Catalysis Letters Vol. 88, Nos. 1–2, May 2003 (© 2003)

Evolution of transition metal speciation in the preparation of supported catalysts: halogenoplatinate(IV) on silica*

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Received 5 December 2002; accepted 4 March 2003

H_2PtCl_6 adsorption on silica and the evolution of the Pt(IV) speciation upon drying and rewetting were studied by ^{195}Pt NMR, UV–visible, and EXAFS spectroscopies. Upon drying at 40 °C, H_2PtCl_6 forms outer-sphere complexes with silica. At 90 °C, inner-sphere complexes are formed; this grafting is reversible upon rehydration. Each surface Pt(IV) species is characterized by a specific reduction temperature, as evidenced by TPR.

KEY WORDS: silica; platinum; speciation; catalyst; preparation; Pt NMR; UV–vis diffuse reflectance; EXAFS; TPR.

1. Introduction

The preparation of supported transition metal catalysts, in spite of its huge economical importance, is still poorly understood at the fundamental level and the industry often relies on empirical recipes reached by a trial-and-error process. However, every practitioner in the field can quote examples where the modification of a single experimental parameter, even at the earliest steps of the preparation procedure, leads to dramatic modification of the final catalyst performance. We have earlier stressed the importance of a molecular-level understanding of all catalyst preparation steps [1–4], in particular of the adsorption mechanism of transition metal precursor complexes on oxide surfaces in the initial deposition step. Several case studies have shown that different adsorption mechanisms may entail differences in the subsequent reactivity upon thermal treatments. In a series of papers [5–7] we have thus investigated the interactions of H_2PtCl_6 solutions with γ-Al_2O_3, which are the main components of reforming catalysts. In the presence of such acidic solutions ($pH = 1.6$–2.0), the alumina surface bears a strong positive charge, and $[PtCl_6]^{2-}$ first forms well-defined outer-sphere complexes (OSC) with Al–$(OH_2)^+$ groups, which may be followed by thermally activated grafting with the formation of inner-sphere complexes (ISC). We have undertaken the present research to determine if a similar level of molecular characterization could be reached for the deposition of H_2PtCl_6 on amorphous silica, a support with quite different properties; in particular, its point of zero charge (PZC) of about 2 should cause a smaller degree of positive charging on the surface. Recently, the interaction of positive precursor complexes ($[Pt(NH_3)_4]^{2+}$) with a silica surface has been investigated in detail [8], but we are not aware of any similar studies concerning negative precursors such as chloroplatinates.

2. Experimental

2.1. *Materials and procedures*

The silica used in this work was a fumed Aerosil 380 from Degussa with a specific surface area of 380 m^2/g, and a mean particle size of around 7 nm.

A stock 5×10^3 M H_2PtCl_6 solution was prepared by diluting an 8 wt% aqueous solution of H_2PtCl_6 (Aldrich) with water.

H_2PtCl_6/SiO_2 samples were prepared by the wet impregnation method: 1.5 g of silica were added to 50 ml of the H_2PtCl_6 solution with continuous stirring at 20 °C, and the slurry was left under stirring to equilibrate for 2 h. After impregnation, the samples were first dried in a rotary evaporator at 40 °C, then in air at 90 °C, and finally re-exposed to ambient humidity. As discussed below, significant changes in sample color were observed in the course of these treatments.

2.2. *UV–visible measurements*

Diffuse reflectance UV–vis spectra of H_2PtCl_6/SiO_2 samples were recorded with a Cary-5 instrument using

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* The authors wish to dedicate this work to Prof. P. Gouzerh (Université Pierre et Marie Curie) on the occasion of his 60th birthday.

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a $BaSO_4$ pellet as a reference sample. The scan range was from 600 to 190 nm with a 1.0 nm interval, and the averaging time at each point was 1.0 s.

2.3. ^{195}Pt NMR measurements

The 86 MHz ^{195}Pt NMR spectra were recorded at room temperature with a Bruker MSL-400 spectrometer that could be fitted with a multinuclear probe for liquid-state NMR, or with a MAS probe (7 mm zirconia rotors) spinning at 4 kHz. A simple one-pulse sequence was employed in all cases; the pulse width was 5 μs, the dead time before acquisition was 20 μs, and the delay between two successive pulses was 0.5 s. 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 an external 8 wt% aqueous $[PtCl_6]^{2-}$ solution ($\delta_{PT} = 0$ ppm).

2.4. EXAFS measurements

EXAFS experiments were carried out at the LURE synchrotron radiation facilities at 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 11 450–12 450 eV range. The counting time was 1 s/point.

The data analyses were performed using the "EXAFS pour le Mac" package [9]. A linear fit for the pre-edge 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 fitting of experimental and calculated EXAFS spectra was carried out with a simplex algorithm [9].

2.5. TPR measurements

Temperature-programmed reduction (TPR) experiments were carried out using an Ar/H_2 (95/5%) mixture with a flow of 25 ml/min. The sample weight was 50 mg and the rate of heating was 7.5 °C/min. The hydrogen consumption was measured with a catharometer.

3. Results and discussion

3.1. Color changes during preparation

The initial hexachloroplatinate solutions are yellow. After deposition of those complexes on silica and drying at 40 °C, the resulting samples are also yellow. Drying under more severe conditions (90 °C under air) caused the samples to turn amber. This change can be made reversible by simple exposure of the samples to ambient humidity at room temperature: a yellow color is observed again after a few minutes. Furthermore, when the H_2PtCl_6/SiO_2 system dried at 90 °C and rewetted is contacted with H_2 at room temperature, its color immediately turned light gray, whereas after reduction at 350 °C samples are black.

In order to understand the color changes and the associated speciation of platinum, the H_2PtCl_6/SiO_2 system was characterized after the successive steps of drying at 40 °C, drying at 90 °C, and rewetting. Moreover, TPR experiments were done starting from a sub-ambient temperature. For the H_2PtCl_6 on silica dried at 90 °C, all characterizations were carried out under inert atmosphere to avoid water adsorption.

3.2. Speciation of Pt(IV) during the early stages of preparation followed by spectroscopy

3.2.1. UV–visible data: evidence of outer- and inner-sphere complexes

Figure 1 shows the UV–visible spectra of H_2PtCl_6 on silica at the different steps of the preparation procedure. The system H_2PtCl_6/SiO_2 dried at 40 °C, and the one dried at 90 °C and re-exposed to ambient humidity, exhibit very similar spectra with two intense ligand $\longrightarrow$ metal charge transfer bands at high energy, and two *d–d* transition bands at lower energy. The positions of these bands, and the overall spectrum shape, are close to those of the transmission spectrum of H_2PtCl_6 solutions [10–13]. Unfortunately, it is hard to discriminate chloroplatinate species with different degrees of aquation on the basis of UV–visible spectra: band shifts and changes in relative intensities are observed on aquation but they are not of sufficient magnitude to be diagnostic.

The H_2PtCl_6/SiO_2 sample dried at 90 °C without rewetting exhibits a spectrum quite different from those of the other two systems. The maxima are ill-resolved, but definitely shifted to lower energies, which is especially apparent for the first charge transfer band (222 instead of 198 nm). A similar spectrum was observed for H_2PtCl_6/Al_2O_3 catalysts at some stages of their preparation [6], tentatively assigned to grafted *cis*-$(AlOH)_2PtCl_4]$ species. We can assume that the analog *cis*-$[(SiOH)_2PtCl_4]$ would have a similar spectroscopic signature. Thus, the UV–visible data suggest the hypothesis of formation of inner-sphere complexes, or grafting, upon drying at 90 °C. This hypothesis will be discussed later on the basis of ^{195}Pt NMR data. Note, however, that this potential grafting is reversible upon rewetting as the UV–visible spectrum then recovers its original shape.

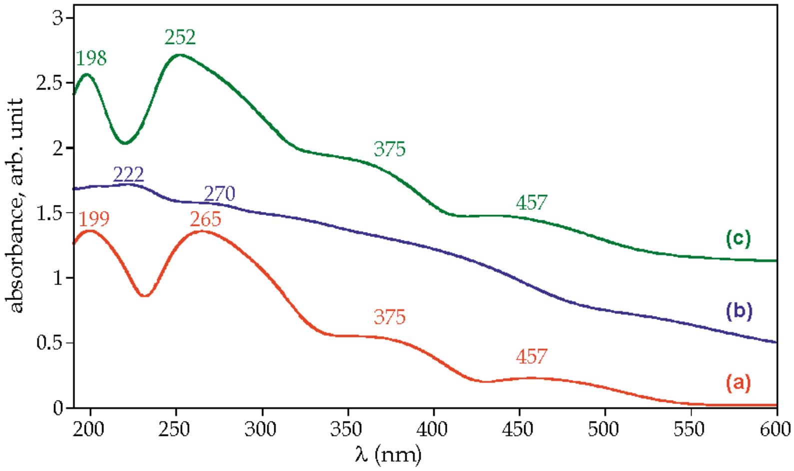

Figure 1. UV–vis spectra of H_2PtCl_6/SiO_2 system: (a) dried at 40 °C, (b) dried at 90 °C, (c) dried at 90 °C then exposed to ambient humidity.

3.2.2. ^{195}Pt NMR data: evolution of the speciation of Pt(IV)

In the presence of water, hexachloroplatinates undergo aquation reactions leading to the formation of aquachloroplatinate species according to the equilibrium

$$\begin{aligned}[Pt^{IV}Cl_6]^{2-} + H_2O &\rightleftharpoons [Pt^{IV}Cl_5(H_2O)]^- + Cl^- \\ [Pt^{IV}Cl_5(H_2O)]^- + H_2O &\rightleftharpoons [Pt^{IV}Cl_4(H_2O)_2] + Cl^-\end{aligned} \quad (1)$$

etc.

The speciation, defined as the distribution of species in a particular sample or matrix [14], can be determined for the case of platinum by ^{195}Pt NMR because the peak position is highly sensitive to ligand substitutions in the coordination sphere of Pt(IV) [15–17]. $[PtCl_6]^{2-}$ taken as reference is thus observed at 0 ppm, $[PtCl_5(H_2O)]^-$ at 504 ppm, and $[PtCl_4(H_2O)_2]$ at 1016 ppm (*cis* isomer) or/and 1167 ppm (*trans* isomer). Even a single deprotonation, equivalent to an OH^-/H_2O ligand substitution in the coordination sphere, results in a +160 ppm down field shift of the corresponding ^{195}Pt resonance.

Indeed, the ^{195}Pt NMR spectrum of the H_2PtCl_6 stock solution exhibits three peaks corresponding to the species previously described (figure 2(a)). The relative intensities of these peaks, identified by their chemical shift in table 1, indicate that the predominant species in solution is $[PtCl_5(H_2O)]^-$.

After deposition of H_2PtCl_6 on silica and drying at 40 °C (figure 2(b)), only two peaks are observed at −2 ppm (80% of total integrated intensity) and +493 ppm (20%) (table 1). In view of the large separation between the resonances of the different Pt(IV) complexes, these signals are unambiguously assigned to $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$, respectively.

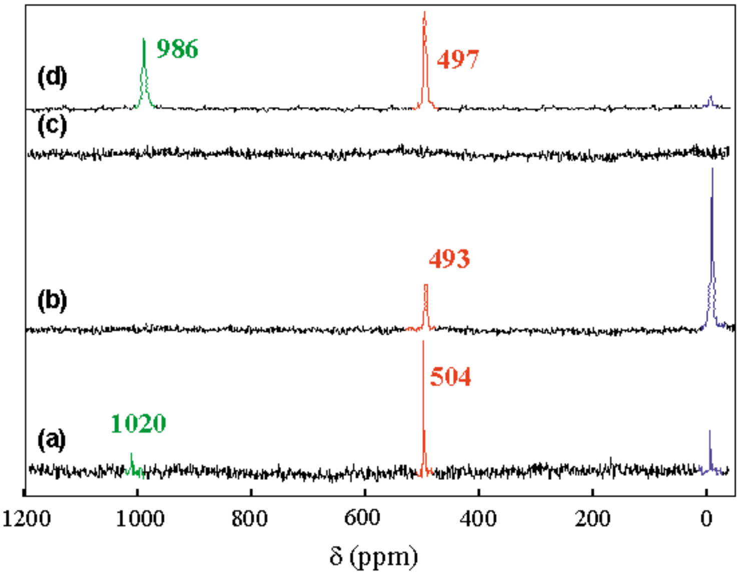

Figure 2. NMR spectra recorded at room temperature: (a) 5×10^{-3} M H_2PtCl_6 solution, (b) H_2PtCl_6/SiO_2 dried at 40 °C, (c) H_2PtCl_6/SiO_2 dried at 90 °C, (d) H_2PtCl_6/SiO_2 dried at 90 °C then exposed to ambient humidity.

Table 1
Chemical shift (δ_{PT}) and relative intensities of the $[PtCl_{6-x}(H_2O)_x]^{2-x}$ lines in ^{195}Pt NMR spectra of H_2PtCl_6 solution and of the H_2PtCl_6/SiO_2 system

Species	H_2PtCl_6 solution (5×10^{-3} M)		H_2PtCl_6/SiO_2 dried at 40 °C		H_2PtCl_6/SiO_2 dried at 90 °C then humidified at RT	
	δ_{PT} (ppm)	RI [a]	δ_{PT} (ppm)	RI [a]	δ_{PT} (ppm)	RI [a]
$[PtCl_6]^{2-}$	0	2	−2	4	0	1
$[PtCl_5(H_2O)]^-$	504	5	493	1	497	8
cis-$[PtCl_4(H_2O)_2]$	1020	1	–	–	986	6

[a] RI, relative intensity.

The predominance of $[PtCl_6]^{2-}$, and the disappearance of *cis*-$[PtCl_4(H_2O)_2]$, can easily be explained by the reversal of aquation reactions (equilibria (1)) following the decrease of the concentration of water upon drying.

However, another interesting feature is apparent from the spectrum of figure 2(b). A small but significant change in peak position is observed for the $[PtCl_5(H_2O)]^-$ species in the presence of silica, which is observed at 493 instead of 504 ppm in solution (table 1). This shift is too low to be due to a modification of the inner coordination sphere, but has the expected order of magnitude for *outer* (solvation) sphere modifications [18,19]. Moreover, the peak widths, while too small for immobilized platinic species, are, however, more important than those of their solution analogs. This broadness corroborates the hypothesis of OSC formation between platinic species and the silica surface: these complexes would have a mobility intermediate between free complexes in solution and immobilized species in a solid matrix.

When the H_2PtCl_6/SiO_2 system is dried at 90 °C, the ^{195}Pt NMR spectrum (figure 2(c)) does not show any peak. The non-observation of adsorbed species may have several causes, but the most likely is the formation of immobile, low-symmetry species. For instance, it is known that the D_{4h} complex $[PtCl_4]^{2-}$ as a solid salt is hardly observable, even under MAS conditions, due to its huge chemical shift anisotropy [20].

A likely reaction of Pt(IV) complexes in the presence of an oxide surface is grafting [5,6], i.e. formation of ISC with surface groups according to mechanisms such as

$$\begin{aligned}&[Pt^{IV}Cl_6]^{2-}, 2H^+ + SiOH \rightleftharpoons [Pt^{IV}Cl_5(SiOH)]^-, \\ &\qquad\qquad\qquad\qquad H^+ + HCl \\ &[Pt^{IV}Cl_6]^{2-}, 2H^+ + 2SiOH \rightleftharpoons [Pt^{IV}Cl_4(SiOH)_2] \\ &\qquad\qquad\qquad\qquad + 2HCl.\end{aligned} \tag{2}$$

Such a grafting of platinum species on silica should indeed induce a decrease in their symmetry; from O_h to C_{4v} for $[PtCl_5(SiOH)]^-$ species and to C_{2v} for *cis*-$[PtCl_4(SiOH)_2]$. The resulting platinum species are thus in molecular environments of very low symmetry and immobile at the NMR timescale.

The analysis of gases evolved during the drying step (the analysis of chlorine was performed in a separate experiment by trapping the evolved gas in water then measuring the pH of the resulting solution and performing a silver nitrate test) proved the presence of HCl, which corroborates the proposed grafting mechanism (2). In addition, elemental analysis of the sample dried at 90 °C indicated a Cl/Pt molar ratio of 4.5 (as opposed to 5.8 after drying at 40 °C), indicating the elimination, on average, of 1.5 Cl per Pt upon drying at 90 °C.

When the H_2PtCl_6/SiO_2 sample dried at 90 °C is re-exposed to ambient humidity, NMR peaks are again observed (figure 2(d)). However, the speciation of platinum is different from that observed after drying at 40 °C; $[PtCl_6]^{2-}$ is still present at 0 ppm, but in rather small amounts, while two stronger peaks appear at 497 ppm ($[PtCl_5(H_2O)]^-$) and 986 ppm. The latter signal is rather close to that of *cis*-$[PtCl_4(H_2O)_2]$ in solution: it exhibits a −34 ppm upfield shift with respect to it. We assign this peak to an OSC formed between *cis*-$[PtCl_4(H_2O)_2]$ and the silica surface, for the same reasons as previously discussed. It should be emphasized that the peak shift upon the formation of an OSC is in the same direction, but approximately four times greater than for $[PtCl_5(H_2O)]^-$.

If we suppose that all the surface platinic species can be observed by NMR at this step, and that all the chlorine atoms are coordinated to platinum, the quantification of the NMR signals would give a Cl/Pt molar ratio of 4.65, in good agreement with the elemental analysis value obtained after drying at 90 °C.

Figure 3 shows the models that describe the evolution of Pt(IV) speciation for the different steps of catalyst preparation.

3.2.3. *EXAFS data: evidence of grafting*

Figure 4 presents the EXAFS spectra of the H_2PtCl_6/SiO_2 system at the different steps of drying. The moduli of Fourier transforms (k^3, Kaiser window) as well as calculated $k\chi(k)$ functions (filter of the first shell) are shown in figure 5.

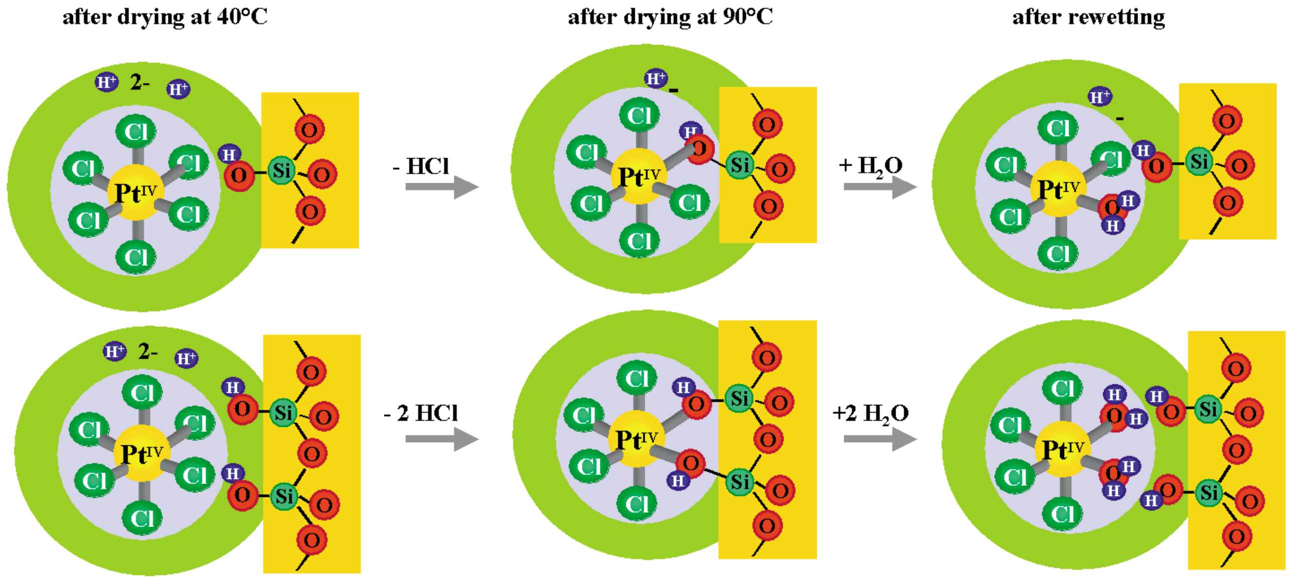

Figure 3. Evolution of platinum speciation: upon drying at 40 °C formation of outer-sphere complexes, upon drying at 90 °C formation of inner-sphere complexes by grafting, which is reversible by rewetting, leading to outer-sphere complexes.

The fitted structural parameters after EXAFS data processing are gathered in table 2, where *N*(Cl), *N*(O), and *N*(Si) are the number of chlorine, oxygen, and silicon atoms in the first coordination sphere of Pt complexes, respectively. *R*(Pt–Cl), *R*(Pt–O), and *R*(Pt–Si) are Pt–Cl, Pt–O, and Pt–Si distances, respectively. The last column refers to the quality of the spectral fit.

After drying at 40 °C, no silicon atom second neighbor is observed, in accordance with ^{195}Pt NMR and UV–visible data, which suggested OSC formation

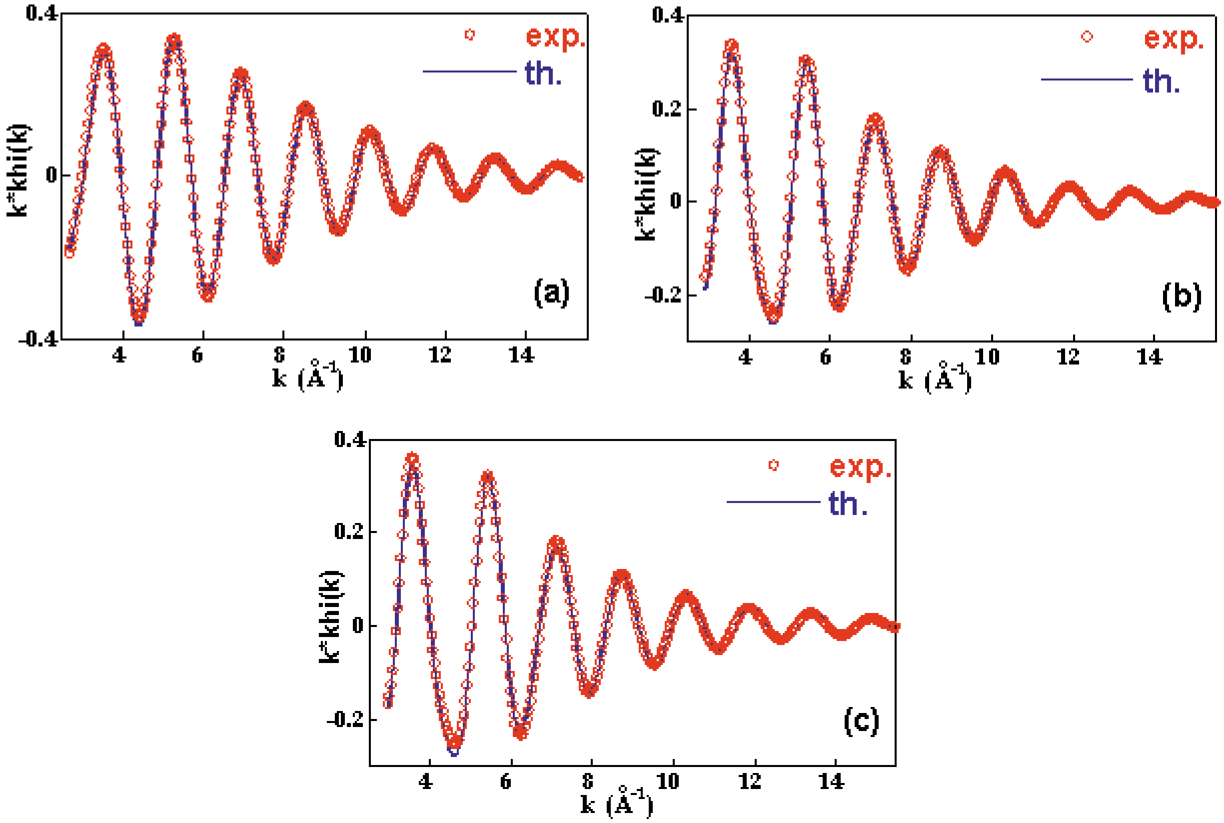

Figure 4. Experimental (circles) and modeled (full lines) EXAFS contribution around Pt atom (filter of the first shell): (a) H_2PtCl_6/SiO_2 system dried at 40 °C, (b) dried at 90 °C, (c) dried at 90 °C then exposed to ambient humidity.

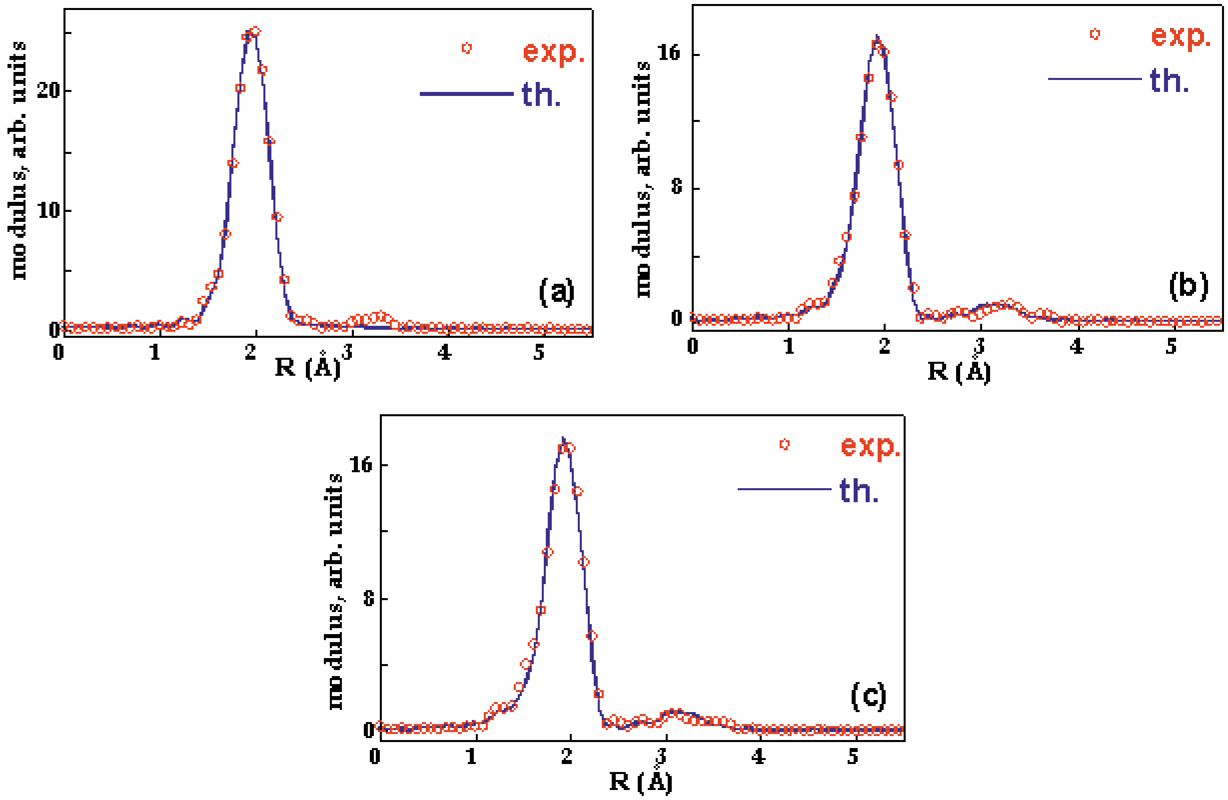

Figure 5. Moduli of Fourier transforms for the H_2PtCl_6/SiO_2 system: (a) dried at 40 °C, (b) dried at 90 °C, (c) dried at 90 °C then exposed to ambient humidity.

without grafting. As regards the first coordination sphere, it corresponds to a coordination number of 6 and an average composition of $Cl_{5.5}O_{0.5}$, in good agreement with NMR and elemental analysis.

In contrast, upon drying at 90 °C, silicon atoms are observed as second neighbors of platinum, whose number corresponds to that of first-neighbor oxygen atoms. Thus, EXAFS data confirm the grafting of platinum onto silica, already suggested by ^{195}Pt NMR and UV–visible data. They also confirm the elimination of approximately 1.5 Cl atoms per Pt at this step of drying.

For the H_2PtCl_6/SiO_2 system dried at 90 °C and rewetted, the composition of the first coordination sphere does not change much in comparison to the drying step at 40 °C. However, a surprising result was obtained as regards the second neighbors of platinum: silicon atoms are observed, again in a number equivalent to that of oxygen atoms. This result is not consistent with UV–visible and NMR data, which suggest the disappearance of grafted complexes. The quality of the EXAFS fit was somewhat lower for this sample, probably indicating higher structural disorder. It is also possible that the conditions of EXAFS data recording (samples were pressed into pellets with a cellulose binder) may have prevented the rehydration observed with other techniques: this point would necessitate further investigation.

3.3. *Speciation of Pt(IV) evidenced by temperature-programmed reduction*

When the H_2PtCl_6/SiO_2 system dried at 90 °C and rewetted was contacted with the H_2/Ar flow in the TPR experiment at room temperature, partial platinum reduction immediately started, as inferred from the change of

Table 2

Structural parameters determined from EXAFS analysis of the H_2PtCl_6/SiO_2 system at the different steps of drying at the L_{III} edge of Pt

Treatment	*N*(Cl)	*R*(Pt–Cl) (Å)	*N*(O)	*R*(Pt–O) (Å)	*N*(Si)	*R*(Pt–Si) (Å)	Fit ($\times 10^3$)
Dried at 40 °C	5.5	2.32	0.5	1.92	–	–	3.57
Dried at 90 °C	4.3	2.29	1.7	1.94	1.7	3.54	3.91
Dried at 90 °C then humidified at RT	4.2	2.29	1.8	1.95	1.8	3.53	5.23

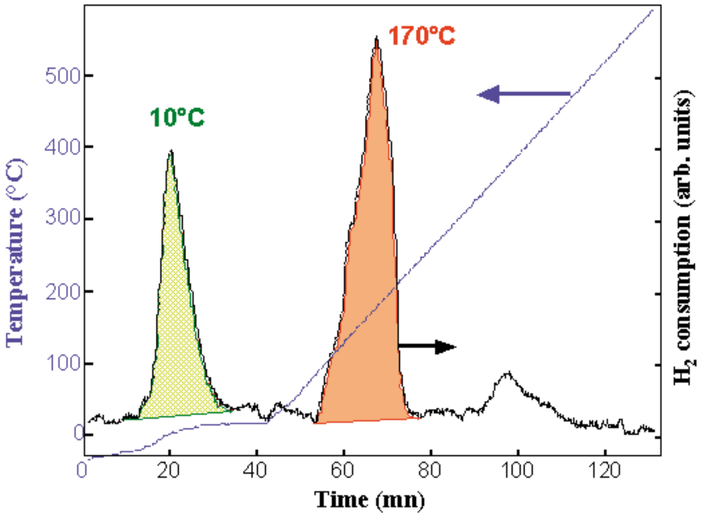

Figure 6. TPR curve of the H_2PtCl_6/SiO_2 system dried at 90 °C then exposed to ambient humidity.

color of the sample, which turned light gray. However, upon heating, a well-defined reduction peak was still observed at 170 °C indicating that platinum reduction takes place at different temperatures. A sub-ambient TPR experiment, starting at the temperature of acetone ice (ca. −95 °C), was then carried out on the same sample: it revealed two peaks at about 10 and 170 °C (figure 6).

Since according to the ^{195}Pt NMR results this sample contains comparable amounts of *cis*-$[PtCl_4(H_2O)_2]$ and $[PtCl_5(H_2O)]^-$, we hypothesized that each TPR peak might correspond to the total reduction ($Pt^{IV} \longrightarrow Pt^0$) of a particular surface platinic species. To investigate this possibility, we carried out a series of experiments where the speciation of platinum in the H_2PtCl_6/SiO_2 system was controlled by adding NaOH to the H_2PtCl_6 impregnating solution prior to deposition. The experimental conditions have been described previously [18]. These systems were studied after drying at 90 °C and exposure to ambient humidity by ^{195}Pt NMR (figure 7) and TPR (figure 8).

The main effect of NaOH addition is the titration of the two strongly acidic protons of H_2PtCl_6. When the OH/Pt ratio exceeds 2, conversion of $[PtCl_5(H_2O)]^-$ to $[PtCl_5(OH)]^{2-}$ starts to occur. However, we found that in the commercial H_2PtCl_6 solution, which contained an unspecified concentration of HCl, an OH/Pt ratio of 2.4 was necessary for complete neutralization of the acidic protons to occur.

This initial titration had an important influence on the speciation of platinum during the drying at 90 °C. ^{195}Pt NMR revealed that after drying at 90 °C and rewetting the formation of $[PtCl_4(H_2O)_2]$ was suppressed. This is perfectly understandable according to our model of supported Pt(IV) reactivity (mechanism (2)), since removal of the chloride ligands requires the availability of protons on the surface. Thus, the speciation of platinum *after rewetting* could be changed to

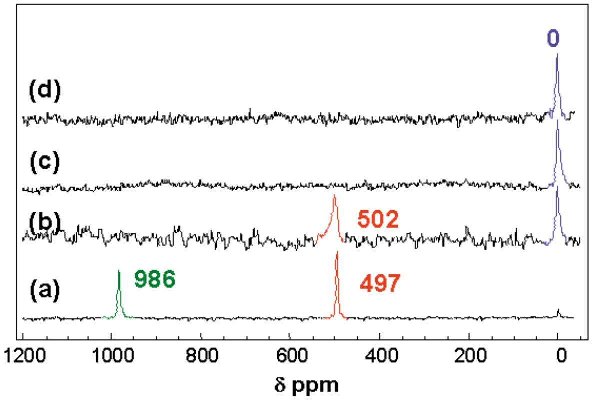

Figure 7. ^{195}Pt NMR spectra of the H_2PtCl_6/SiO_2 system dried at 90 °C then exposed to ambient humidity with addition of NaOH to the H_2PtCl_6 impregnating solution: (a) OH/Pt = 0, (b) OH/Pt = 0.8, (c) OH/Pt = 1.6, (d) OH/Pt = 2.4.

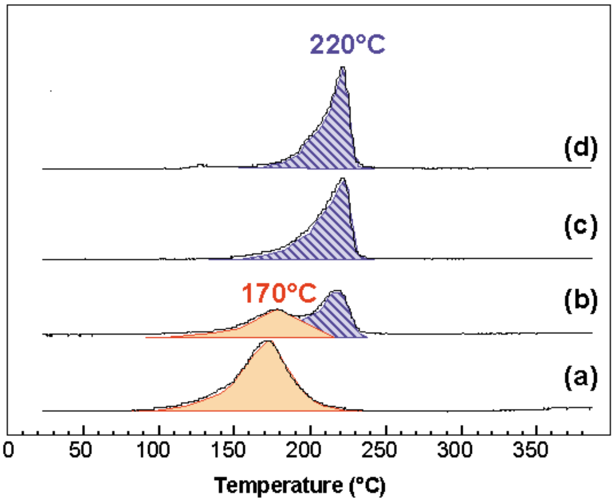

Figure 8. TPR curves of the H_2PtCl_6/SiO_2 system dried at 90 °C then exposed to ambient humidity with addition of NaOH to the H_2PtCl_6 impregnating solution: (a) OH/Pt = 0, (b) OH/Pt = 0.8, (c) OH/Pt = 1.6, (d) OH/Pt = 2.4.

$\{[PtCl_5(H_2O)]^- + [PtCl_6]^{2-}\}$ at moderate OH/Pt ratios (figure 7(b)), and to mostly $[PtCl_6]^{2-}$ at higher OH/Pt ratios (figures 7(c) and (d)).

A very good correlation was observed between the TPR behavior and the speciation after rewetting (compare figures 7 and 8). Room temperature reduction was suppressed by initial NaOH titration, strongly suggesting that the only species that can be reduced at room temperature is the *cis*-$[PtCl_4(H_2O)_2]$ OSC. When $[PtCl_5(H_2O)]^-$ was present, a TPR peak appeared at 170 °C; when $[PtCl_6]^{2-}$ was present, a TPR peak appeared at 220 °C. The intensity ratios of the TPR peaks were also very similar to those of the NMR signals of the corresponding species.

Thus, we can conclude that each surface platinum species is indeed reduced at a characteristic temperature: *cis*-$[PtCl_4(H_2O)_2]$ at ambient or sub-ambient, $[PtCl_5(H_2O)]^-$ at 170 °C, and $[PtCl_6]^{2-}$ at 220 °C. The following correlation can be proposed: species resonating at low field are easily reduced while species resonating at high field are more difficult to reduce. This could well have a physical basis: a species resonating at higher field has a higher electron density around the Pt nucleus, and consequently the $H_2 \longrightarrow Pt(IV)$ electron transfer should be more difficult. However, in view of the complex factors that determine chemical shifts of Pt complexes, this correlation is probably only valid in a series of closely related complexes such as the ones studied in this work.

4. Conclusions

The present work shows that the speciation of platinum in the H_2PtCl_6/SiO_2 system can be understood at the molecular level for the first steps of supported catalyst preparation: deposition, drying, rewetting (a step that certainly occurs upon storage of the catalysts unless special precautions are taken), and hydrogen reduction.

The general trends are quite similar to those reported for the deposition of H_2PtCl_6 on alumina [7], with an initial interaction through outer-sphere complex formation, followed by thermally activated grafting; however, interesting differences are also apparent, and both supports do not exhibit the same coordination chemistry.

While silanols (SiOH) as well as aluminols (AlOH) can act as ligands towards supported Pt^{IV} complexes, the resulting inner-sphere complexes are unstable in the presence of water for the H_2PtCl_6/SiO_2 system with a rapid substitution of (SiOH) ligands by (H_2O) ligands. However, the resulting supported *cis*-$[PtCl_4(H_2O)_2]$ and $[PtCl_5(H_2O)]^-$ species still interact with the surface, forming well-defined outer-sphere complexes with silanols. The former, especially, has no equivalent on alumina. In addition, it is possible to control the speciation between OSC $[PtCl_4(H_2O)_2]$, $[PtCl_5(H_2O)]^-$, and $[PtCl_6]^{2-}$ through titration of the initial solution.

We have also shown that each of these surface platinic species exhibits a specific reactivity towards molecules in the gas phase, as witnessed by the strong correlation between TPR and ^{195}Pt NMR. This opens up the possibility of selectively modifying a single-surface Pt(IV) species while leaving the other untouched, a direction of research on which we will report in a future publication.

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