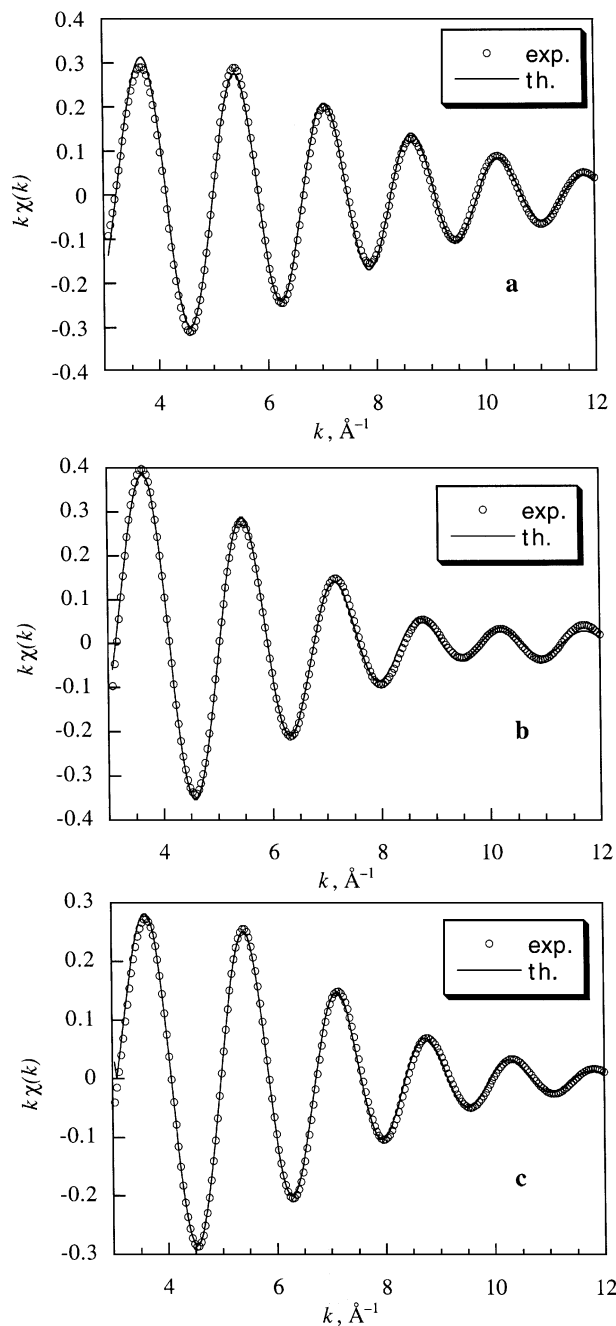


FIG. 13. Experimental (circles) and modeled (full lines) EXAFS contribution around Pt atom (filter of the first shell): (a) sample 1, (b) sample 6, and (c) sample 10 (Table 5).

TABLE 6
Structural Information on Adsorbed Platinum Complexes in the H₂PtCl₆/γ-Al₂O₃ System upon Impregnation and Subsequent Drying

Technique	Procedure	Structures of adsorbed Pt complexes	
		Untreated alumina	Acidified alumina
Step A: Wet impregnated samples			
¹⁹⁵ Pt NMR and UV-Vis	Impregnation with H ₂ PtCl ₆ solutions	[PtCl ₆] ²⁻ ; [PtCl ₅ (OH)] ²⁻	[PtCl ₆] ²⁻ ; {[H[PtCl ₆]} ⁻
¹⁹⁵ Pt NMR and UV-Vis	Aging of the wet impregnated solids	[PtCl ₆] ²⁻ ; [PtCl ₅ (OH)] ²⁻ ^a	[PtCl ₆] ²⁻ ; {[H[PtCl ₆]} ⁻
Step B: Drying at 20°C and rewetting			
¹⁹⁵ Pt NMR	Drying	No signal	[PtCl ₆] ²⁻ (MAS)
	Rewetting	[PtCl ₆] ²⁻ ; [PtCl ₅ (OH)] ²⁻ ^b	[PtCl ₆] ²⁻ ; {[H[PtCl ₆]} ⁻
UV-Vis	Drying	Structures are not identified	[PtCl ₆] ²⁻
	Rewetting	[PtCl ₆] ²⁻ ; [PtCl ₅ (OH)] ²⁻ ^b	[PtCl ₆] ²⁻
EXAFS	Drying	PtCl ₄ O ₂ (pH 1) PtCl ₃ O ₃ (pH 3)	PtCl ₆
Raman	Drying	ν(Pt-Cl) + ν(Pt-O)	ν(Pt-Cl)
Step C: Drying at 90°C and rewetting			
¹⁹⁵ Pt NMR	Drying	No signal	[PtCl ₆] ²⁻ (MAS)
	Rewetting	No signal	[PtCl ₆] ²⁻ ; {[H[PtCl ₆]} ⁻
UV-Vis	Drying	Structures are not identified	[PtCl ₆] ²⁻
EXAFS	Drying	PtCl ₄ O ₂ (pH 1) PtCl ₃ O ₃ (pH 3)	PtCl ₆
Raman	Drying	ν(Pt-Cl) + ν(Pt-O)	ν(Pt-Cl)

^a The [PtCl₆]²⁻/[PtCl₅(OH)]²⁻ ratio decreases with impregnation time.

^b The same spectrum as that of the wet impregnated sample.

treated alumina is well described by assuming electrostatic fixation of [PtCl₆]²⁻, {H[PtCl₆]}⁻, and [PtCl₅(H₂O)]⁻ on positively charged protonated hydroxyl groups (reactions [6]–[8], [12], and [13]) and by proposing deprotonation of H₂PtCl₆, {H[PtCl₆]}⁻, and [PtCl₅(H₂O)]⁻ by the basic surface alumina hydroxyls (reactions [9], [10], and [14]). No marked ligand exchange or grafting of the adsorbed Pt species was found to occur for the wet solids.

In contrast, when Al₂O₃(un) is impregnated with a less acidic H₂PtCl₆ solution at pH 2.8, NMR data indicate a stronger interaction of the adsorbed Pt species with alumina which leads to a loss in the integral intensity of the NMR signals (Fig. 4(2)). The reaction leading to this interaction is slow at room temperature (typically 10–20 h).

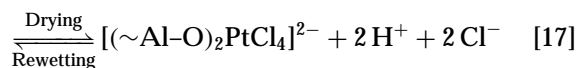
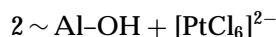
Upon aging the impregnated solids, the aquation of adsorbed [PtCl₆]²⁻ occurs (reaction (16)) followed by deprotonation of the resulting aqua complex to give rise to [PtCl₅(OH)]²⁻ (ads) as discussed above. The aquation reaction is hindered in the presence of an excess of Cl⁻ ions, and, therefore, [PtCl₆]²⁻ (ads) is much favored on the surface of HCl treated alumina Al₂O₃(dt).

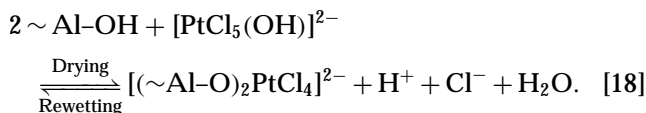
A final comment that must be made on wet samples is that we never observed any evidence of mixed Pt–Al species. In other words, alumina dissolution, if it occurs to any appreciable extent, does not induce changes in Pt speciation, in contrast to systems such as heptamolybdate/Al₂O₃ (29)

or [M^{II}(NH₃)₆]²⁺/Al₂O₃ (30). As regards the extent of alumina dissolution, it was not investigated in this work, but it is probably less extensive than might be deduced from the low initial pH values, due to the buffer effect of the alumina surface.

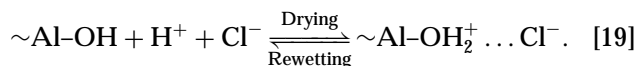
Following drying of H₂PtCl₆/Al₂O₃(un) at 20°C, the NMR signals disappear, and no reliable information about the structures of adsorbed Pt species can be obtained from the rather featureless UV-Vis spectra (Fig. 8(1c)). Thus, at this stage of catalyst preparation (step B in Table 6) some conclusions can be drawn only from EXAFS and Raman data.

The EXAFS data evidence the presence of PtCl₄O₂ (or possibly PtCl₃O₃) as the major adsorbed species on Al₂O₃(un) depending on the initial pH of the impregnating H₂PtCl₆ solutions. The Raman data also show the formation of the Pt–O bond in the dried samples. These findings can be rationalized by assuming Cl⁻ ligand exchange in the coordination sphere of adsorbed [PtCl₆]²⁻ and [PtCl₅(OH)]²⁻ with surface hydroxyls as depicted by the following scheme:





Upon drying, physisorbed water and structural water, which is held by the alumina surface, are removed. Thus, the Pt species can approach the surface hydroxyls for ligand exchange. The resulting Pt species can be considered as grafted. The H^+ and Cl^- produced by reactions [17] and [18] can be stabilized on the surface by the protonation of OH groups:



It should be emphasized that the ligand exchange at step B is completely *reversible*, since, following rewetting of the dried solids, the ^{195}Pt NMR and UV-Vis spectra that are characteristic of nondried samples can be restored. When water is added to the dried samples, the protons are released by reversed reaction [19] and can hydrolyze the Al-O-Pt bond, thus regenerating the initial Pt species. Reversed reactions [17] and [18] are facilitated upon rewetting due to a gain in the energy of aquation of the Pt species and alumina surface.

In the case of the HCl treated alumina impregnated with an acidic H_2PtCl_6 solution, the data of all techniques evidence no transformation of $[\text{PtCl}_6]^{2-}$ (ads) and no entering of oxygen atoms into the Pt coordination sphere upon drying at 20°C (Table 6). This implies that ligand-exchange reaction [17] does not take place, probably, because most of the alumina hydroxyls are protonated.

Drying the impregnated $\text{Al}_2\text{O}_3(\text{un})$ at 90°C results in *irreversible* transformations of the adsorbed Pt species, since no NMR signal can be restored upon rewetting the dried solids (Table 6, step C). Also, the modifications of the UV-Vis spectra upon drying the solids at 90°C point to a change in the Pt atom environment, although specific structures cannot be identified by this technique (Fig. 8(1e)). At the same time, EXAFS data show no significant change in the number of Cl and O atoms bonded to the central Pt atom. We may suggest that, upon heating at 90°C , the adsorbed protons and Cl^- are eliminated as HCl:



Therefore, after drying at 90°C , the initial Pt species can no longer be regenerated by rewetting with water, but they can be partly restored upon treating the dried solids with aqueous HCl (reversed reactions [17] and [18]).

CONCLUSIONS

The combined use of different spectroscopic techniques allowed us to identify Pt complexes adsorbed on the alu-

mina support from acidic H_2PtCl_6 solutions and to follow their transformations upon various treatments such as drying, rewetting, and further calcination of the impregnated solids.

The following conclusions emerge from this study:

(i) Platinum adsorbs on alumina from H_2PtCl_6 solutions as $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{OH})]^{2-}$. The $[\text{PtCl}_6]^{2-}/[\text{PtCl}_5(\text{OH})]^{2-}$ ratio is strongly dependent on the pH of the impregnating solution, the acidity of the alumina support, and the impregnation time. The speciation of adsorbed Pt is quite different from that in the solution.

(ii) No marked grafting of the adsorbed Pt species to the alumina surface occurs for wet samples impregnated with the more acidic H_2PtCl_6 solution at pH 1.15. The Pt anion complexes are held on alumina by electrostatic interaction, probably accompanied by a more specific, although rather weak, interaction with surface sites (specific adsorption or outer-sphere complex formation). In contrast, when alumina is impregnated with the less acidic H_2PtCl_6 solution at pH 2.8, a part of adsorbed Pt complexes becomes grafted. This process is, however, slow at room temperature (typically, 10–20 h).

(iii) Upon removal of physisorbed water at 20°C from $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3(\text{un})$, Cl^- ligands in the Pt coordination sphere exchange with surface OH groups. This process gives rise to grafted Pt complexes of lower symmetry. The ligand exchange is found to be **reversible** and the initial non-grafted Pt species can be restored upon rewetting the dried solids.

(iv) Upon drying $\text{H}_2\text{PtCl}_6/\text{Al}_2\text{O}_3(\text{un})$ at 90 and 150°C , the grafting of adsorbed Pt complexes becomes **irreversible**; i.e., the initial species cannot be restored by subsequent rewetting. However, a partial restoration is possible upon treatment of the dried solids with aqueous HCl.

(v) There is no evidence for ligand exchange and grafting of $[\text{PtCl}_6]^{2-}$ adsorbed on the doubly HCl treated alumina upon drying at temperatures as high as 150°C , presumably, because of a too high concentration of protonated hydroxyls for ligand exchange to occur.

(vi) After drying, the compositions of the grafted Pt complexes do not change markedly upon calcination in air up to $270\text{--}350^\circ\text{C}$.

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