



# In situ observations of tetraamineplatinum(II) hydroxide adsorption from its aqueous solution on heulandite (0 1 0) surface by atomic force microscopy

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## Abstract

Adsorption of tetraamineplatinum(II) hydroxide, a Pt catalyst precursor, from its aqueous solution onto a (0 1 0) surface of a natural zeolite heulandite was observed, in situ, by atomic force microscopy (AFM). The Pt complex exhibited certain adsorption habits on the surface, frequently forming a short chain along the zeolite *a*-axis, separated by three times the *c* unit cell length in the *c* direction. Possible adsorption sites on the surface were identified and discussed. The present work constitutes the first in situ atom-level observation of a liquid-phase preparation process of supported metal catalysts.

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## 1. Introduction

Solid catalysts in common use are typically in the form of small metal crystallites dispersed on the (inner) surfaces of porous support materials such as silica, alumina or zeolite. Such supported metal catalysts are commonly prepared by a process called impregnation, in which the support material in a

powder or pellet form is soaked in a liquid, often aqueous, that contain one or more desired catalyst metal precursors [1]. During this impregnation process, the dissolved catalyst metal precursor is adsorbed on the (inner) surface of the porous support material. Then, the impregnated catalyst support material is dried and then treated in various ways to bring the catalyst metal precursors into its catalytically active form.

While this impregnation process, and the adsorption process involved in it, is known to affect the performance of the finished catalyst in great extent [1], its detail at atomic level has not been well understood,

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mostly due to the facts that the process is performed in liquid-phase and that the support materials employed are insulators, both of which refuse the application of microscopy techniques that employ electrons. Atomic force microscopy (AFM), with its applicability to insulators and under liquid environments, should enable us to explore the systems heretofore inaccessible.

Thus, with AFM, we have successfully observed in situ atomic images of natural zeolite surfaces, heulandite and stilbite (0 1 0), under aqueous environments [2–4], and molecular images of aqueous-phase-adsorbed pyridine bases and other molecules on these surfaces [3–8]. The unprecedented resolution of the AFM imaging on these adsorption systems enabled us to determine, for the first time, the atomic arrangements on these zeolite surfaces including extra-framework cations and the array and orientation structures of the adsorbed molecules on these surfaces.

The present paper exploits those unparalleled characteristics of AFM for the study of in situ catalyst preparation process, and observes the aqueous-phase adsorption of a Pt-containing molecule, tetraamineplatinum(II) hydroxide, often used as a Pt catalyst precursor, on a heulandite (0 1 0) surface. The observations revealed certain adsorption habits of the Pt complex on the zeolite surface, and also enabled us to estimate the possible adsorption sites for the complex molecules.

## 2. Experimental

Tetraamineplatinum(II) hydroxide (Strem Chemicals) was used as a representative Pt catalyst precursor. The Pt complex ion  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  is planar with four ammonia groups surrounding the center  $\text{Pt}^{2+}$ . The nuclei–nuclei distance between Pt and N is 0.206 nm, and thus, the size of the planar ion is somewhere around 0.5 nm, considering the N–H arm lengths and their van der Waals radii.

Natural heulandite (HEU) from Puna, India, was used as a representative catalyst support. The mineral, with a nominal composition of  $\text{Ca}_4[\text{Al}_8\text{Si}_{28}\text{O}_{72}]$ , has a monoclinic crystal structure with the unit cell lattice parameters of  $a = 1.77$  nm,  $b = 1.79$  nm,  $c = 0.74$  nm, and  $\beta = 116^\circ$  [9]. Micropores consisting of ten- and eight-membered rings run

along the [0 0 1] direction and eight-membered ones along the [1 0 0]. Thus, these channels are running parallel to the (0 1 0) (i.e.,  $ac$ ) plane, which is the plane that is exposed by cleaving (cf. Fig. 4). On the cleaved (0 1 0) surface, two oxygen atoms per unit cell are protruding out from the plane, lining up along the  $a$ -axis with unequal spacings, 0.71 nm for the shorter and 1.06 nm for the longer. These top-most oxygen atoms are most likely in the form of OH under ambient or aqueous conditions in which the present experiments were performed, and we refer them as surface hydroxyls, hereafter.

Atomic force microscopy examinations were performed using a Nanoscope II contact-mode AFM (Digital Instruments) equipped with a laser beam deflection type scan head. Type NP cantilevers (Digital Instruments) were employed, which have  $\text{Si}_3\text{N}_4$  tips and force constants equal to 0.12, 0.38 or 0.58 kN/m. The tip load applied was about 5 nN. When a contact-mode AFM is applied on a soft, layered material with high surface symmetry with high tip loads, it is known that sometimes the flakes of the sample layer sticks on the tip apex and give a false atomic image due to the multiple tip effect. The present work employs a very low tip load, and the sample is not soft, layered nor possess high surface symmetry, and the images obtained are considered to reflect actual atom or molecular positions. A discussion will be given later about the resolution of the contact-mode AFM. Line scans were obtained in height mode at a frequency range between 5.7 and 19.3 Hz. All images were presented as obtained, without any filtering.

The zeolite sample was cleaved with a razor blade along its (0 1 0) [or (0 2 0)] plane under ambient conditions and immediately placed in a sealed AFM liquid cell, which was then filled with deionized and membrane-filtered water (conductivity of ca. 90 S/cm). The cleaved HEU (0 1 0) surface showed a bulk-terminated atomic arrangement, as reported previously [3]. After images of HEU (0 1 0) surface under pure water were taken, the liquid contents in the cell were substituted with 0.7 wt.% Pt aqueous solution, left overnight (18 h) in order to allow the liquid-phase adsorption to equilibrate, and then the surface was examined by AFM. When necessary, the liquid cell content was changed back to pure water, so that weakly adsorbed Pt complex are desorbed.

### 3. Results and discussion

First we examine images taken after the weakly adsorbed Pt complex was desorbed in pure water, since the procedure tends to produce higher resolution images. Fig. 1 shows one such example. On the upper right side of the image, a characteristic oxygen atom (or hydroxyl) array of the bulk-terminated HEU (0 1 0) surface, indicated by small open circles representing each oxygen atom (or hydroxyl group) and arrows pointing  $c$  direction, is apparent. On the other part of the image (mainly on the upper area), bright structures higher and larger than those attributed to topmost hydroxyl groups, and measure ca. 0.5 nm in size, are found. Their arrangement on the surface is quite different from the bulk-terminated oxygen (hydroxyl) arrangement of HEU (0 1 0), and along with their size (see the inset Pt complex model), we attribute those to the adsorbed Pt complex ion. Particularly noteworthy is the two four-peaked structure on the upper part (one is indicated by an arrow): the diagonal distance between the peaks within a structure measures about 0.5 nm, and the structure is considered

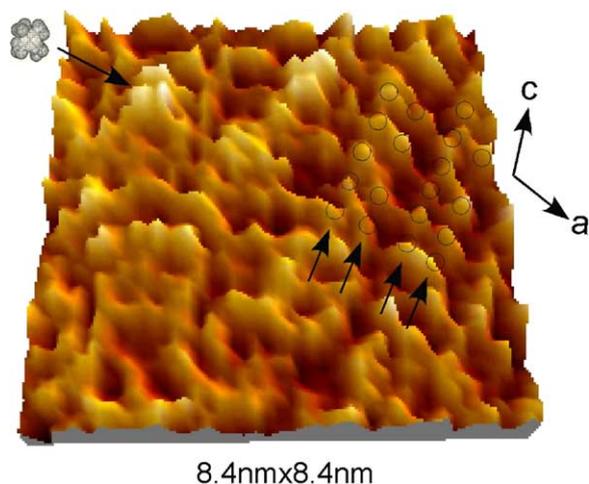


Fig. 1. An AFM image on a Pt-adsorbed HEU (0 1 0) surface, taken after weakly adsorbed Pt complex was desorbed in pure water. Scan size is 8.4 nm  $\times$  8.4 nm and the gray scale is 0.8 nm full-scale. On the upper right, a characteristic oxygen atom (or hydroxyl) array of the bulk-terminated HEU (0 1 0) surface is indicated with small circles representing oxygen atom (or hydroxyl group) and arrows pointing  $c$  direction. On the upper area, bright structures attributable to Pt complexes are found. One of them, with the wire-grid model of the complex at the end of arrow, shows four lobes that are attributable to resolved ammonia ligands.

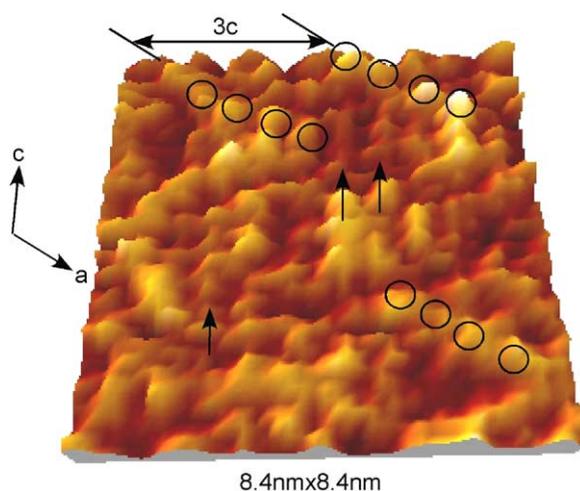


Fig. 2. An AFM image taken in a Pt complex solution. Scan size is 8.4 nm  $\times$  8.4 nm and the gray scale is 1.2 nm full-scale. Substrate structure is indicated by arrows in a  $c$  direction. Three Pt complex chains are highlighted with large circles each representing one molecule. Two of them at the top of the image are separated three times the  $c$  unit cell length.

to be a Pt complex with all the four ammonia ligands resolved.

In almost all the cases, the images taken under Pt complex solution gave lower resolution, and rarely showed a part of the substrate surface. One possible reason for this may be that Pt complexes are adsorbed at the apex of the AFM tip, increasing the apex curvature, reducing the space resolution and also prohibiting the tip to penetrate fine corrugation existing on the surface. Fig. 2, which is taken under Pt complex solution, shows ranges of large bright spots, highlighted with large open circles and measuring about 0.5 nm, attributed to individual Pt complex ions. At the bottom of these Pt complex ranges, one may be able to see substrate atomic structures, indicated by arrows, in the  $c$  direction.

In Fig. 2, we may be able to make a few observations about the adsorption habits and adsorption sites of the Pt complex ions on this surface. First, it appears that Pt complex ions tend to form short chains. Those chains appear to be a few molecules long, and orient themselves either along  $a$ - or  $c$ -axis. In Fig. 2, both  $a$ - and  $c$ -axis orientation are apparent, with dominant  $a$ -axis orientation. It is further noted that in some cases, but not always, the  $a$ -axis-oriented chains are separated from each other by three times the  $c$  unit cell

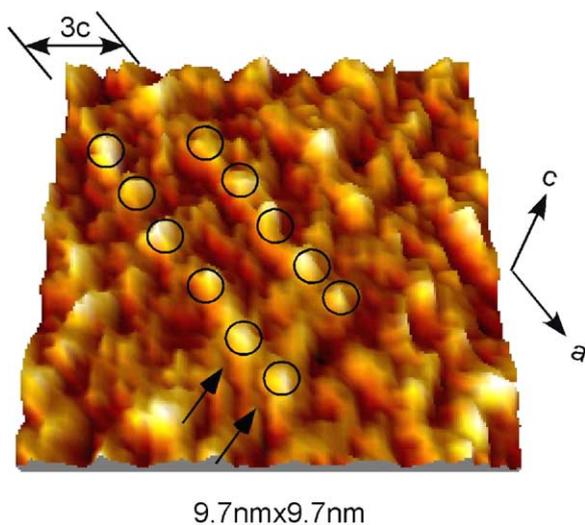


Fig. 3. Another AFM image taken in a Pt complex solution. Scan size is  $9.7 \text{ nm} \times 9.7 \text{ nm}$  and the gray scale is  $0.8 \text{ nm}$  full-scale. Two Pt complex chains are highlighted with large circles each representing one molecule. The two chains are separated three times the  $c$  unit cell length.

length, as an example being indicated at the top of Fig. 2. Finally, the bright spots attributable to Pt complex ions position themselves, more often than not, not on the positions of the topmost protruding framework oxygen atoms (hydroxyls) of the HEU substrate surface, but among those oxygen atoms (or hydroxyl groups).

In Fig. 3, which is also taken under Pt complex solution, we see a few substrate surface atoms indicated by arrows along the  $c$ -axis. Again, we find short Pt complex chains, each molecule indicated by large open circles, aligned mostly along the  $a$ -axis. The chains are again separated from each other by three times the  $c$  unit length along the  $c$ -axis.

There may be a few possible origins for the apparent adsorption habits observed in the present experiment. Firstly, the Pt complexes seem to be adsorbed among the protruding oxygen atoms (hydroxyl groups), but not on top of them. This would be reasonable if we consider the nature of Pt complex adsorption as ionic or electrostatic. Then, instead of binding to only one surface OH group, it may be more stable to interact with more than one OH. This would lead the complexes to position themselves among the topmost OH groups. Furthermore, this position among the OH groups is actually a valley, as may be found in Fig. 4 which shows a ball-and-stick model of heulandite  $1 \times 0.5 \times 2$  unit cell. The figure views  $(0\ 0\ 1)$  (or  $ab$ ) plane along the  $a$ -axis. All the dangling bonds produced by cutting the bulk crystal are terminated with hydrogen atoms. The top part of this figure is the cleaved  $(0\ 1\ 0)$  plane showing two valleys along the  $a$ -axis flanked by protruding oxygen atoms (hydrolyzed), with the separation between the oxygen ridges being  $0.74 \text{ nm}$ . This is actually a part of the eight-membered channel running along  $[1\ 0\ 0]$  cleaved into half. Apparently these valleys (or grooves) on the  $(0\ 1\ 0)$

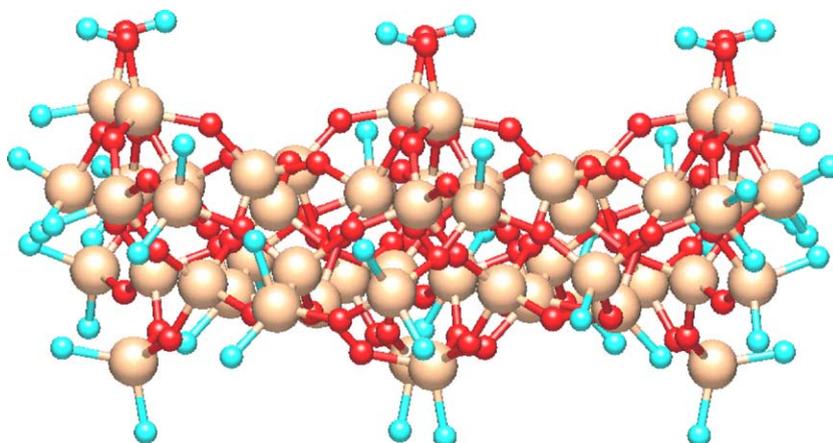


Fig. 4. A ball-and-stick model of heulandite  $1 \times 0.5 \times 2$  unit cell, showing  $(0\ 0\ 1)$  (or  $ab$ ) plane viewed along the  $a$ -axis. All the dangling bonds produced by cutting the bulk crystal are terminated with hydrogen atoms. The top part is the cleaved  $(0\ 1\ 0)$  plane showing two valleys along  $a$ -axis flanked by protruding oxygen atoms (hydrolyzed), with the separation between the oxygen ridges being  $0.74 \text{ nm}$ .

surface consisting of the cleaved eight-membered channels are wide enough to accommodate the present Pt complex ion into them. Similar channels (eight- and ten-membered) also run along *c*-axis. This way, the complexes fallen in the channels may appear to form chains either along *a*- or *c*-axis, as may be found in the present work. The reason for dominant *a*-axis alignment of these chains, however, is not apparent.

Another apparent adsorption habit, the  $3c$  spacing when chains are aligned along *a*-axis, is rather difficult to interpret at this moment. This is not necessarily a rule, as stated above by noting that one may occasionally find chains even next to each other, but it is an often-observed phenomenon. The distance between the chains, when they are apart  $3c$  length, is about 2 nm normal to the *a*-axis, and it must be a relatively long-range repulsive force to invoke such an order among the adsorbates. Considering the fact that they produce short chains (which obviously mean that they are not very repulsive to each other), it is difficult to envision such a long-range repulsive force working among the adsorbates.

It may also be possible to seek the origin of this ordering (including the *a*-axis alignment of the chains) to the substrate structure. Again assuming that the present adsorption is ionic in nature, the distribution of substrate electronic charge, including the extraframework cations, would have strong influence on the Pt complex adsorption habits. In the case of heulandite of different origin [2], any of the extraframework cations exposed on (0 1 0) surface did not show systematic ordering with  $3c$  unit length, but there are a few more cation sites below (0 1 0) face, and if there exist any crystal habits for those extraframework cations as a whole (which is obviously controlled by the aluminum distribution within the zeolite framework), it would be reflected in the adsorption habits like the one observed here.

Finally, a word is added about the resolution of contact-AFM. There exist a widespread notion that contact-mode AFM is not able to attain atomic resolution, contrary to our own experience [2–7]. One such view is expressed by Heuberger et al. who, in their continuum mechanics analysis of AFM imaging [10], find that atomic resolution is not possible at the tip load of the level of nN. Taking elastic deformations of both the tip and the sample into consideration, they calculated the deformation as a function of Young's

modulus as well as of applied force, and defining the range of deformation to give “true” atomic resolution as “a contact area which is smaller than the size of a single atom” they draw a line at an “estimated contact radius” of  $10^{-10}$  m.

If we stand on a very common definition of “resolution” in any microscopy, it appears that this line for “true” atomic resolution should be defined, not as “the size of an atom,” but as “the distance between two atoms” on the surface plane, since if two atoms are separated by a distance much larger than the atom size, then deformation of a single atom size still does not interfere with imaging of a single atom on the surface plane within the framework of their analysis.

Take our system, for example. In our HEU zeolite system examined in the present paper, we were able to resolve surface oxygen (or hydroxyl) routinely under the present experimental conditions [2–7]. The reason for this is, if we follow the argument of Heuberger et al. [10] with the modification of the definition of resolution indicated above, that it is because the two surface oxygen (or hydroxyl) are separated at least 0.71 nm (shortest atomic distance on the surface plane). Then, for the “true” atomic resolution on this surface plane, a line should be drawn at 0.71 nm in Fig. 3(b) of [10], and this will place their “true” atomic resolution limit at this separation between 1 and 10 nN applied force for the materials with a “surface” Young's modulus of above 10 GPa. Bulk Young's modulus of a silicate is in the order of  $10^2$  GPa (no Young's modulus data for HEU available), and our tip load is ca. 5 nN, thus, we may safely be able to claim that we are within the range of atomic resolution within the continuum analysis by Heuberger et al. [10].

Considering the fact that we do not know the surface Young's modulus for many surfaces examined by AFM, as well as for many adsorbed molecular systems, it may appear premature to claim or declare that contact-AFM per se is not able to attain atomic resolution.

#### 4. Conclusions

An in situ atom-level observation of a liquid-phase preparation process of supported metal catalysts was attempted using AFM for the first time. Adsorption of tetraamineplatinum(II) hydroxide, a Pt catalyst pre-

cursor, from its aqueous solution on a (0 1 0) surface of a natural zeolite heulandite was examined. The Pt complex exhibited certain adsorption habits on the surface, frequently forming a short chain along the substrate *a*-axis, separated by three times the *c* unit cell length in the *c* direction. The complex ion seems to be adsorbed in the valley formed by the oxygen atoms (OH group) protruding out of the *ac* plane.

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