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In-situ monitoring of transition metal complex adsorption on oxide surfaces during the first stages of supported metal catalyst preparation

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ABSTRACT

In the preparation of supported catalysts by deposition, in solution, of a transition metal complex (TMC) on an oxide support, the interactions occurring at the solid/liquid interface between the TMC and the oxide have a crucial impact on the properties of the final catalyst. However, these interactions remain difficult to investigate and monitor as most of the spectroscopic characterization techniques can only be used once the solvent has been removed, which eliminates an essential partner of the interaction. In this paper, we show that Quartz Crystal Microbalance with dissipation monitoring (QCM-D), a highly sensitive technique operating *in situ* at the solid/liquid interface, can be used to undo this technical lock. QCM-D was used to study two well-known systems: the adsorption of $[Pt(NH_3)_4]^{2+}$ on silica at high pH and the adsorption of $[PtCl_6]^{2-}$ on alumina at low pH, in order to demonstrate that QCM-D can be a very useful tool for the investigation of the interaction between a TMC and an oxide surface in solution.

1. Introduction

Preparation of supported catalysts by *deposition–reduction* involves first the deposition of an ionic metal precursor, often a transition metal complex (TMC), on a support, often an oxide, either by wet or incipient wetness impregnation or by ion exchange. Depending on the choice of the TMC, of the support and of other experimental conditions – such as the pH of the solution – the interaction between the TMC and the support may simply be electrostatic in nature (strong electrostatic adsorption model, SEA, developed by Regalbuto and colleagues [1,2]) or include the formation of outer or inner sphere complexes [3–5]. It is now well established that interactions occurring in solution (and more precisely at the solid/liquid interface) between the metal complex and the oxide support have a lasting influence over all subsequent steps of the catalyst preparation procedures, and on the properties of the final catalyst [6–10]. Therefore, understanding these initial steps of the adsorption of transition metal complexes on oxide surfaces is of prime importance for mastering the synthesis of supported metal catalysts [11].

Nevertheless, determining the mode of adsorption and the structure of the deposited species in solution remains challenging, as most of the spectroscopic characterization techniques require the removal of the solvent, an essential partner in the interaction. For this reason, a large part of the conclusions involving the complex/surface interaction in solution are based on the measurement of adsorption isotherms and on potentiometric titration data [8,10,12,13]. These measurements are highly time-consuming and knowledge of the adsorption mode of metal complexes on surfaces is therefore currently limited to very few metal/oxide systems and very specific conditions of pH and temperature.

Newly developed *in situ* techniques, such as Quartz Crystal Microbalance (QCM) show great promise in helping us understand the phenomena occurring at the solid/liquid interface. A QCM

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sensor consists of a quartz single crystal sandwiched between two conductive gold films. In addition, an oxide coating (such as silica or alumina) may be deposited onto one of the gold electrodes, providing a surface for molecules of interest to adsorb on. Detection is based on the modification of the oscillations of the piezoelectric quartz by the adsorbed layer[1], and the frequency change can be correlated to the mass uptake, down to the ng cm^{-2} scale, using the Sauerbrey equation [14]. Although QCM was initially developed in the 1950s [14], it is only recently that its scope was successfully extended to the liquid/solid interface, a step which requires taking into consideration the viscoelasticity of the solution. This was achieved with the help of dissipation monitoring, or QCM-D [15]. Until now, this technique has mostly been used to study the adsorption of biomolecules [16–19] and never been applied to the adsorption of metal ions on oxide surfaces, whether in the field of catalyst preparation or in other domains, such as corrosion, storage or transport of contaminants in the environment.

In this context, we have undertaken to use QCM-D to probe the solid/liquid interface for two well-known systems: the adsorption of $[Pt(NH_3)_4]^{2+}$ on silica at high pH and of $[PtCl_6]^{2-}$ on alumina at low pH. Our objective is to determine whether QCM-D can be used to monitor, in real time and in the presence of the solvent, the adsorption of TMCs. We will compare the results obtained with results from the literature on divided powders.

2. Experimental/methodology

In this study, we investigated the adsorption of anionic and cationic platinum complexes on QCM quartz crystals coated with silica or alumina. The adsorptions were carried out at pH values below and above the point of zero charge (PZC) of each oxide.

For the adsorption of $[Pt(NH_3)_4]^{2+}$, the pH of a 10^{-3} M solution of $[Pt(NH_3)_4](NO_3)_2$ (Sigma-Aldrich) was adjusted to pH = 4 by addition of HNO_3 and to pH = 10 by addition of NaOH. Solutions at pH = 4 and pH = 10 were also prepared without the addition of $[Pt(NH_3)_4](NO_3)_2$.

For the adsorption of $[Pt(Cl_6)]^{2-}$, the pH of a 10^{-3} M solution of $H_2[PtCl_6]$ (natural pH ≈ 2.7) was adjusted to 3 and to 11 by addition of NaOH. Solutions at pH = 3 and pH = 11 were also prepared without the addition of $H_2[PtCl_6]$ using, respectively, HCl and NaOH.

The water used for the preparation of these solutions was ultrapure (Milli-Q, Millipore, France).

The adsorption of metal complexes on oxide surfaces (either SiO_2 or Al_2O_3) was followed *in situ* by quartz crystal microbalance with dissipation monitoring. Measurements were performed with a QCM-D Q-Sense E4 system (Gothenburg, Sweden, detection limit 0.5 ng cm^{-2}) at a temperature of 22.0 (±0.1° C). The crystal used (1 cm^2) was a thin AT-cut (*i.e.* 35°15′ from the *Z* axis of the crystal), gold coated quartz covered with a thin film of the desired oxide (thickness: ≈40 nm for SiO_2; ≈100 nm for Al_2O_3) provided by Q-Sense. The surface roughness of these oxide coatings, as measured by Kelesoglu et al. using AFM, is below 2 nm (1.6 ± 0.4 nm) [20]. Therefore, the excess surface area (compared to the geometrical surface of the quartz) induced by this roughness is below 10%, and we used the geometrical surface of the quartz (1 cm^2) for the calculation of the surface density of adsorbed complexes [21]. Prior to measurement, the quartz surfaces were rinsed in ethanol and subjected to 20 min of UV–O_3 cleaning [22]. Experiments were performed in dynamic conditions using a peristaltic pump operating at a flow rate of 100 μl min^{-1}. Data were simultaneously acquired at the fundamental frequency *F* of 5 MHz (*N* = 1) and at several overtone frequencies (15, 25, 35, 45, and 55 MHz, *i.e.* *N* = 3, 5, 7, 9, and 11). For clarity, only the data for the seventh harmonic are reported. Two physical parameters were measured: the changes in the oscillation frequency (*F*), and the changes in energy dissipation (*D*). This dissipation increases upon adsorption of an imperfectly rigid layer, making it impossible to directly quantify the mass of the adsorbate. The evolution of the dissipation was therefore monitored to confirm the validity of the Sauerbrey model [14], which relates the frequency change to the mass of the adsorbed layer as long as the dissipation change is low:

$\Delta F = -N\Delta m/C_f$ where C_f is the mass sensitivity constant (=17.7 ng cm^{-2} Hz for a crystal with *F* = 5 MHz), *N* is the harmonic number and Δm is expressed in ng cm^{-2}.

In a typical experiment, before flowing the solution containing the platinum complex, a platinum-free solution at the same pH was flowed through the setup until the QCM signals were stable. After switching to the platinum solution and waiting for the signals to stabilize (*ca.* 15 min), the platinum-free solution at the same pH was flowed through the cell in order to remove loosely adsorbed platinum complexes. It is essential to use a solution of the same pH as a reference since the frequency and the dissipation are significantly modified by the pH of the solution.

3. Results and discussion

For this preliminary study, we investigated two systems for which the interaction between the metal complex and the oxide support is electrostatic according to the literature (with the possible formation of outer sphere complexes) [23]. Strong electrostatic adsorption is indeed the simplest interaction that can occur between a complex and a surface and is a widely used technique for the preparation of supported metal nanoparticles as it ensures a high dispersion of the active phase [24,25]. The only requirement for electrostatic adsorption is that the oxide surface and the metal complex have opposite charges. Every oxide support has a point of zero charge (PZC), defined as the pH at which the surface is neutrally charged. PZC values vary from very acidic (*e.g.* SiO_2, PZC ≈ 4) to very basic (*e.g.* MgO, PZC ≈ 12.4). Since the support has —OH functional groups on its surface, these hydroxyl groups will become protonated and positively charged when the pH of the solution is below the PZC, and the surface can then adsorb anionic metal complexes (Fig. 1, left). The same groups become deprotonated and negatively charged when the pH of the solution is above the PZC of the oxide support, and thus positively charged species can be adsorbed onto the support [12]. SEA corresponds to the accumulation of the metal complex in the mobile diffuse layer (which extends up to *ca.* 10–12 Å from the support surface), and where the metal complex retains most of its mobility. Electrostatic adsorption in solution may be followed by the establishment of stronger interactions, with the formation of outer sphere complexes (*e.g.* through hydrogen bonds) or inner sphere complexes (where surface hydroxyls are directly bound to the metal).

We first describe the adsorption of $[Pt(NH_3)_4]^{2+}$ on silica. Since the PZC of silica is close to 4 [13], the positive charge developed by the surface at pH close to and below 4 should prevent electrostatic adsorption of this complex, whereas the negative charge developed by the surface at pH above 4 makes the adsorption of the cation possible. As expected, the frequency and dissipation values remained unchanged upon switching from a pH = 4 Pt-free solution to a pH = 4 $[Pt(NH_3)_4]^{2+}$ solution, indicating the absence of adsorption of $[Pt(NH_3)_4]^{2+}$ on silica in these conditions (see Fig. 2).

Fig. 3 shows the frequency and dissipation changes *vs.* time, for the sequence of reagents described above the figure. The switch from a pH = 10 Pt-free solution to a pH = 10 $[Pt(NH_3)_4]^{2+}$ solution at *t* ≈ 5 min leads to an initially sharp then smooth decrease in the frequency, without modification of the dissipation, indicating

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[1] The mass uptake also includes water molecules trapped in the adsorbed layer and in the hydration sphere of the complex.