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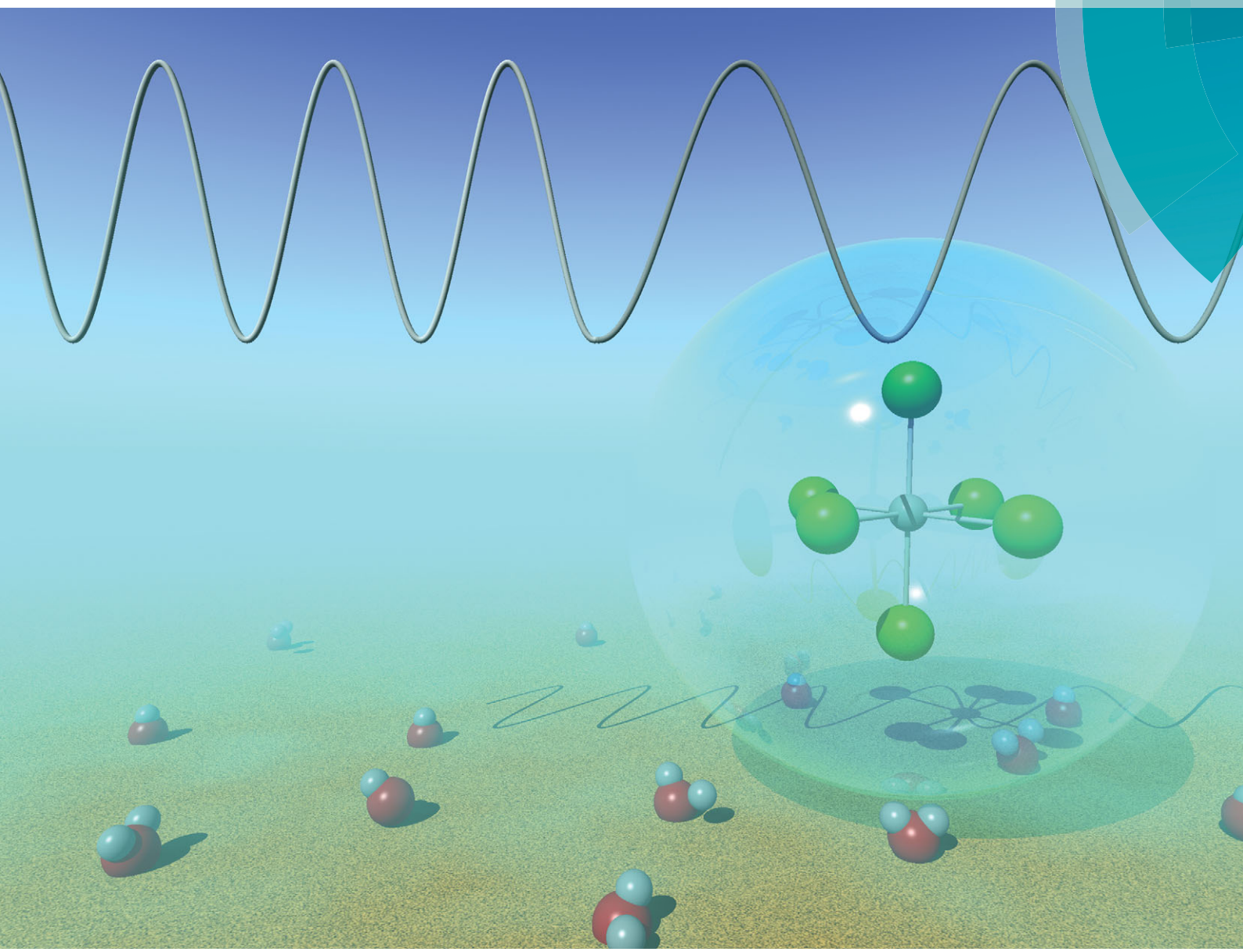

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Understanding the interactions between metal complexes and oxide surfaces is crucial to the synthesis of supported metal catalysts. Recently developed *in situ* techniques have made it possible to closely characterize the solid/liquid interface. For the first time, the adsorption of platinum complexes on alumina and silica has been probed using a quartz crystal microbalance; we were able to observe the adsorption of metal complexes in real time, and to observe the reversibility of this adsorption.

Understanding the adsorption of transition metal complexes (TMCs) on oxide surfaces in the aqueous phase is of prime importance for the synthesis of supported metal catalysts, as this initial deposition step has a lasting influence over all subsequent steps of the catalyst preparation procedures and ultimately on the catalytic properties.[1–3] Attempts to establish the exact nature of the interaction between TMCs and oxide surfaces have led to numerous studies on this subject, which have settled on three possible mechanisms: inner sphere complexation, outer sphere complexation and strong electrostatic adsorption.[4–6] In some cases, the interaction was found to be specific enough to lead to molecular recognition phenomena between TMCs and specific sites on oxide surfaces.[7] In other studies, the adsorption of TMCs on oxide surfaces was considered to be mainly governed by electrostatic interactions; in the first stage of the adsorption, the approach onto the surface is controlled exclusively by these interactions (albeit within the limits imposed by steric hindrance and the solvation sphere).[4] However, all of these conclusions were drawn based on characterization performed after removal of the solvent. This is problematic, since the solvent is responsible, by definition, for the solvation of the TMCs, and for the oxide surface charges, by means of protonation/deprotonation of the OH groups.[8,9] The missing link in a complete understanding of these phenomena is a real time and *in situ* investigation at the solid/liquid interface.

The recent development of highly sensitive *in situ* techniques, such as quartz crystal microbalance (QCM) or surface plasmon resonance (SPR),[10–12] paves the way for the characterization of the solid/liquid interface and for a better understanding of its physical chemistry. Though today these techniques are mainly devoted to the interactions of biomolecules with surfaces,[13,14] their sensitivity is high enough to study the adsorption of small size complexes. In two recent reviews, Francisco Zaera even described this type of exploration as one of the main challenges facing the surface science community.[15,16] In this context, we undertook to probe by QCM the solid/liquid interface during the adsorption of anionic and cationic TMCs on oxide surfaces. Our goal is to observe, in real time and in the presence of the solvent, the adsorption of TMCs and to determine its reversibility.

We investigated the adsorption of anionic and cationic platinum complexes on oxide surfaces, namely CPA, chloroplatinic acid $[PtCl_6]^{2-}$ and PTA, platinum tetra-ammine $[Pt(NH_3)_4]^{2+}$, on alumina and silica, respectively. The adsorption was carried out at pH values below and above the point of zero charge (PZC) of each oxide, 2–4 and ~8 for silica and alumina, respectively,[17–19] with the expectation that ionic adsorption would occur according to Scheme 1. The adsorption is expected to be reversible if the pH is modified enough to reverse the charge of the oxide surface and thus induce repulsion of TMCs.

Adsorption monitoring was carried out in the flow cell of a quartz crystal microbalance with dissipation measurement (QCM-D, E4 model, Q-sense AB, Sweden) at 22 ± 0.1 °C. AT-cut, gold-coated quartz crystals with a nominal frequency F of 5 MHz, and covered by a thin layer of alumina or silica, were purchased from Lot-Oriel, France. Solutions were flowed at 100 μL min^{-1} over the oxide surface using a peristaltic pump. Mass uptake was derived from the Sauerbrey equation (1), which is based on the assumption that the layers deposited on the quartz surface are rigid:[20]

$$\Delta F = -\frac{N\Delta m}{C_f} \quad (1)$$

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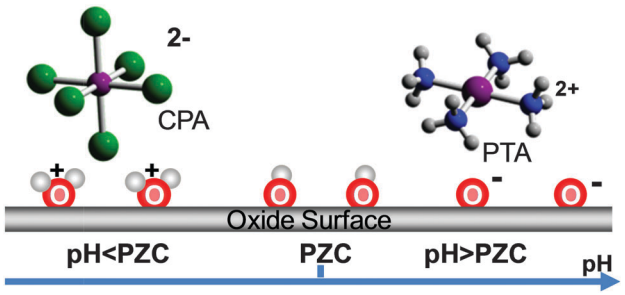

Scheme 1 Schematic representation of platinum complex electrostatic adsorption on the oxide surface depending on pH.

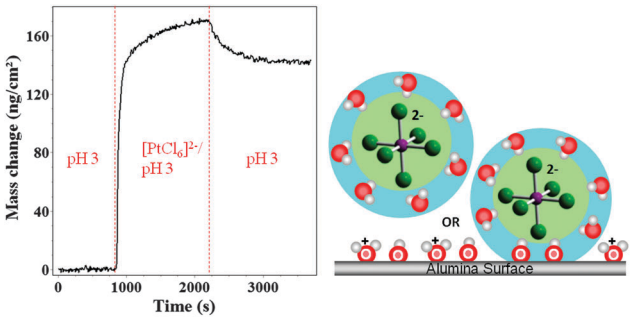

Fig. 2 Changes in adsorbed mass calculated from the Sauerbrey model upon $[PtCl_6]^{2-}$ adsorption on alumina at pH 3, along with the proposed adsorption model.

where C_f (17.7 ng cm^{-2} Hz^{-1}) is the mass sensitivity factor at F = 5 MHz and N (1, 3, 5, 7...) the harmonic number. The rigidity of the layer can be estimated by measuring the energy dissipated, or dissipation factor D; if D is low, then the Sauerbrey equation can be applied. In the figures below, the curves of the seventh harmonic (1 measurement per 5 ms) are shown for both frequency and dissipation changes.

In the first step, we focused on $[PtCl_6]^{2-}$ (CPA) adsorption on alumina. When the pH is below the PZC of alumina, which is close to 8, the surface is positively charged, which should favor the adsorption of this anionic complex by electrostatic interactions (Scheme 1). The adsorption was carried out at pH = 3 and followed by QCM as shown in Fig. 1.

First, frequency was stabilized in a hydrochloric acid solution at pH 3. Upon injection of a solution of H_2PtCl_6 at the same pH, the frequency decreased by 9.5 Hz, indicating the adsorption of Pt complexes on the surface. In the last part of the measurements, the initial solution, free from the platinum complex, was injected again to remove the weakly bound species; this leads to a slight increase of F to −8 Hz. The changes in the dissipation recorded at this stage remained below 2 × 10^{-7}, indicating that the system is well within the limits of the Sauerbrey equation (Fig. 2).

Fig. 2 shows that the saturation coverage, after rinsing with pH 3 solution, is reached for an adsorbed complex mass of 145 ng cm^{-2}. This value may seem surprising, since the coverage calculated after drying for this system was between 0.16 and 0.2 nmol cm^{-2}, or 65 to 81 ng cm^{-2}.[4] The difference is due to the co-adsorption of water molecules. For CPA, the hydration shell was indeed estimated to be 20 H_2O molecules per complex,[21] which leads to 123–154 ng cm^{-2} for the 0.16–0.2 nmol cm^{-2} coverage, in perfect agreement with the mass of adsorbed complexes deduced from QCM. Moreover, taking into account some geometrical considerations, this coverage corresponds to a monolayer of hydrated CPA on alumina, confirming for this system that the main factors governing the adsorption are electrostatic and steric. It is important to note that the injection of an alkaline solution of CPA on alumina did not lead to any decrease in frequency, *i.e.* to any adsorption, as expected from Scheme 1.

QCM also makes it possible to explore the reversibility of the adsorption (results in Fig. 3).

When a solution of sodium hydroxide at pH 12 was flowed in the QCM cell, the vibration frequency of the quartz quickly increased without returning to its initial value. Dissipation was greatly disturbed, an indication that the solvent change is interfering with the crystal vibration frequency. The subsequent injection of the hydrochloric acid solution at pH 3 led the frequency and dissipation to return to their initial values, showing the total reversibility of the adsorption of $[PtCl_6]^{2-}$ on the alumina surface. These operations were repeated several times, producing nearly identical adsorption–desorption cycles. It is nevertheless important to note that the frequency variation in these cycles is greater than that observed during the very first adsorption measurements (Fig. 1), indicating the adsorption of a higher amount of CPA

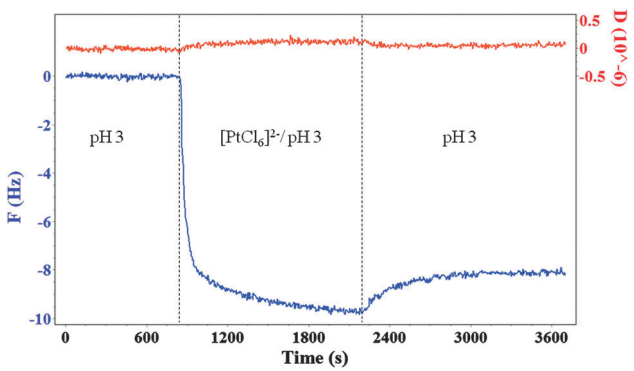

Fig. 1 Frequency changes (F) and dissipation measurements (D) upon adsorption of $[PtCl_6]^{2-}$ on alumina at pH 3.

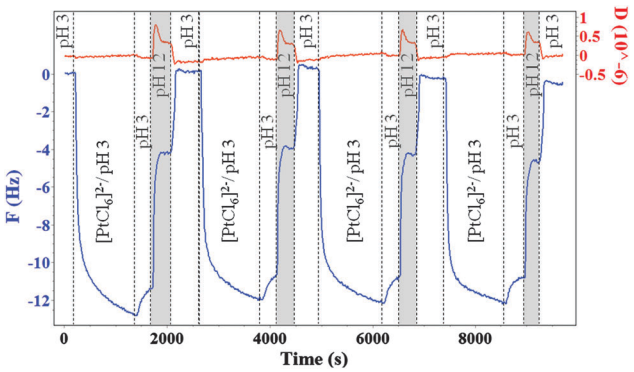

Fig. 3 Frequency changes and dissipation measurements upon reversible adsorption of $[PtCl_6]^{2-}$ on alumina.

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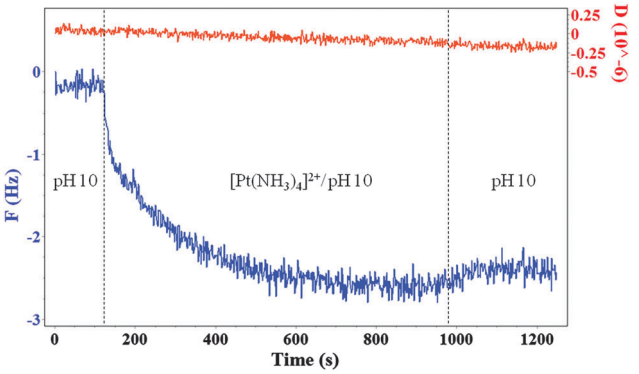

Fig. 4 Frequency changes and dissipation measurements upon $[Pt(NH_3)_4]^{2+}$ (PTA) adsorption on silica at pH 10.

on the alumina surface. One possible reason for this difference is an increase in the alumina surface roughness after treating with the pH 12 solution (alumina can dissolve or form a boehmite phase at high pH[22]); changes in root mean square surface roughness of just a few nanometers can indeed lead to a significant increase in the specific surface area.[23,24] We surveyed by AFM the topography of alumina covered quartz prior to and after immersion in the pH 12 solution and images corroborated this hypothesis. Consequently, the measured amount of adsorbed CPA per cm^2 was overestimated in the second series of experiments due to the underestimation of the surface area. This result highlights the difficulty in applying this innovative technique to the analysis of small molecules; the adsorption of biomolecules is indeed much less affected by the nanometer-scale roughness of the substrate due to their larger size. As a result, biomolecules produce more accurate results when relying on the value of the geometrical surface of the quartz. However, this difficulty in no way diminishes the considerable potential of quartz crystal microbalance for exploring TMC adsorption, since adequately accurate surface area measurements can be performed using atomic force microscopy.[23,24]

The same approach was applied to study the adsorption of cationic $[Pt(NH_3)_4]^{2+}$ (PTA) on silica at pH 10 (Fig. 4).

Real time monitoring of PTA adsorption on silica was again successfully performed using a QCM, despite the smaller molecular weight of this complex (263.1 *vs.* 407.8 g mol^{-1} for CPA). Changes in dissipation remained low enough to allow the calculation of the mass uptake (35 ng cm^{-2}), which is consistent with the adsorption of a monolayer of hydrated PTA.[25,26] Finally, we also clearly observed that this adsorption is reversible: switching to a solution at pH 4, which leads to a positive surface charge on the silica, causes the PTA to desorb from the surface. For this system no changes in frequency were observed during the regeneration at low pH, possibly because silica is resistant to acidic media.

Using QCM, we were able to monitor *in situ*, at the solid–liquid interface, the interaction between transition metal complexes and oxide surfaces, and by doing so, to mimic the first stage of the preparation of supported metal catalysts. This approach paves the way for new exploration of the initial deposition step. Charge effects are the first obvious phenomena to study, but beyond this, using larger ligands, such as bromine, rather than the chlorine of $[PtCl_6]^{2-}$, would allow us to establish the relative importance of steric hindrance and surface charge in this adsorption model. Going further, using labile ligands would make it possible to observe, in real time, the formation of the inner sphere complex, often presumed in the literature to occur at this stage, but never actually proven. The adsorption, the kinetics, and the reversibility of the interaction could therefore be explored on a broader scale and applied to many support–precursor pairs or support–precursor–solvent systems.

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