

Molecular-level studies of transition metal–support interactions during the first steps of catalysts preparation: platinum speciation in the hexachloroplatinate/alumina system

B.N. Shelimov^a, J.-F. Lambert^{b,*}, M. Che^{b,1}, B. Didillon^c

^a *Zelinskii Institute of Organic Chemistry, Moscow, Russia*

^b *Laboratoire de Réactivité de Surface, Université Pierre et Marie Curie, Paris, France*

^c *Institut Français du Pétrole, Rueil-Malmaison, France*

Abstract

This paper summarizes recently published results on the mechanisms of chloroplatinate adsorption onto alumina, as revealed by the joint use of ¹⁹⁵Pt NMR and other spectroscopic techniques. Molecular models of solution species and conceivable adsorbed species are presented. It is shown that the adsorption of hexachloroplatinate-derived species is initially electrostatic, but accompanied by weak specific bonding to the surface (probably H-bonding; these are the “specifically adsorbed” ions of triple-layer theory). This initial electrostatic adsorption can be followed by a slow, thermally activated grafting, i.e., by the formation of inner-sphere complexes with two surface (AlOH) groups. Upon drying at elevated temperatures, grafting becomes irreversible. However, modification of the alumina surface by chlorination prior to Pt deposition efficiently prevents grafting, opening the possibility of a chemical control of adsorbed Pt speciation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Platinum/alumina catalysts; Pt speciation; Adsorption mechanisms; Hexachloroplatinate; Nuclear magnetic resonance, of ¹⁹⁵Pt; Specific adsorption; Triple layer

1. Introduction

Alumina-supported Pt catalysts based on hexachloroplatinate precursors are largely used industrially, especially in the field of reforming. For this reason, their preparation has been studied by several research groups [1–7]; yet, a unified picture of the chemical phenomena oc-

curing during their preparation has failed to emerge so far.

We have reinvestigated this system in the conceptual frame of interfacial coordination chemistry [8–11]. The emerging picture that is briefly exposed here summarises several recent publications [12–14]. We have started from the assumption that it was worth considering in detail the initial steps of supported Pt preparation: speciation in the precursor solution, contact with the support, and drying. Thus, the present communication mainly focuses on these

* Corresponding author.

¹ Member of “Institut Universitaire de France”.

initial steps while the obtention of the final catalyst and its characterisation will be dealt with in forthcoming publications.

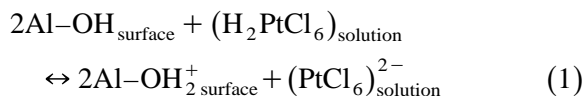
We will often use the term of platinum “speciation”, borrowed from the fields of geochemistry and soil science, to denote its distribution between different molecular species.

1.1. Interfacial coordination chemistry: a view of Pt speciation at the molecular level

As soon as one wishes to go beyond, or even to explain in molecular terms, the simple “strong/weak adsorption” distinction, two main contenders appear for the adsorption mechanism: electrostatic adsorption and inner-sphere complex formation, often called “grafting”. Fig. 1 schematises these two situations in terms of changes in the coordination and solvation spheres of adsorbed platinum.

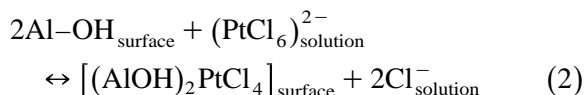
In electrostatic adsorption (Fig. 1A), both the coordination and solvation spheres of adsorbed chloroplatinates remain unaffected and similar to what they were in solution. In addition, the chloroplatinate anions are very mobile in the “diffuse layer”, whose negative charge compensates the positive charge of the surface plane. The latter results from protonation of surface

Al–OH groups by the acidic solutions of H_2PtCl_6 , so that the overall adsorption reaction may be assimilated to a simple acid–base reaction:

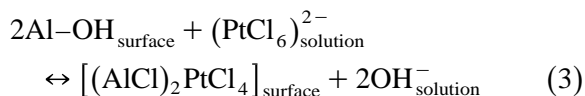


In Section 2, we will indicate that other anionic platonic species are present in solution and they too may be electrostatically adsorbed.

As for grafting (Fig. 1B), two different mechanisms may be considered. In the first one (Fig. 1B1), the Al–OH surface groups replace some of the initial ligands of the chloroplatinates in a ligand substitution reaction:



There is, however, another conceivable grafting mechanism (Fig. 1B2), where the labile groups would be the hydroxide ligands of the surface Al^{3+} :



The common feature between reactions (2) and (3) is the formation of Al–L–Pt linkages, where

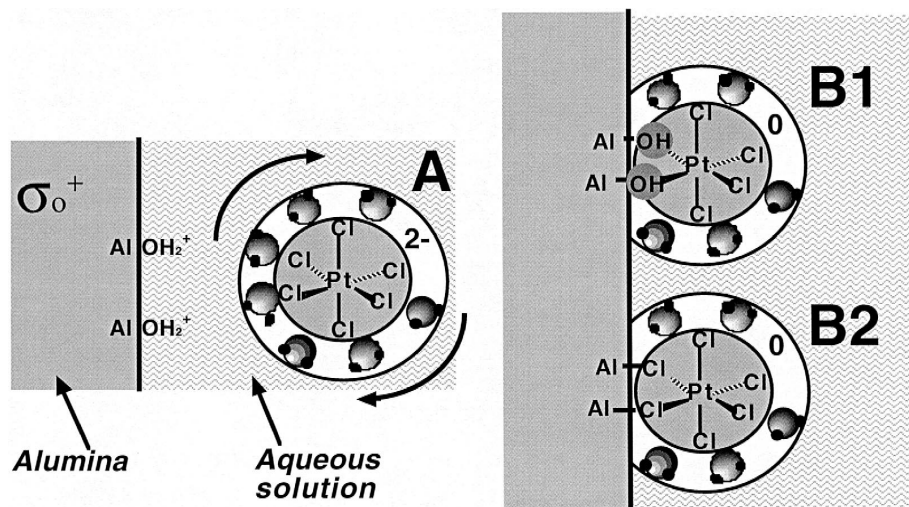


Fig. 1. The two basic models for hexachloroplatinate adsorption, viewed in terms of interfacial coordination chemistry. (A) Electrostatic adsorption; (B1) inner-sphere complex formation or grafting, with OH bridging ligands; (B2) grafting, with Cl bridging ligands.

the bridging ligand L is either OH^- or Cl^- . However, if reaction (2) occurs, the coordination sphere of Pt^{IV} in the resulting grafted species has composition $(\text{PtO}_2\text{Cl}_4)$, while if reaction (3) occurs, its composition is (PtCl_6) . We will see later that electrostatically adsorbed species can also have different coordination spheres. Thus, the adsorption mechanism and the composition of the coordination sphere are two problems that have to be treated separately.

In general, a third possible class of phenomena has to be considered during TMC deposition on an oxide surface, namely, support dissolution followed by the formation of a mixed species [15,16]. However, available information suggests that this does not happen in the present case [7,17].

1.2. Sources of information on chloroplatinate adsorption: macroscopic techniques

Much information can be gained on the mechanism of chloroplatinate adsorption by macroscopic measurements, which can be interpreted along one or the other of the models proposed above (Section 1.1), as has long been known by colloid chemists and geochemists [18]:

- Adsorption isotherms (not systematically exploited so far)
- pH dependence [5,7]; for instance, a reaction like (3) would be pH-dependent since it releases OH^- ,
- amount of free chloride ions [7]; these are liberated by the adsorption reaction (2), but also by Pt speciation in solution (cf Section 2).
- dissolution of Al^{3+} [3,7]
- ion strength dependence, which is expected for electrostatic adsorption, but not for grafting [7].

Deriving an adsorption mechanism uniquely from macroscopic data requires a considerable amount of experimental data, and those models that suggest a coexistence of two or more ad-

sorption mechanism suffer from a too great number of adjustable parameters. In addition, the kinetics of adsorption are generally not taken into account and the implicit assumption is often made that adsorption equilibria have been attained, which is far from certain in view of the kinetic inertness of Pt^{IV} . In view of this, independent confirmation of the adsorption models by spectroscopic techniques sensitive to the molecular environment of Pt is desirable.

1.3. Sources of information on chloroplatinate adsorption: molecular-level information from spectroscopic techniques

Because of the strong support absorption in the IR, vibrational spectroscopy is mostly limited to Raman spectroscopy. The Raman spectra of mixed halogenoplatinates have been thoroughly studied by Preetz et al.; although species with aqua or hydroxo ligands have not been investigated, data concerning the chlorofluoro complexes $[\text{PtCl}_{6-x}\text{F}_x]$ [19–21] should be relevant due to the close molecular weights of F^- and (Aq) (where $\text{Aq} = \text{H}_2\text{O}$ or OH^-). In a diatomic approximation, Pt–Cl and Pt–Aq bonds should be clearly discriminated, with bands at 330–350 and 570 cm^{-1} , respectively.

Another source of molecular-level information is to be found in UV–visible spectroscopy. Although UV–visible spectra of chloroplatinate/alumina systems have been reported several times [22–24], their interpretation remains open to doubt. The chloroplatinate complexes should have both d–d electronic transitions and $\text{Cl}^- \rightarrow \text{Pt}^{\text{IV}}$ charge transfer (CT) bands. Whereas d–d transitions appear as small shoulders with little diagnostic value, the spectra in the CT region are more information-rich and, until a more rigorous treatment is available, we have proposed the following rule-of-thumb [14]: two bands at 205 and 260 nm correspond to $\text{Cl}^- \rightarrow \text{Pt}^{\text{IV}}$ CT in free chloroplatinates and aquachloroplatinates, while an additional band at 220–240 nm indicates grafted species.

As could be expected, X-ray absorption spectroscopy has been applied to these systems by several authors [2,14,25]. In cases we are aware of, this potentially powerful technique in fact only indicates the (average) atomic composition of the platinum coordination sphere, e.g., $[\text{PtCl}_{6-x}\text{O}_x]$. As we have mentioned, this is not sufficient to clarify the adsorption mechanism of chloroplatinates.

We have recently shown that very useful information on the initial Pt speciation in chloroplatinate/alumina could be obtained by the use of ^{195}Pt NMR spectroscopy ([12–14]; a first mention was made in Ref. [4]). This technique is sensitive not only to the first coordination sphere of platinum (IV), but also to longer-range effects (solvation sphere). It allows in situ observation of both adsorbed and free Pt species, and also provides information on the mobility of these species. Its main drawback is that grafted complexes are not mobile on the NMR timescale, and are thus unobservable in the current state of technology due to their high anisotropy. In spite of this, the use of ^{195}Pt NMR played a key role in determining the evolution of platinum speciation during deposition and drying, as will be sketched in the following paragraphs.

2. Pt speciation in the original solution

Hexachloroplatinic acid in commercial solutions (typically, 8% H_2PtCl_6 in weight, with $\text{pH} = 1.5$ to 2) is almost completely dissociated to $[\text{PtCl}_6]^{2-}$. The latter complex anion can undergo two different types of reactions (Fig. 2).

(1) Hydrolysis or aquation, i.e., substitution of the original chloride ligands by solvent H_2O molecules:

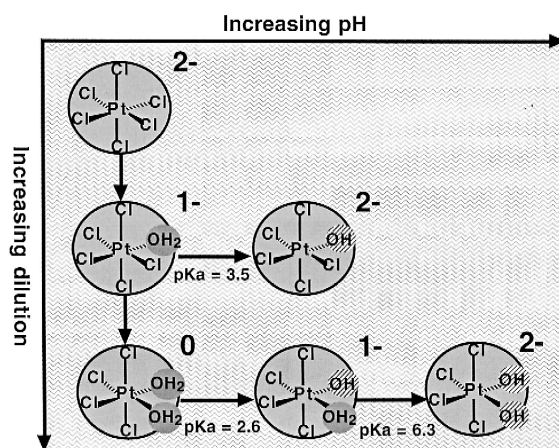
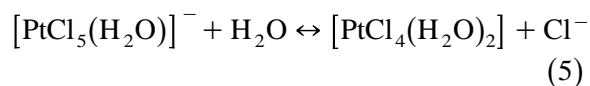
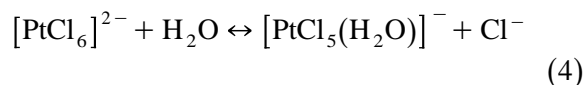
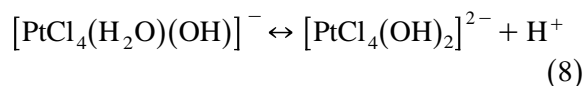
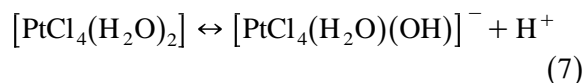
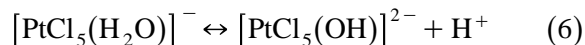


Fig. 2. Chloroplatinates speciation in aqueous solutions, as a function of dilution and pH.

Theoretically, the process could go on, providing more deeply hydrolyzed (and cationic!) Pt complexes. However, further aquations are in fact not observed unless basic pH and/or high temperatures are applied to the solution.

- Deprotonation of the aqua complexes formed in Eqs. (4) and (5):



(Note that the above picture is already simplified in that it neglects the *cis-trans* isomerism of tetrachloroplatinate complexes).

The possibility of these reactions is generally recognised; it follows that Pt species in solution can have coordination spheres $[\text{PtCl}_6]$, $[\text{PtCl}_5\text{O}]$, and $[\text{PtCl}_4\text{O}_2]$, and the same is true for electrostatically adsorbed species. As regards quantitative evaluation, it is hampered by the rather different values that have been reported for the respective equilibrium constants [26,27]. We estimate $\log K_4$ to be about -1.7 , and we have evaluated the acidity constants of reactions (6–8) (Ref. [13] and Fig. 2).

The interest of ^{195}Pt NMR is therefore twofold. Not only does it allow to estimate the precise equilibrium composition of precursor solutions, independently of published constants, but it can also provide information on the kinetics of Pt speciation, which may be an important factor. For instance, while reactions (6–8) are very fast, being proton transfers, they necessarily follow reaction (4) or reaction (5), which are ligand substitutions on an inert low-spin d^6 complex, and therefore very slow.

Thus, if one titrates a chloroplatinate solution with a strong base, the pH initially rises quickly and then decreases over several weeks (when aged at room temperature).

3. Pt speciation on initial contact with the alumina support

We will first discuss the simplest deposition procedure in which one starts with a diluted (say, 5×10^{-3} to 7×10^{-2} M in Pt) commercial solution, possibly containing added HCl but not modified otherwise. Such a solution is very acidic (pH = 1.5 to 2) and mostly contains $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, and a minor amount of $[\text{PtCl}_4(\text{H}_2\text{O})_2]$. If one observes the *adsorbed* species immediately after contact between the solution and the alumina support (Fig. 3), it appears that the following occurs.

-The NMR signal of $[\text{PtCl}_6]^{2-}$ is still present, but shifted upfield by a few ppm. Such a small shift corresponds to a second-sphere effect: the coordination sphere of Pt^{IV} is still $[\text{PtCl}_6]$, but its more remote environment (solvation sphere) is significantly modified with respect to free aqueous $[\text{PtCl}_6]^{2-}$. Closer inspection of the spectra obtained as a function of initial solution pH reveals that two different modified forms can exist, with $\delta = -1.4$ and -6.2 ppm with respect to free $[\text{PtCl}_6]^{2-}$.

-The signal of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ (504 ppm) disappears and is replaced by a broad signal at a δ value of 638–660 ppm, i.e., close to that of $[\text{PtCl}_5(\text{OH})]^{2-}$ in solution (but probably also

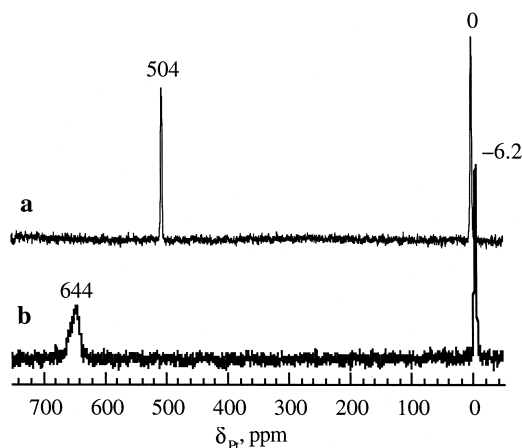
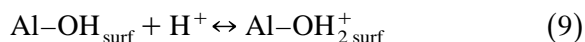


Fig. 3. ^{195}Pt NMR spectra of: (a) A commercial hexachloroplatinate solution diluted to $[\text{Pt}] = 6 \times 10^{-2}$ M. (b) The same, contacted with γ -alumina.

shifted upfield by a few ppm). The peak width indicates reduced mobility. (It should be noted that the integrated intensity of the NMR signal remains constant when the starting solution is contacted with alumina, which means that all or most of the Pt species are detected).

These observations can be interpreted as follows. Upon contact with the acidic solution, the surface hydroxyl groups of alumina are immediately protonated, consuming free protons in solution and thus leading to a bulk pH increase (“basic effect” of alumina):



The surface is then positively charged and can act as an anion exchanger, retaining chloroplatinate anions electrostatically. So far the picture is in good agreement with the “physical adsorption” model developed by Regalbuto et al. [7], but the significant decreases in δ values and the evidence of reduced mobility indicate that this model has to be refined. All observations can be accounted by a “triple layer” model, in which the adsorbed platinum species are mostly located in close vicinity to the surface, in the “Stern layer”, interacting with surface groups through rather weak, but specific, bonding (e.g., hydrogen bonds). Beyond that, there is the diffuse layer, containing free H_3O^+ and Cl^- ions, pos-

sibly with a very small amount of free chloroplatinates, in the relative amounts required to obtain electroneutrality. Fig. 4 is a graphic summary of this model, illustrating two possible specifically adsorbed Pt^{IV} species:

$\text{Al}-\text{OH}_2^+ \cdots [\text{PtCl}_6]^{2-} \cdots \text{Al}-\text{OH}_2^+$ (species C) and $\text{Al}-\text{OH}_2^+ \cdots [\text{PtCl}_6]^{2-}$ (species D). Similar sketches could be presented for the specifically adsorbed $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ species.

As regards the predominance in the adsorbed phase of $[\text{PtCl}_5(\text{OH})]^{2-}$ over $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, it seems that it cannot be entirely attributed to the bulk basic effect mentioned above, but is partly due to the localized interaction between the alumina surface and the adsorbed pentachloroplatinates. This point needs further investigation.

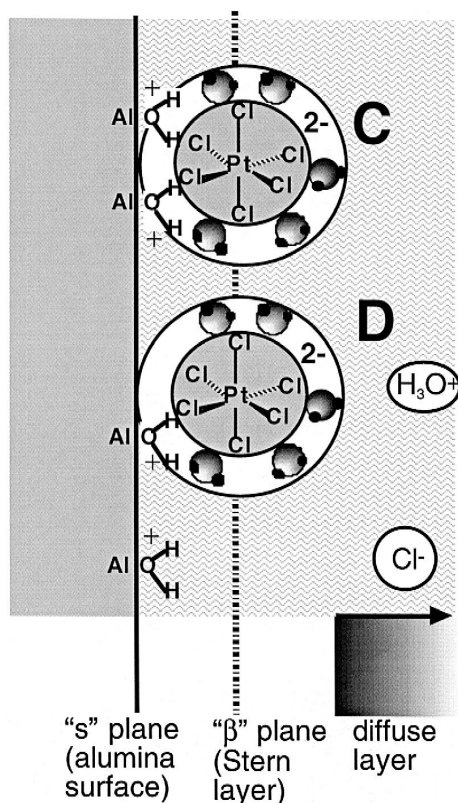


Fig. 4. Molecular mechanism of the initial adsorption of chloroplatinates on alumina. C and D are two different forms of "specifically adsorbed" Pt complexes (electrostatic adsorption + outer-sphere interaction).

Other experiments have been carried out with chloroplatinate solutions partly titrated by NaOH. Even in this case, the *initial* interaction was essentially electrostatic (with contribution of localized, outer-sphere interaction but no grafting).

4. Pt speciation on ageing

The Pt/surface interaction may be altered on prolonged contact with the solution, revealing the occurrence of phenomena with slow kinetics. Two cases have to be distinguished here.

(A) When raw chloroplatinate solutions with low initial pH were contacted with alumina and the resulting suspensions were then aged at room temperature, the $[\text{PtCl}_5(\text{OH})]^{2-}/[\text{PtCl}_6]^{2-}$ ratio increased over a time range of a few hours to 20 h, but no other species formed; in particular, there was no grafting and the adsorption models of Fig. 4 remained valid. The reasons for additional $[\text{PtCl}_6]^{2-} \rightarrow [\text{PtCl}_5(\text{OH})]^{2-}$ transformation after adsorption are not fully understood. Reaction (4) could be drawn to the right if a slow chloride-consuming mechanism occurred, and an interesting suggestion to that effect was made by Regalbuto et al. [7]: the alumina support slowly dissolves under these pH conditions, and the dissolved $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ species could be able to complex Cl^- ligands. Then, although no mixed Al/Pt species are formed, alumina dissolution would indirectly influence Pt speciation.

(B) When NaOH-titrated chloroplatinate solutions with higher pH were used, *or* when the temperature was raised to 60–80°C, the above transformation still took place, but in addition the total integrated intensity of ^{195}Pt NMR spectra decreased much over time [14]. Much of the Pt then transformed into an NMR-unobservable form. By analogy with the transformations observed on drying, we think that temperature-activated grafting is happening in these experiments (see Section 5). Apparently, at moder-

ately high pH values, grafting can occur slowly even at room temperature.

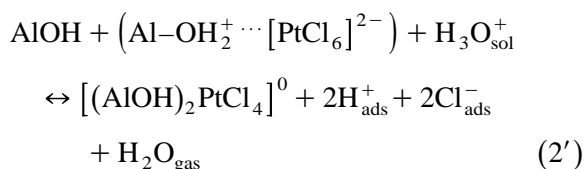
5. Pt speciation on drying

In general, when chloroplatinate/alumina systems were thoroughly dried, the ^{195}Pt NMR signals disappeared completely, complicating the task of molecular-level understanding of Pt speciation. A consideration of other spectroscopic data, notably UV [13], still allowed reasonable hypotheses to be made, however. It was observed that the effects of drying could be reversible or irreversible, according to the conditions. For instance,

- After drying at 20°C over P_2O_5 under vacuum, the original ^{195}Pt NMR signals could be restored by resuspending the catalyst in water.
- After drying at 90°C in an oven, no NMR spectrum was apparent even after rewetting. However, post-drying treatment with HCl solutions caused the appearance of a $[\text{PtCl}_6]^{2-}$ signal.

Drying most probably causes the transformation of all Pt complexes in the triple layer into

digrafted species, such as those shown in Fig. 1B; EXAFS showed these to have coordination sphere $(\text{PtCl}_4\text{O}_2)$ [14], and they might thus be represented by form B1 in Fig. 1. There is uncertainty as to the degree of protonation of the bridging ligands; the formula may be written as $[(\text{AlOH})_2\text{PtCl}_4]^0$, $[(\text{AlO})(\text{AlOH})\text{PtCl}_4]^-$ or $[(\text{AlO})_2\text{PtCl}_4]^{2-}$, each deprotonated species being compensated by a proton adsorbed somewhere else on the surface. Obviously, the passage from a coordination sphere of (PtCl_6) or (PtCl_5O) after deposition to a coordination sphere of $(\text{PtCl}_4\text{O}_2)$ after drying requires the liberation of chloride ligands, which also remain adsorbed on the surface since the process is reversible if carried out under mild conditions. One can then write, for instance, the transformation of form D ($\text{Al}-\text{OH}_2^+ \cdots [\text{PtCl}_6]^{2-}$) into form B1 upon drying as a variant of Eq. (2) above (Section 1):



The adsorbed protons, “ H^+_{ads} ”, would certainly protonate more basic AlOH groups. There is some uncertainty as to the state of “ Cl^-_{ads} ”, but

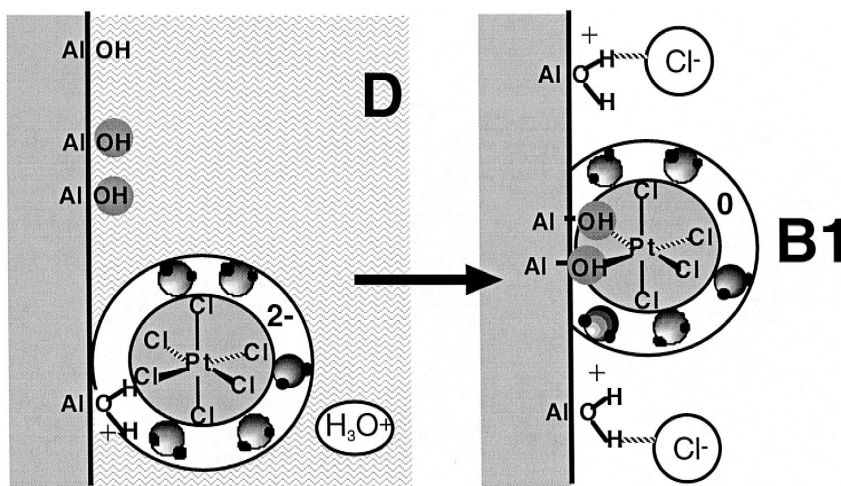


Fig. 5. The mechanism of transformation of surface species D on drying. One of the products is species B1 from Fig. 1.

we do not think that they form covalent bonds with Al^{3+} ions at this stage. Thus, a still more complete version of Eq. (2) would be:

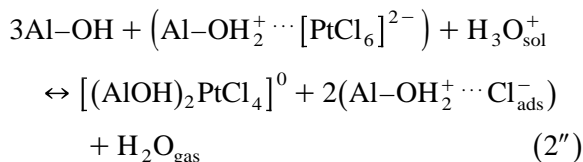
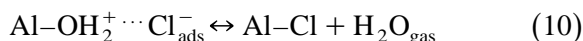


Fig. 5 presents a graphic illustration of this reaction. There is no difficulty in adapting it for the transformation of other “triple-layer” species, or in changing the degree of deprotonation.

When harsher drying conditions are applied, reaction (2'') is followed by elimination of “ H_{ads}^+ ” and “ Cl_{ads}^- ”. It could be thought that they are eliminated together as gaseous HCl; however, elemental analysis indicates that the Cl/Al molar ratio decreases only slightly after drying at 90°C. In addition, gaseous HCl could not be evidenced at this step by mass spectroscopy or AgNO_3 precipitation test. A possible alternative mechanism for the elimination of these surface species would be:



At any rate, grafting can then be considered as irreversible, since some of the products of reaction (2'') have been removed. As additional evidence, resupplying them as aqueous HCl again displaces reaction (2'') to the left.

Additional experiments have to be carried out to separate the respective roles of H^+ and Cl^- .

After drying, grafted species are apparently stable up to 300°C at least under oxidising atmospheres.

6. Control of Pt speciation by modification of the support surface

As already suggested by reaction (10), the question of Pt speciation in chloroplatinate/alumina systems necessarily involves consideration of the problem of surface chlorination.

Besides, in industrial preparations, chlorination pretreatments are often empirically applied to alumina supports prior to Pt deposition. We were then led to investigate the effect of a simple support pretreatment with aqueous HCl on the mechanisms of Pt speciation. The results were unambiguous: this kind of chlorinating pretreatment completely inhibits grafting, not only at the oxide/solution interface (where the only NMR-detectable species is now $[\text{PtCl}_6]^{2-}$, without any aqua- or hydroxo complex), but also after drying up to 150°C and even after thermal treatment up to 350°C, when EXAFS indicates that the number of Cl neighbors of supported Pt is only slightly inferior to 6. This preservation of $[\text{PtCl}_6]^{2-}$ species was confirmed by Raman and UV-visible spectroscopies. Their existence at high temperatures is likely to have important consequences for the final Pt/ Al_2O_3 catalyst, since $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ is known to self-reduce to $\text{Pt}^{\text{II}}\text{Cl}_2$ and later Pt^0 , even under oxidising atmospheres [28,29]. The conclusion of such experiments is that a molecular understanding of Pt^{IV} speciation in supported catalysts opens the way to its efficient control, with lasting consequences on the final properties of the catalyst.

7. Conclusion

We have tried to present a unified picture of Pt speciation in the chloroplatinate/alumina system, both during adsorption from the aqueous solution and on subsequent drying. To do this we have used the languages that are most suited to such systems, i.e., those of coordination chemistry and colloid chemistry, and we have written precise chemical equations for all reactions postulated. While the exercise has been attempted before [5], we feel that it is now better substantiated because of the possibility of direct spectroscopic identification of the platinum species by ^{195}Pt NMR [12–14]. Added confidence in the above model can be gained from its compatibility with published literature

data (for instance, we essentially agree with the contention by Regalbuto et al. [7] that for short contact times, the mechanism of chloroplatinate adsorption is essentially “physical”, i.e., electrostatic). In fact, apparently opposing opinions can often be reduced to divergences in the use of terminology, which could be settled without difficulty.

In summary, we think that the mechanisms of chloroplatinate/alumina interaction are now qualitatively well established, and could easily be brought to quantitative understanding. Obtaining such a molecular-level understanding of metal precursor/support interaction is a perfectly realistic goal for many other systems, although it is greatly facilitated by the availability of a spectroscopic technique sensitive to the molecular environment of the target metal.

References

- [1] P. Lagarde, T. Murata, G. Vlaic, E. Freund, H. Dexpert, J.P. Bournonville, *J. Catal.* 84 (1983) 333.
- [2] J. Berdala, E. Freund, J.-P. Lynch, *J. Phys., Colloque C8* 47 (1986) 269.
- [3] X. Huang, Y. Yang, J. Zhang, *Appl. Catal.* 40 (1988) 291.
- [4] J.H.A. Martens, R. Prins, *Appl. Catal.* 46 (1989) 31.
- [5] T. Mang, B. Breitscheidel, P. Polanek, H. Knözinger, *Appl. Catal., A* 106 (1993) 239.
- [6] V.A. Matyshak, T.I. Khomenko, N.K. Bondareva, V.I. Panchishnyi, V.N. Korchak, *Kin. Katal.* 39 (1998) 93.
- [7] J.R. Regalbuto, A. Navada, S. Shadid, M.L. Bricker, Q. Chen, *J. Catal.* 184 (1999) 335.
- [8] M. Che, O. Clause, L. Bonneviot, in: *Proc. 9th Int. Congr. Catal., Calgary, 1988*, p. 750.
- [9] M. Che, *Stud. Surf. Sci. Catal.* 75A (1993) 31.
- [10] J.F. Lambert, M. Che, *Stud. Surf. Sci. Catal.* 109 (1997) 91.
- [11] C. Lepetit, M. Che, *J. Mol. Catal.* 100 (1996) 147.
- [12] B. Shelimov, J. Lehman, J.-F. Lambert, M. Che, B. Didillon, *Bull. Soc. Chim. Fr.* 133 (1996) 617.
- [13] B. Shelimov, J.F. Lambert, M. Che, B. Didillon, *J. Am. Chem. Soc.* 121 (1999) 545.
- [14] B. Shelimov, J.F. Lambert, M. Che, B. Didillon, *J. Catal.* 185 (1999) 462.
- [15] X. Carrier, J.-F. Lambert, M. Che, *J. Am. Chem. Soc.* 119 (1997) 10137.
- [16] X. Carrier, J.-F. Lambert, M. Che, *J. Am. Chem. Soc.* 121 (1999) 3377.
- [17] B. Shelimov, J.-F. Lambert, M. Che, unpublished results.
- [18] W. Stumm, *Chemistry of The Solid–Water Interface: Process at the Mineral–Water Interface and Particle–Water Interface in Natural Systems*, Wiley, New York, 1992.
- [19] P. Erhköfer, W. Preetz, *Z. Naturforsch.* 44b (1989) 619.
- [20] P. Erhköfer, W. Preetz, *Z. Naturforsch.* 44b (1989) 1214.
- [21] W. Preetz, P. Erhköfer, *Z. Naturforsch.* 44b (1989) 421.
- [22] T.L.M. Maesen, M.J.P. Botman, T.M. Slaghek, L.Q. She, J.Y. Zhang, V. Ponec, *Appl. Catal.* 25 (1986) 35.
- [23] S. Alerasool, D. Boecker, R.D. Gonzalez, in: *Symp. Prepar. Charact. Catalysts*, ACS, Division of Petroleum Chemistry, Los Angeles, 1988, p. 607.
- [24] S. Alerasool, D. Boecker, B. Rejai, R.D. Gonzalez, G.D. Angel, M. Azomosa, R. Gomez, *Langmuir* 4 (1988) 1083.
- [25] H.C. Choi, S.H. Choi, J.S. Lee, K.H. Lee, Y.G. Kim, *J. Catal.* 166 (1997) 284.
- [26] C.M. Davidson, R.F. Jameson, *Trans. Faraday Soc.* 61 (1965) 2462.
- [27] L.E. Cox, D.G. Peters, *Inorg. Chem.* 9 (1970) 1927.
- [28] J.R. Regalbuto, T.H. Fleisch, E.E. Wolf, *J. Catal.* 107 (1987) 114.
- [29] Le Bel de Penguilly, V., PhD Thesis, Université Pierre et Marie Curie, 1998.