Small Pt nanoparticles on the TiO₂ (110) - (1x2) surface

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ABSTRACT

Scanning tunnelling microscopy (STM) has been used to study the initial stages of Pt deposition on the TiO₂ (110)-(1x2) surface. Experimental STM images recorded for Pt coverage of 0.1 and 0.4 ML, suggest a Volmer-Weber growth. For low coverage and RT deposition, small clusters homogeneously distributed on the surface terraces are observed. However, after annealing at 825K, material agglomeration, with nucleation mainly at the cross-links, is observed as a consequence of Pt diffusion on the surface. Finally, the structure of small clusters has been determined, in good agreement with previous theoretical calculations.

Keywords: titanium oxide; STM; Pt/TiO₂; surface reconstruction

INTRODUCTION

The (110) face of rutile TiO_2 presents several terminations depending on its reduction level. Among all of them, the most studied and widely used are the (1x1) and the (1x2) surface terminations. The (1x1) surface is characteristic of stoichiometric and low reduced substrates and it is well understood from the morphological and electronic points of view [1]. This bulk truncated surface is composed by oxygen rows (bridging oxygen atoms, O_{br}), which protrude approximately 0.15 nm from the surface [2] and in-plane five-fold coordinated Ti rows ($\text{Ti}_{5\text{f}}$), both running along the [001] surface direction [3]. On the other hand, the (1x2) surface termination has been less studied due to the extra complexity to form it (heavily reduced substrates and high temperature annealing are mandatory). Its structure has been a matter of debate for several years. Different models, based on different experimental techniques and theoretical calculations, have been proposed for this reconstruction [4-7]. A few years ago, a complete structural study combining STM, LEED-IV and DFT calculations managed to yield a fully consistent structure [8]; it was shown that the best fitting structural model for the (1x2) $\text{TiO}_2(110)$ surface is an 'added Ti_2O_3 rows' model similar to that proposed by Onishi et al [5]. Of particular importance here is the low R-factor value obtained for the LEED structural analysis and the nice agreement between LEED and DFT calculations. Such agreement could not be obtained for other models proposed in the literature [9], which clearly indicates that the best candidate so far is related to the positions and stoichiometry proposed in ref. [8]. In this model, Ti_2O_3 rows run along the [001] direction with a [1-10] periodicity of 1.3 nm.

On this reconstructed surface it is common to find two kinds of ordered surface defects: the so-called “single-links” and “cross-links” [10-16]. They are associated to TiO_2 and Ti_2O_3 units, respectively, which diffuse on the surface until they are trapped between two neighboring Ti_2O_3 rows. This gives rise to the formation of rows running along the $[1-10]$ direction, interrupting the characteristic rows of the reconstruction.

Titanium dioxide is used in a wide range of technological applications, e.g. in catalysis, gas sensors, optical coating, etc. [1]. In fact, TiO_2 is one of the most extensively used catalytic supports and its combination with noble metals such as Pt, Pd, Ir, etc. is much utilized for industrial applications. The (110) face has been a model surface to depict an atomistic view of these processes. However, as commented above, most of the noble metal adsorption studies have been performed on the stoichiometric (1x1) surface. Special attention has been paid to Pt, as it is a very common and useful catalyst, complementing in different ways the properties of metallic oxides. Previous studies on Pt films on the rutile TiO_2 (110)-(1x1) surface have shown a Volmer-Weber growth with randomly distributed clusters on it [17,18]. For Pt coverages of 25 ML and upon annealing at high temperature, the majority of the clusters presented a quasi-hexagonal shape, although some square clusters were also visible [19]. These Pt clusters undergo encapsulation by titanium oxides after the subsequent annealing process at high temperature [19-22].

On the other hand, concerning the (1x2) surface termination of TiO_2 (110), the deposition of some noble metals like Rh [23,24], Ir [25,26], Au [27] and Pt [28,29] have also been undertaken. The case of Pt adsorption on the (1x2) reconstruction has been previously addressed in two different works. Gan et al.

in ref. [29], dealt with the Pt cluster size effects and its role on the adsorption chemistry of CO. Although they assumed a Ti_3O_5 model for the (1x2) surface reconstruction they successfully arrived to show that Pt forms small clusters distributed on the surface. The work reported on ref. 28 theoretically describes the preferential adsorption sites for Pt_n clusters ($n=1 - 4$). Those results have been calculated considering a surface structural model based on added-rows with a Ti_2O_3 stoichiometry.

In this paper we study by means of STM the initial stages of Pt growth on the rutile TiO_2 (110)-(1x2) surface reconstruction. A Volmer-Weber (VW) growth is proposed in agreement with previous works [29]. Additionally, after annealing at 825K, diffusion of the clusters at the cross-link nucleation sites as well as an increase in their size and height is observed. Contrary to the 1x1 surface, we show that for small particle sizes there are not evidences of encapsulation of Pt nanoparticles.

EXPERIMENTAL DETAILS

All the experiments have been carried out under ultra-high vacuum (UHV) conditions (pressure below 1.5×10^{-10} mbar) in a chamber equipped with Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and room temperature Scanning Tunneling Microscope (STM) techniques. A commercial rutile TiO_2 (110) single crystal has been prepared under UHV conditions by sputtering and annealing cycles (1100K) until a sharp (1x2) symmetry was observed by LEED. The cleanliness and quality of the surface was checked by AES and STM.

Platinum has been evaporated on the substrate by direct heating of a 99.99% pure Pt filament. The coverage and evaporation rate have been calibrated by STM. Coverage has been evaluated by estimating the area covered by adsorbates and evaporation rates were of the order of several Å per minute. To identify single atoms, the smallest atomic bump has been squared in a box of about $0.5 \times 0.5 \text{ nm}^2$. Therefore, we assigned the value of 0.25 nm^2 to a single atom.

All STM images have been measured in the constant current mode using only positive voltages applied to the sample. STM images were analyzed by with the WSxM software [30].

RESULTS

An atomic model for the rutile TiO_2 (110)-(1x2) surface reconstruction is depicted on figure 1 a). Figures 1 b) and c) show STM images for this surface, with a black arrow representing the [001] direction. Bright strips running along the [001] direction correspond to the Ti_2O_3 rows of the reconstruction [1]. Since the images were measured using positive sample voltages, the tunneling current flows from the tip into the empty states of the sample, which have predominant Ti 3d character [3]. For this reason, the bright features into the long strips correspond to Ti atoms inside the Ti_2O_3 rows. Extra brilliant structures extending along the [1-10] direction and linking some of the bright rows of the reconstruction appear in the STM images of figures 1 b) and c). These linking features are known as “single-links (SL) and cross-links (CL)” (marked with arrows in fig. 1b) [10]. CLs have been associated in the literature to Ti_2O_3 molecules trapped at the surface troughs altering the reconstruction

structure [10]. Figure 1 c) exhibits a closer view of the CLs perpendicular to the Ti_2O_3 rows of the TiO_2 (110)-(1x2) surface reconstruction. Within the cross-links region of this atomic resolution image, it is possible to distinguish some main bright spots arranged in a cross-shape, which are in agreement with a previous proposed model for the linked structures [10]. On the other hand, the SL have been considered as one-half of a fully CL [11], and ascribed to TiO_2 or TiO units between added rows [10]. Although the formation of both CL and SL is reported to take place when re-annealing an oxygen-treated TiO_2 (110) surface in UHV [10-15], they have been also observed by annealing in UHV at high temperatures (1200 K) [16], as evidenced in our STM images.

Using the previous surface as a template, platinum atoms have been deposited at room temperature for two different coverages, 0.1ML (figure 2 a) and 0.4ML (figure 2 b). From these images it is evident that the material is homogeneously distributed on the surface, with no important step decoration. Bright features with different dimensions can be observed. These features can be associated to simple Pt atoms, although there are also particles composed of several atoms. This indicates that Pt atoms present a low diffusion rate on the surface at RT. Pt particles are mainly located at the bright rows of the (1x2) reconstruction. This result is more evident for the low coverage images, due to the moderate amount of Pt, which makes it easily observable. At small coverage, line scans allow to extract nanoparticle diameters and heights, ranging from approximately 0.5 to 1.5 nm and from 0.15 to 0.45 nm, respectively. A deeper analysis of the Pt clusters dimensions will be given below. For the case of the high coverage deposition, the diameter and height of the clusters extend from approximately 0.5 up to 2.5 nm and from 0.15 to up to 0.6 nm, respectively. These values are

consistent with a three-dimensional growth of the Pt clusters on the $\text{TiO}_2(110)$ surface. This growth mode, also known as Volmer-Weber growth, is characterized by the nucleation of islands coexisting with the bare substrate at low coverage [31]. On the other hand, no long-range ordering for Pt clusters can be observed in the STM images in both submonolayer regimes, in accordance to the case of Pt deposition on the $\text{TiO}_2(110)-(1 \times 1)$ surface [32].

The thermal stability of the Pt clusters has also been investigated for the lower coverage case. In previous works performed on Pt deposition on the $\text{TiO}_2(110)-(1 \times 1)$ surface, some interesting processes were detected in the range of 800-1000K [17,18]. This is the case, for example, of the encapsulation process, where the Pt islands are covered by an overlayer of Ti oxides, observed upon annealing the Pt films on $\text{TiO}_2(110)-(1 \times 1)$ up to 800K [17]. Figure 3 shows the surface with 0.1ML of platinum after annealing at approximately 825K. A noticeable increase of material at the CLs is observed. Additionally, the size and height of the clusters has increased in detriment of the number of dispersed ones. Both effects indicate a migration of the Pt atoms from initial nucleation sites on the bright rows towards the junction between these Ti_2O_3 chains and CLs. It is interesting to mention that both effects, i.e. the increase of the cluster size upon annealing and the preferential cluster site at the CLs have been also observed for the growth of Au on $\text{TiO}_2(110)-(1 \times 2)$ [27]. It was concluded that the Au particles diffuse along the surface rows while the diffusion was suppressed at the CL sites. Our observation for Pt is similar; therefore, we can deduce that the same effect is taking place for the Pt particles.

By analyzing in detail the STM images, a small number of small clusters can also be detected. In those cases, the initial stages of the cluster formation can

be followed. As an example, figures 3 d) and e) show a dimer and a trimer of Pt atoms on the bright Ti_2O_3 rows, indicating the tendency of the isolated atoms to agglomerate after the annealing. In the case of the dimer we observe a tendency to align along the direction perpendicular to the surface rows, i.e. they are aligned along the $[1-10]$ direction, with one of the atoms coming out of the reconstruction row into the trough. When a third atom joins the dimer, the cluster adopts a triangular shape with the atom placed in the trough moving towards the row in order to increase the coordination. These geometries appear in nearly all the dimers and trimers we have imaged.

It is interesting to note that these results are in nice agreement with previous theoretical calculations on the adsorption sites of Pt clusters on the TiO_2 (110)-(1x2) surface [28]. For the case of one isolated Pt atom deposited on the surface, it can be observed from Fig. 3 c) that it gets favorably adsorbed on top of the reconstruction bright rows. These rows correspond to the Ti_2O_3 groups. However, the Pt dimer energetically prefers to be located in the trough hollow in a position very close to the two reactive Ti cations of the added row. Finally, the trimer preferential site is on top of the Ti_2O_3 row.

A qualitative and comparative study on the size of the Pt clusters before and after thermal treatment has been performed. Figure 4 shows two different histograms representing the area and height distributions of the clusters before and after the annealing (figure 4 a) and b), respectively). In both cases we have included the values of the bright features already present at the clean surface, which can be associated to small adsorbates coming from the residual gas, as H_2O , OH, etc. They present a mean area of 1 nm^2 and a mean height of 0.1 nm. In the bar graph of the clusters area distribution it is possible to observe that

before the annealing the mean area for the clusters is around 0.5 nm^2 . One can attribute an area of 0.25 nm^2 to a single Pt atom, as it is deduced experimentally from our STM images (see experimental details section). Thus, within the first purple box in the histogram we merge all events corresponding to one atom area, within the second box we merge events corresponding to two atom areas and so on. Consequently, it is clear from the data of Figure 4 that before annealing, clusters of 1, 2 or 3 Pt atoms dominate the statistics (green bars). However, after the annealing treatment, a larger variety of clusters is obtained, and even clusters formed by nine Pt atoms can be seen. Regarding the height of these clusters (figure 4 b), before annealing their mean height is around 0.3 nm, which corresponds to one or two Pt atoms. On the other hand, after annealing the distribution shifts to higher clusters with a mean height of approximately three Pt atoms (0.5 nm), and smaller contributions from 1, 2 or 4 Pt atoms height. These data indicate that before annealing, the clusters are small and randomly distributed on the surface as a consequence of weak diffusion mechanism that leads to very low diffusion rates at room temperature. However, when thermal energy is supplied through an annealing at 825K, Pt atoms start diffusing on the surface with a tendency to form bigger clusters. Curiously, after annealing the number of small clusters increases. This fact can be related to nucleation at defect sites (oxygen vacancies, SLs or CLs). As the diffusion is enhanced, the structural defects act as nucleation points.

Finally, it should be mentioned that from the STM images, no encapsulation of the Pt clusters by Ti oxides was detected after annealing for the low coverage regime. This result contrasts with previous observation on the TiO_2 (110)-(1x1) surface [10-16]. Two possible reasons can contribute to this phenomenon. First,

because our aim is to investigate the early stages of Pt growth, we have used lower coverages than those used in the case of encapsulation of Pt at the (1x1) surface. Second, the catalytic properties of the (1x1) and (1x2) surface terminations of TiO₂ (110), which are fundamental for determining the metal-support interaction, are different. This fact implies that these Pt clusters should present a higher catalytic activity towards H₂ and CO adsorption than encapsulated systems observed on the (1x1) surface.

CONCLUSIONS

We present a study of the initial stages of the growth of Pt on the rutile TiO₂ (110)-(1x2) surface. For submonolayer coverage the growth mode at room temperature is three-dimensional islanding, i.e. VW-like. When depositing at room temperature, the Pt atoms cluster in small particles formed by 1, 2 or 3 Pt atoms, with an area smaller than 1 nm². The mean height of these clusters is 0.3 nm approximately. These small nanoparticles are homogeneously distributed on the surface. The preferential nucleation sites for Pt_n clusters (n=1-3) observed in the STM images are corroborated by previous theoretical calculations. On the other hand, after annealing at about 825K, an increase in the mean area and height of these clusters is observed (in detriment of the amount of them). Thermally activated, these clusters diffuse on the surface and nucleate at the cross-links of the (1x2) surface reconstruction. For these coverages, no evidences of cluster encapsulation after annealing at 825 K are observed.

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Figure captions:

Fig. 1. a) Model for the $\text{TiO}_2(110)-(1 \times 2)$ surface with the blue and red spheres representing the titanium and oxygen atoms, respectively. STM images corresponding to this surface on an area of b) 50×50 and c) $8 \times 8 \text{ nm}^2$. The black arrow indicates the $[001]$ direction. Bias voltage and tunnel current are 1.2 V and 0.1 nA, respectively.

Fig. 2. STM images ($50 \times 50 \text{ nm}^2$) of the $\text{TiO}_2(110)-(1 \times 2)$ surface after deposition of Pt for a coverage of a) 0.1 ML ($I = 0.13 \text{ nA}$ and $V = +1.5 \text{ V}$) and b) 0.4 ML ($I = 0.11 \text{ nA}$ and $V = +1.5 \text{ V}$).

Fig. 3. STM images of the $\text{TiO}_2(110)-(1 \times 2)$ surface with a 0.1 ML Pt coverage after annealing at 825 K for an area of a) 50×50 , b) 20×20 , c) 2.9×2.9 (isolated Pt atoms), d) 2.5×2.7 (dimer) and e) $2.4 \times 2.3 \text{ nm}^2$ (trimer). $I = 0.15 \text{ nA}$, $V = +2.0 \text{ V}$.

Fig. 4. a) Area and b) height distribution of the Pt clusters for the clean $\text{TiO}_2(110)-(1 \times 2)$ surface (red bars), the surface after 0.1 ML Pt deposition (green bars) and 0.1 ML Pt plus annealing at 825 K (blue bars).

Figure 1

Figure 2

Figure 3

Figure 4