

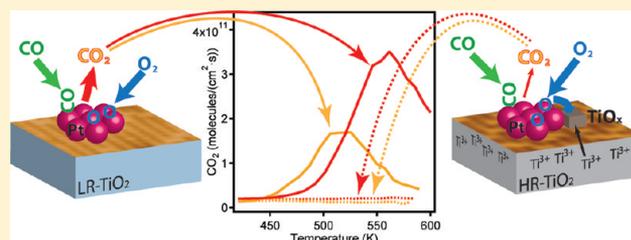
# Effect of the TiO<sub>2</sub> Reduction State on the Catalytic CO Oxidation on Deposited Size-Selected Pt Clusters

Simon Bonanni, Kamel Ait-Mansour,\* Wolfgang Harbich, and Harald Brune\*

Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

**S** Supporting Information

**ABSTRACT:** The catalytic activity of deposited Pt<sub>7</sub> clusters has been studied as a function of the reduction state of the TiO<sub>2</sub>(110)-(1 × 1) support for the CO oxidation reaction. While a slightly reduced support gives rise to a high catalytic activity of the adparticles, a strongly reduced one quenches the CO oxidation. This quenching is due to thermally activated diffusion of Ti<sup>3+</sup> interstitials from the bulk to the surface where they deplete the oxygen adsorbed onto the clusters by the formation of TiO<sub>x</sub> ( $x \simeq 2$ ) structures. This reaction is more rapid than the CO oxidation. The present results are of general



relevance to heterogeneous catalysis on TiO<sub>2</sub>-supported metal clusters and for reactions involving oxygen as intermediate.

## 1. INTRODUCTION

In order to improve the efficiency and selectivity of modern catalysts, a detailed understanding of the interplay of the underlying physical and chemical processes is needed. This will depend on the size, composition, and morphology of the active material, and, equally importantly, on the chemical composition, morphology, and charge state of the support. Metal nanoclusters supported on well-defined single-crystal metal oxide substrates serve as model systems where these parameters can be controlled on the atomic scale.<sup>1–20</sup> Their catalytic properties have been studied as a function of the cluster size,<sup>1–6</sup> shape,<sup>8,9</sup> composition,<sup>10</sup> as well as of oxide support chemistry, surface stoichiometry,<sup>14</sup> and thickness.<sup>16</sup>

Pioneering studies by Heiz et al. have shown that the CO oxidation reaction rate over small size-selected platinum clusters supported on MgO films grown on Mo(100) is strongly influenced by the cluster size.<sup>1</sup> Yoon et al. have found that size-selected gold clusters adsorbed on an MgO(001) surface catalyze the CO oxidation at low temperature only in the presence of surface oxygen vacancy defects due to charging of the clusters.<sup>14</sup> However, on very thin MgO films (2 or 3 monolayers, ML) grown on Mo(001), catalysis of the CO oxidation by two-dimensional gold clusters has been shown to occur in the absence of the surface defects.<sup>15,16</sup> The two-dimensional configuration of the gold clusters has been found to be stable on 3 ML but not on 8 ML MgO films on Ag(001).<sup>17</sup> These studies clearly manifest the influence of the cluster-support interaction on the morphology, charge state, and catalytic activity of the clusters.

Rutile TiO<sub>2</sub> is one of the most studied metal oxide supports for model catalysts based on metal nanoclusters. It can be reduced by heating in vacuum creating bulk oxygen vacancies which are readily detected by the crystal changing from transparent to blue.<sup>21</sup> The density of bulk vacancies goes hand

in hand with the one of surface vacancies, the abundance of which is therefore a measure of the bulk reduction state.<sup>21,22</sup> Bulk oxygen vacancies are accompanied by bulk Ti<sup>3+</sup> interstitials. These are very reactive to any adsorbed oxygen once they diffuse to the subsurface region.<sup>23,24</sup> Recent papers by Benz et al. have shown that Ti<sup>3+</sup> interstitials are responsible for breaking the CO double bond in benzaldehyde to form stilbene.<sup>25,26</sup> At elevated temperatures and under oxidative conditions they segregate to the surface where they form TiO<sub>2</sub> leading to the reoxidation of the crystal.<sup>27–29</sup>

It is well established that if TiO<sub>2</sub> is sufficiently reduced, supported nanoparticles of Pt, Ir, Rh, Ni, and Pd lose their H<sub>2</sub> and CO chemisorption capacity after annealing above 700 K<sup>30</sup> due to their encapsulation by a reduced titania layer.<sup>31,32</sup> This state is known as strong metal–support interaction (SMSI) state. It suppresses the catalytic activity of the nanoparticles, e.g., toward CO oxidation.<sup>33</sup>

In this work, we demonstrate the decisive role of the TiO<sub>2</sub>(110) bulk reduction state on the catalytic CO oxidation over supported size-selected platinum clusters (Pt<sub>7</sub>). Atomic resolution scanning tunneling microscopy (STM) images reveal the TiO<sub>2</sub> surface oxygen vacancies, and the formation of surface TiO<sub>x</sub> ( $x \simeq 2$ ) species after the reaction on strongly reduced supports. CO<sub>2</sub> production rates on the Pt clusters are 2 orders of magnitude higher when they are supported on a slightly reduced TiO<sub>2</sub> than on a strongly reduced one. The quenching of the CO oxidation on the strongly reduced support is identified as being caused by the surface segregation of Ti<sup>3+</sup> interstitials and their consumption of the adsorbed oxygen from the Pt clusters by spillover. This reoxidation of strongly reduced bulk titania is activated at 430 K and much more rapid

Received: October 20, 2011

Published: January 10, 2012

than the CO oxidation aimed for. We further show that the Pt clusters are clean on both supports and that the surface oxygen vacancies are not responsible for the difference in the catalytic activity, which highlights the importance of  $\text{Ti}^{3+}$  interstitials for the surface chemical reaction. The results are of general relevance to any catalytic reaction involving oxygen on titania-supported metal nanoclusters.

## 2. EXPERIMENTAL SECTION

The measurements have been performed in an ultrahigh vacuum (UHV,  $p_{\text{tot}} \leq 1 \times 10^{-10}$  mbar) chamber combining size-selected cluster deposition, low-temperature STM,<sup>34</sup> and catalytic activity measurements with a highly sensitive detector.<sup>35</sup>

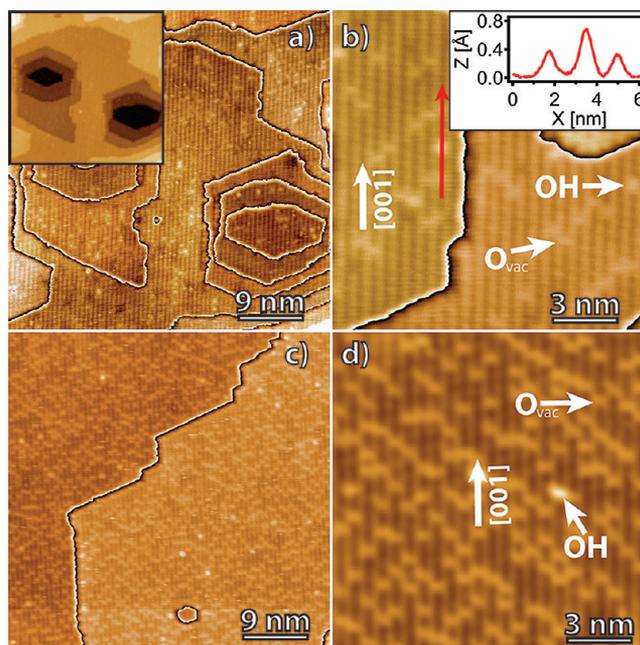
The  $\text{TiO}_2(110)$  surfaces have been prepared in UHV by repeated sputtering-annealing cycles. Oxygen is preferentially removed from the crystal leading to a  $\text{TiO}_{2-x}$  stoichiometry ( $0 < x < 1$ ). This induces the formation of defects such as surface oxygen vacancies ( $\text{O}_{\text{vac}}$ ), bulk oxygen vacancies, and bulk interstitial  $\text{Ti}^{3+}$  atoms.<sup>21,36,37</sup> The bulk defects give rise to color centers. Increasing their concentration changes the crystal color from transparent for a perfectly stoichiometric crystal to pale yellow, light blue, dark blue, and finally black, with increasing reduction of the crystal.<sup>21</sup>  $\text{TiO}_{2-x}$  with  $x > 1 \times 10^{-3}$  results in a black crystal with shear plane lattice defects.<sup>28</sup> From two initially perfectly stoichiometric  $\text{TiO}_2$  crystals (MTI Corporation), one was transformed into a low reduction state (LR- $\text{TiO}_2$ ) and the other into a high reduction state (HR- $\text{TiO}_2$ ). The LR- $\text{TiO}_2$  had blue color and was prepared by 8 cycles of  $\text{Ar}^+$  sputtering (1 kV, 1.3  $\mu\text{A}$ , 13 h) and annealing at 900 K for 1 h, while the HR- $\text{TiO}_2$  was black and resulted from a hundred cycles of  $\text{Ar}^+$  sputtering (1 kV, 1.3  $\mu\text{A}$ , 13 h) and annealing at 1100 K for 1 h. The surface reduction states of both crystals have been determined by counting the  $\text{O}_{\text{vac}}$  densities from atomic resolution STM images.

$\text{Pt}_7$  clusters were deposited with a kinetic energy of 7 eV/atom on both crystal surfaces at room temperature with a density of  $2 \times 10^{-2}$  clusters per  $\text{TiO}_2(110)-(1 \times 1)$  unit cell corresponding to a Pt coverage of 5% ML, where 1 ML is defined as the atomic density of Pt(111) ( $1.5 \times 10^{15}$  atoms/ $\text{cm}^2$ ). The  $\text{Pt}_7^+$  current density during deposition was  $1.6 \pm 0.1$  nA/ $\text{cm}^2$  leading to a deposition time of  $18 \pm 1$  min.

The CO oxidation rate has been determined by measuring the  $\text{CO}_2$  signal as a function of sample temperature raised at a rate of 1 K/s from 300 to 600 K. The reactants  $\text{O}_2$  and CO have been pulsed alternately with a delay of 5 s during this temperature ramp.<sup>35</sup> To distinguish the product from  $\text{CO}_2$  in the residual gas, we have dosed  $^{13}\text{C}^{16}\text{O}$  and  $^{18}\text{O}_2$  and detected the yield of  $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ . Each CO pulse corresponds to an exposure of 0.1 Langmuir (L,  $1 \text{ L} = 1.33 \times 10^{-6}$  mbar  $\cdot$  s) and each oxygen pulse to 0.6 L. The CO oxidation activity of the Pt/HR- $\text{TiO}_2$  sample has also been measured by exposing it to a constant  $\text{O}_2$  pressure ( $2.8 \times 10^{-6}$  mbar) and pulsing CO (0.1 L) every 10 s. Thermal desorption spectroscopy (TDS) of CO has been performed after the CO oxidation measurement by exposing the samples to 60 L of CO at 100 K, and subsequently increasing the temperature up to 600 K at a rate of 1 K/s. The atomic scale morphologies of the pristine  $\text{TiO}_2(110)-(1 \times 1)$  surfaces and of the ones with  $\text{Pt}_7$  clusters before and after the reaction have been measured by STM at 80 K. The STM images have been recorded in the constant-current mode; the tunnel voltages given in the figure captions refer to the sample potential. The STM tips have been electrochemically etched from a tungsten wire. The WSxM software<sup>38</sup> has been used to process the STM images.

## 3. RESULTS AND DISCUSSION

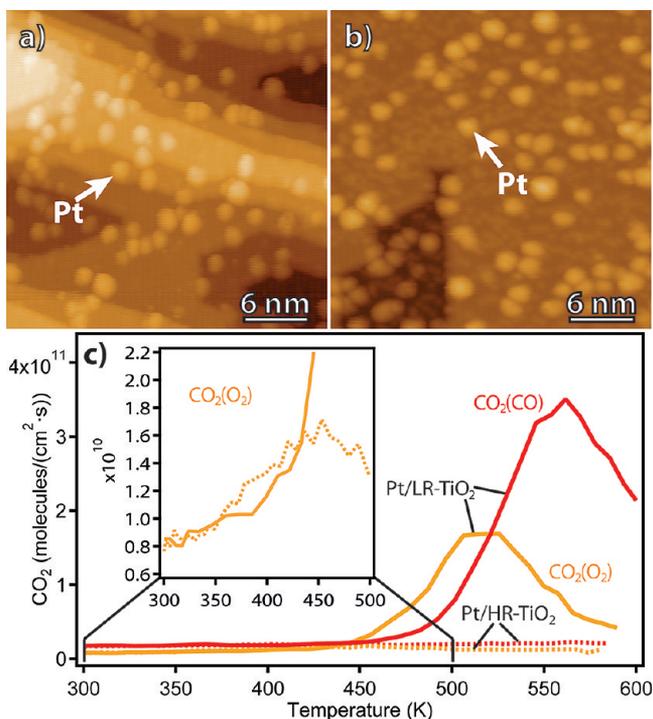
Figure 1(a,b) shows STM images of the clean LR- $\text{TiO}_2(110)-(1 \times 1)$  surface. This surface exhibits small terraces with an average size of 5 nm as determined from large scale images such as Figure S2a in Supporting Information, (SI). The close-up STM image reveals the typical  $\text{TiO}_2(110)-(1 \times 1)$  empty state pattern whose contrast is inverted with respect to the atomic



**Figure 1.** STM images of the clean LR (a,b) and HR (c,d)  $\text{-TiO}_2(110)-(1 \times 1)$  surfaces (+1.5 V, 0.1 nA, 80 K). In (a–d), the color scale has been applied to each terrace in order to enhance the contrast. Inset in (a) shows the same as (a) with a color code revealing the terrace heights. Inset in (b), the height profile along the red arrow indicated in (b) shows the apparent heights of three point defects, two  $\text{O}_{\text{vac}}$  and one OH in between.

structure, i.e., the bright and dark lines are attributed to the  $[001]$ -oriented 5-fold-coordinated titanium atoms and protruding bridging oxygen atoms, respectively.<sup>21</sup> It also reveals the presence of two types of surface point defects,  $\text{O}_{\text{vac}}$  and hydroxyls (OH), which can be discerned by their apparent heights of 0.3 and 0.7 Å, respectively (see the height profile in the inset in (b)). The  $\text{O}_{\text{vac}}$  density on the surface serves as a measure of the reduction state of the crystal,<sup>23</sup> and amounts to 3.4% ML (two OH are considered as one  $\text{O}_{\text{vac}}$ <sup>39–41</sup>), where 1 ML is defined as the density of the  $\text{TiO}_2(110)-(1 \times 1)$  unit cells ( $5.2 \times 10^{14}$   $\text{cm}^{-2}$ ). Comparing this  $\text{O}_{\text{vac}}$  concentration with reported values,<sup>21,36,37,42</sup> we conclude that the crystal is slightly reduced. The STM images of the clean  $(110)-(1 \times 1)$  surface of the HR- $\text{TiO}_2$  are shown in Figure 1(c,d). This surface exhibits much larger terraces (we determine a mean terrace width of 30 nm from Figure S2b of the SI), and a considerably higher  $\text{O}_{\text{vac}}$  concentration of 13.2% ML indicative of a strongly reduced crystal. However, the bulk stoichiometry must be  $\text{TiO}_{2-x}$  with  $x$  below  $10^{-3}$ , since higher reductions are known to give rise to shear planes,<sup>28</sup> which we do not observe in STM.

After deposition of 5% ML  $\text{Pt}_7$  on both LR- and HR- $\text{TiO}_2(110)$  surfaces, randomly distributed clusters are seen in the STM images (Figure 2, parts a and b, respectively). They have an average apparent height of 4 Å, compatible with the apparent height of single-layer Pt clusters on this substrate,<sup>20</sup> and exhibit similar apparent height distributions on both surfaces (see Figure S5 of the SI). In both cases, they are located on the bare terraces as well as at steps, but just because the step density is much higher in the case of the LR- $\text{TiO}_2$ , the cluster abundance at steps is also much higher. As can be seen in Figure 2(a,b), some clusters appear larger and/or higher, which we attribute to the coalescence of two clusters that have



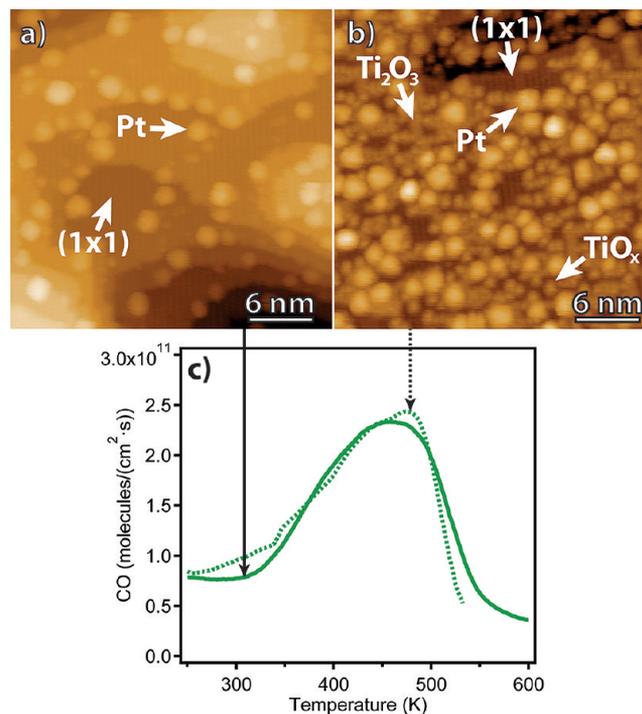
**Figure 2.** STM images after deposition of 5% ML Pt<sub>7</sub> on (a) LR- and (b) HR-TiO<sub>2</sub>(110)-(1 × 1) (+1.5 V, 0.1 nA, 80 K). (c) CO<sub>2</sub> production from Pt<sub>7</sub>/LR-TiO<sub>2</sub> shown as full and from Pt<sub>7</sub>/HR-TiO<sub>2</sub> as dotted line. In both cases, the CO<sub>2</sub> correlated with the CO pulses is shown in red and the one synchronized with the O<sub>2</sub> pulses in orange. The inset displays a zoom of the CO<sub>2</sub>(O<sub>2</sub>) signal from both samples between 300 and 500 K.

been deposited close by. The cluster density measured in STM is comparable with the one determined using the integral of the cluster current during the deposition. Therefore we can conclude that the clusters have a negligible surface diffusion and a mean size of 7 atoms on both TiO<sub>2</sub> crystals. Note that there might well be a small amount of cluster fragmentation which we cannot exclude from the observation of the mean size agreeing with the deposited one.

Figure 2c displays as full lines the CO<sub>2</sub> production from Pt/LR-TiO<sub>2</sub> measured by alternately pulsing CO and O<sub>2</sub>, while the sample is annealed from 300 to 600 K. The CO<sub>2</sub> production synchronized with the CO pulses is displayed in red and labeled CO<sub>2</sub>(CO) and the one synchronized with the O<sub>2</sub> pulses in orange and labeled CO<sub>2</sub>(O<sub>2</sub>) (see Figure S1 of the SI for the individual pulse sequences). At 300 K, we observe no CO<sub>2</sub> production since the Pt clusters are saturated with CO inhibiting O<sub>2</sub> dissociation, which is known as CO poisoning. From 360 K on, CO<sub>2</sub>(O<sub>2</sub>) increases, indicating that CO partially desorbs from the Pt clusters leaving sites for oxygen adsorption, dissociation, and reaction with the remaining CO. The optimum balance for the applied fluxes and time delay between remaining CO and adsorbing oxygen is reached at 520 K, where the maximum of CO<sub>2</sub>(O<sub>2</sub>) is observed. The CO<sub>2</sub>(CO) production starts to increase at 450 K and reaches its maximum at 560 K when oxygen is the dominant species on the Pt clusters so that the supplied CO can react directly with the adsorbed atomic oxygen. The observed reaction rate as function of temperature and reactants is very similar to the one of platinum single crystal surfaces.<sup>43</sup>

In contrast to Pt/LR-TiO<sub>2</sub>, the CO<sub>2</sub> production from Pt/HR-TiO<sub>2</sub> displayed as dotted lines in Figure 2c, red for CO<sub>2</sub>(CO) and orange for CO<sub>2</sub>(O<sub>2</sub>), is almost completely quenched. The inset shows that the CO<sub>2</sub>(O<sub>2</sub>) signal on both samples increases from 360 to 430 K. However, above 430 K the CO<sub>2</sub>(O<sub>2</sub>) production on the HR-TiO<sub>2</sub> surface takes on roughly a constant value, whereas the one on the LR-TiO<sub>2</sub> surface steeply increases. Thus, on the HR-TiO<sub>2</sub> sample the catalytic CO oxidation is quenched by a mechanism activated at 430 K.

After the reaction, the two samples show quite different surface morphologies as can be seen in the STM images of Figure 3(a,b). The surface of the LR-TiO<sub>2</sub> sample exhibits flat



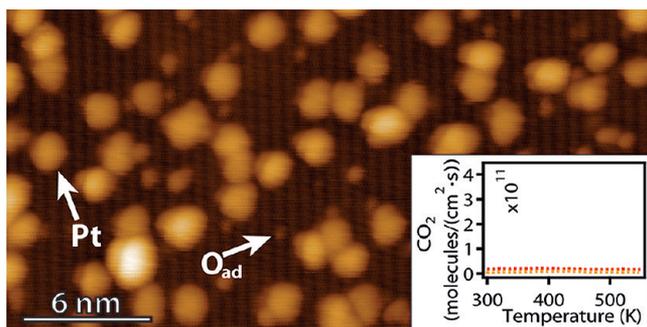
**Figure 3.** STM images after CO oxidation on (a) Pt/LR-TiO<sub>2</sub> and (b) Pt/HR-TiO<sub>2</sub> revealing TiO<sub>x</sub> structures in case (b) (+1.5 V, 0.1 nA, 80 K). (c) TD spectra of CO (after adsorption of 60 L at 100 K) in solid and dotted lines from the samples shown in (a) and (b), respectively.

terraces with Pt clusters, very much as before the reaction; only the mean cluster size has increased from 7 to 10 ± 1 atoms, as inferred from the decrease of cluster density. This coarsening of the clusters is induced by the temperature rise and the exposure to gases.<sup>44,45</sup> The surface of the HR-TiO<sub>2</sub> sample exhibits after the exposure to the reactants and the temperature ramp additional structures with an apparent height of 1.9–3.2 Å coexisting with the Pt clusters appearing 6 Å high. Also on this sample the clusters coarsen; they have an average size of 11 ± 1 atoms after the reaction. We notice that the additional structures also form on the Pt-free HR-TiO<sub>2</sub>(110) after heating to 600 K under O<sub>2</sub> and CO exposure (see Figure S4 of the SI). They are attributed to TiO<sub>x</sub> species similar to those previously observed after exposure of clean reduced TiO<sub>2</sub>(110) surfaces at elevated temperatures to oxygen, due to the oxidation of segregating Ti<sup>3+</sup> interstitials.<sup>27,46</sup> In fact, the Ti<sup>3+</sup> interstitials present in a reduced TiO<sub>2</sub> bulk crystal are mobile above 400 K.<sup>47</sup> Once they reach the subsurface region, they react with any oxygen present at the surface to form a great variety of TiO<sub>x</sub>

structures which are the manifestation of the  $\text{TiO}_2$  reoxidation process.<sup>27,46,47</sup> The fact that the  $\text{TiO}_x$  structures are almost absent on the surface of the LR- $\text{TiO}_2$  sample is attributed to the much lower bulk concentration of  $\text{Ti}^{3+}$  interstitials in this crystal.

In order to investigate whether the Pt clusters are clean or encapsulated by a passivating titania layer,<sup>31–33</sup> we have performed CO TDS measurements on both samples after the reaction. These are displayed in Figure 3c as full and dotted lines, respectively. In both cases, there is a broad peak ranging from  $\sim 350$  to  $\sim 500$  K reminiscent of the desorption of CO from Pt terraces (at  $\sim 400$  K) and steps (at  $\sim 470$  K).<sup>48,49</sup> As expected for our case of small clusters, the CO desorption from low coordinated Pt atoms is found dominant. The two TD spectra of Figure 3c are almost identical revealing that both samples have compatible densities of Pt adsorption sites for CO, which excludes an SMSI state as a reason for the quenching of the catalytic activity on the HR- $\text{TiO}_2$  support.

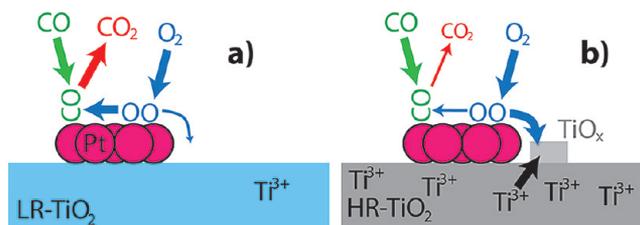
In order to clarify whether the surface  $\text{O}_{\text{vac}}$  are the origin of the absence of catalytic activity of the HR- $\text{TiO}_2$  sample, we have prepared an HR- $\text{TiO}_2$  sample without surface  $\text{O}_{\text{vac}}$ . Exposure of this surface to 50 L of  $\text{O}_2$  at 100 K and subsequent annealing it to 300 K heals the surface  $\text{O}_{\text{vac}}$ .<sup>42</sup> (For an atomic scale image of the resulting surface, see Figure S3 of the SI.) Figure 4 shows this surface after  $\text{Pt}_7$  deposition at 300 K and



**Figure 4.** STM image of 5% ML  $\text{Pt}_7$  on HR- $\text{TiO}_2(110)-(1 \times 1)$  pre-exposed to 50 L of  $\text{O}_2$  at 100 K (+1.5 V, 0.1 nA, 80 K). Inset is the corresponding  $\text{CO}_2$  production displayed with the same color code as in Figure 2c.

reveals that it is still bare of  $\text{O}_{\text{vac}}$ . We find that the  $\text{CO}_2$  production from this sample is negligible (see inset in Figure 4); therefore, the surface  $\text{O}_{\text{vac}}$  are not responsible for the catalytic passivity of the HR- $\text{TiO}_2$ -supported Pt clusters, which has hence to be solely ascribed to bulk defects.

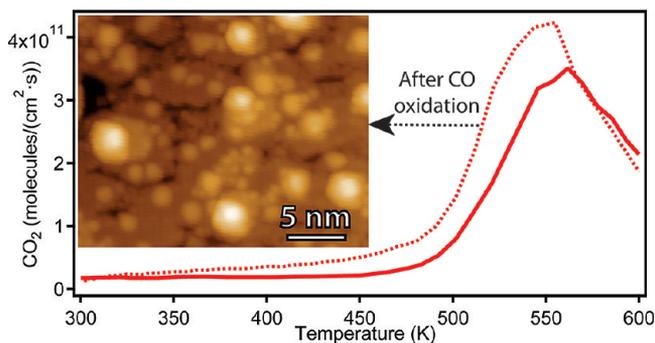
These observations of newly created surface  $\text{TiO}_x$  features, of the cleanliness of the Pt clusters, and of the negligible role of surface  $\text{O}_{\text{vac}}$  suggest the following scenario for the HR- $\text{TiO}_2$  sample. On this sample, the dosed oxygen adsorbed on the Pt clusters is depleted via spillover from the clusters to the support surface where it is consumed by reaction with surface segregating  $\text{Ti}^{3+}$  interstitials (see sketch in Figure 5). Since  $\text{Ti}^{3+}$  interstitials are much more abundant in the HR- $\text{TiO}_2$  subsurface region than in the LR- $\text{TiO}_2$  one, the HR- $\text{TiO}_2$  surface can adsorb much more oxygen than the LR- $\text{TiO}_2$  one.<sup>23,24</sup> This explains why much more  $\text{TiO}_x$  structures are observed after the catalytic CO oxidation on Pt/HR- $\text{TiO}_2$  than on Pt/LR- $\text{TiO}_2$ . The absence of  $\text{CO}_2$  production from Pt/HR- $\text{TiO}_2$  indicates that  $\text{Ti}^{3+}$  interstitials react not only with the oxygen arriving from the gas phase directly at the  $\text{TiO}_2$  surface,



**Figure 5.** Schematic diagram explaining the difference in the catalytic CO oxidation activity between  $\text{Pt}_7/\text{LR-TiO}_2$  and  $\text{Pt}_7/\text{HR-TiO}_2$ . (a) On the LR- $\text{TiO}_2$  sample most of the oxygen remains chemisorbed on the Pt clusters and oxidizes the dosed CO. (b) On the HR- $\text{TiO}_2$  sample oxygen mainly spills over and reacts with  $\text{Ti}^{3+}$  interstitials to form  $\text{TiO}_x$  on the surface, instead of reacting with the dosed CO.

but also with the oxygen adsorbed on the Pt clusters via spillover to the nearby  $\text{TiO}_2$  surface. This reaction is more rapid and energetically more favorable than the CO oxidation since the binding energy of an oxygen atom is higher in  $\text{TiO}$  (6.87 eV<sup>50</sup>) and in  $\text{TiO}_x$  (3.34 eV<sup>36</sup>) than in  $\text{CO}_2$  (2.94 eV<sup>51</sup>). This opens up an effective sink for the adsorbed oxygen which, instead of being consumed by CO to produce  $\text{CO}_2$ , is consumed by  $\text{Ti}^{3+}$  to produce  $\text{TiO}_x$  (Figure 5b). Bennet et al. have observed such an oxygen spillover for larger Pd clusters on strongly reduced  $\text{TiO}_2(110)$  above 550 K,<sup>46</sup> while Kaden et al. have seen no evidence for oxygen spillover up to 500 K for a sample with smaller Pd clusters adsorbed on slightly reduced  $\text{TiO}_2(110)$ .<sup>5</sup> These observations find an explanation in the present results, i.e., oxygen spillover occurs only on strongly reduced  $\text{TiO}_2$  and only above 400 K, where the mobility of  $\text{Ti}^{3+}$  interstitials is activated.

The model schematized in Figure 5 is further corroborated by measuring the  $\text{CO}_2$  production rate from a freshly prepared Pt/HR- $\text{TiO}_2$  sample (as the one in Figure 2b) exposed to a constant  $\text{O}_2$  pressure of  $2.8 \times 10^{-6}$  mbar corresponding to a 30 times higher dose than in the pulsed  $\text{O}_2$  experiments. Now the  $\text{CO}_2$  production at each CO pulse, shown as dotted line in Figure 6, is comparable to the one obtained from Pt/LR- $\text{TiO}_2$



**Figure 6.** Dotted line,  $\text{CO}_2$  production from Pt/HR- $\text{TiO}_2$  obtained by exposing the sample to a constant  $\text{O}_2$  pressure of  $2.8 \times 10^{-6}$  mbar and pulsing CO (0.1 L per pulse). Solid line, the same as in Figure 2c, i.e.,  $\text{CO}_2(\text{CO})$  component of the  $\text{CO}_2$  production from Pt/LR- $\text{TiO}_2$  obtained by alternately pulsing CO (0.1 L) and  $\text{O}_2$  (0.6 L). To facilitate the comparison of the two measurements obtained with different pressure conditions, a  $\text{CO}_2$  background of  $4.9 \times 10^{10}$  molecules/( $\text{cm}^2 \cdot \text{s}$ ) has been subtracted for the dotted line. Inset, STM image of Pt/HR- $\text{TiO}_2$  after the  $\text{CO}_2$  production with the high oxygen exposure (+1.5 V, 0.1 nA, 80 K).

by alternately pulsing CO and  $\text{O}_2$  shown as full line for comparison. Since oxygen is supplied at a much higher rate, the

oxygen spillover mechanism is saturated and the Pt clusters can reach an oxygen coverage comparable to the one of Pt/LR-TiO<sub>2</sub> with 0.6 L O<sub>2</sub> pulses. In addition, this high O<sub>2</sub> exposure of Pt/HR-TiO<sub>2</sub> results in the growth of new complete TiO<sub>2</sub>(110)-(1 × 1) layers beside TiO<sub>x</sub> structures, and finally the coarsening of the Pt clusters is also enhanced, as seen in the STM image of Figure 6.

#### 4. CONCLUSIONS

In summary, we have conducted a systematic UHV study to show the relevance of the bulk reduction state of TiO<sub>2</sub>(110) on the catalytic CO oxidation on supported Pt<sub>7</sub> clusters. We have used two types of TiO<sub>2</sub> supports with low and high reduction (LR, HR) states revealed by their clean (110)-(1 × 1) surfaces containing 3.4% and 13.2% ML O<sub>vac</sub>, respectively. Catalysis measurements performed by alternately pulsing CO and O<sub>2</sub> and simultaneously annealing the sample from 300 to 600 K show that the maximum CO<sub>2</sub> production rate of the Pt clusters is 2 orders of magnitude higher when they are supported on LR- than on HR-TiO<sub>2</sub>. The quenching of the CO<sub>2</sub> production on Pt/HR-TiO<sub>2</sub> is due to the depletion of the dosed oxygen adsorbed on the Pt clusters via spillover to the support and its consumption by reaction with segregating Ti<sup>3+</sup> interstitials. An SMSI state could be excluded and we demonstrated that the role of surface oxygen vacancies is negligible; they only serve as indicator of the bulk reduction state. On the basis of these results, we generally expect that the bulk reduction state of TiO<sub>2</sub> strongly affects the catalytic activity of supported metal clusters in chemical reactions between oxygen and other molecules.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Details of the catalysis measurements and supplementary STM measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

harald.brune@epfl.ch; kamel.ait-mansour@epfl.ch

#### ■ ACKNOWLEDGMENTS

Support from the Swiss National Science Foundation is gratefully acknowledged.

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**Supporting information for:**  
**Effect of the TiO<sub>2</sub> reduction state on the catalytic CO  
oxidation on deposited size-selected Pt clusters**

Simon Bonanni, Kamel Aït-Mansour,\* Wolfgang Harbich, and Harald Brune\*

*Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL),  
CH-1015 Lausanne, Switzerland*

E-mail: harald.brune@epfl.ch; kamel.ait-mansour@epfl.ch

## **Details of the catalysis measurements**

Figure S1 shows the data measured on the Pt/LR-TiO<sub>2</sub> sample from which the CO<sub>2</sub> production curves presented in Figure 2c of the manuscript have been derived. The CO<sub>2</sub> signal exhibits peaks synchronized with the injections of the reactants (CO and O<sub>2</sub>). The inset shows one sequence of reactant and product pressure peaks. The CO<sub>2</sub> peaks synchronized with the O<sub>2</sub> pulses (blue) are labeled CO<sub>2</sub>(O<sub>2</sub>) and shown in orange and those synchronized with the CO pulses (green) are labeled CO<sub>2</sub>(CO) and shown in red. The maxima of the respective peaks are connected with full lines and displayed in Figure 2c. In Figure 6 of the manuscript we performed the reaction with a constant O<sub>2</sub> pressure and CO pulses. In that case there is only one CO<sub>2</sub> curve (red) which is obtained by connecting the CO<sub>2</sub> peaks synchronized with the CO pulses. For further information, the reader can refer to S. Bonanni, et al., Eur. Phys. J. D 63, 241 (2011).

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\*To whom correspondence should be addressed

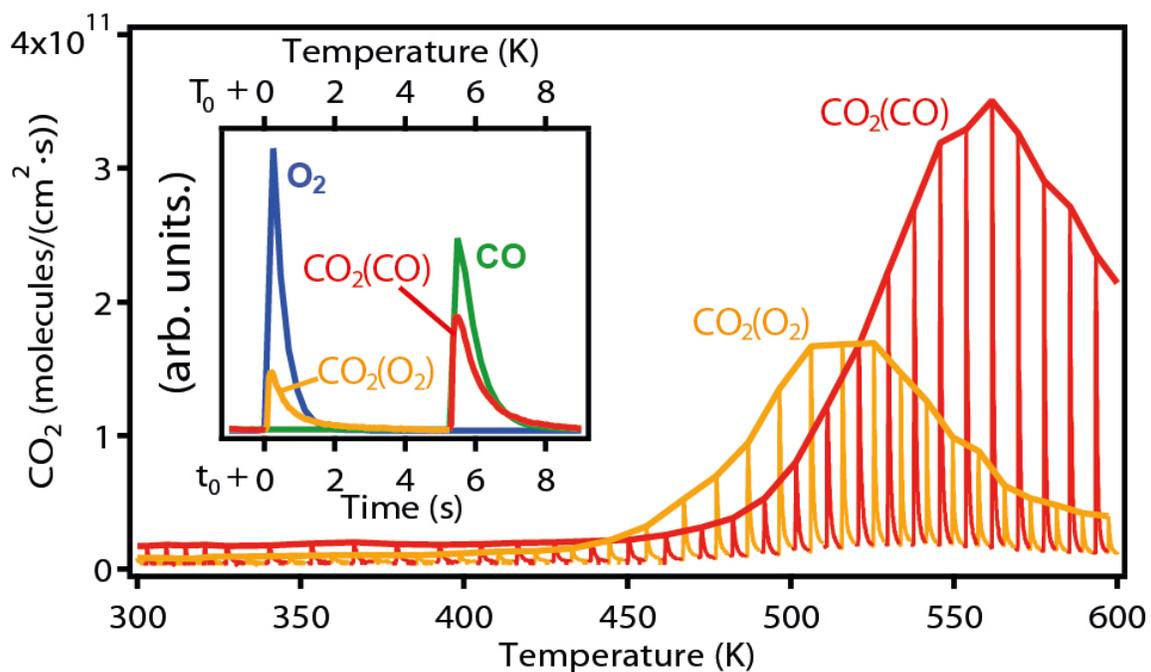


Figure S1: Inset: Single reactant pulse sequence,  $O_2$  blue and CO green, and resulting  $CO_2$  peaks, orange when correlated with  $O_2$  pulse and red when synchronized with CO pulse. Main figure shows individual  $CO_2$  pulses as function of temperature and time (ramp 1 K/s) and their respective peaks connected by curves, such as shown in Figure 2c of the main paper.

## Supplementary STM measurements

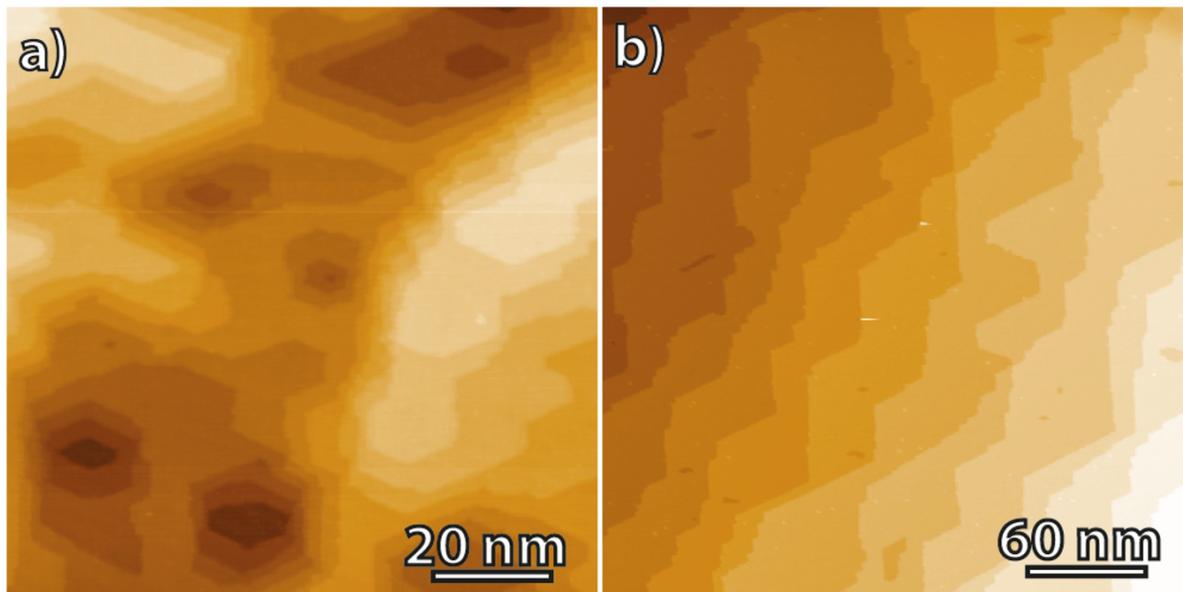


Figure S2: Large scale STM images of the clean (a) LR- and (b) HR-TiO<sub>2</sub>(110)-(1×1) surfaces showing terraces with an average width of 5 and 30 nm, respectively (+1.5V, 0.1 nA, 80 K).

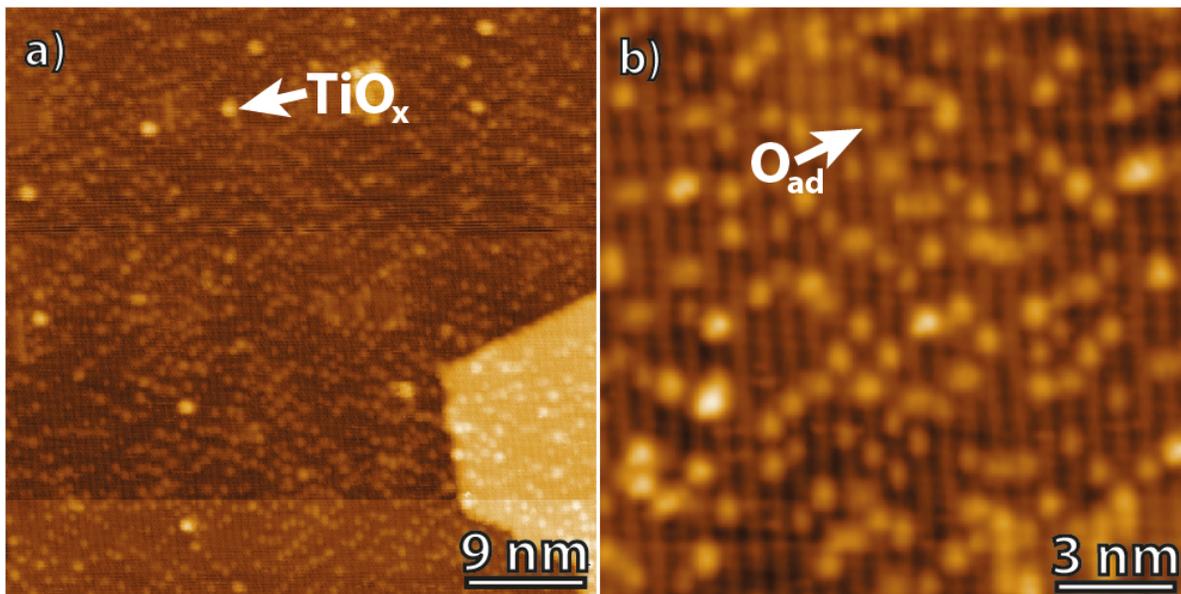


Figure S3: (a,b) Atomic resolution STM images of HR-TiO<sub>2</sub>(110)-(1×1) after oxygen exposure of 50 L at 100 K and annealing to 300 K (+1.5V, 0.1 nA, 80 K). The surface exhibits a coverage of 0.10 ML of oxygen adatoms (*O<sub>ad</sub>*) all of them adsorbed on the Ti rows. The features with the larger apparent height are attributed to TiO<sub>x</sub> nuclei.

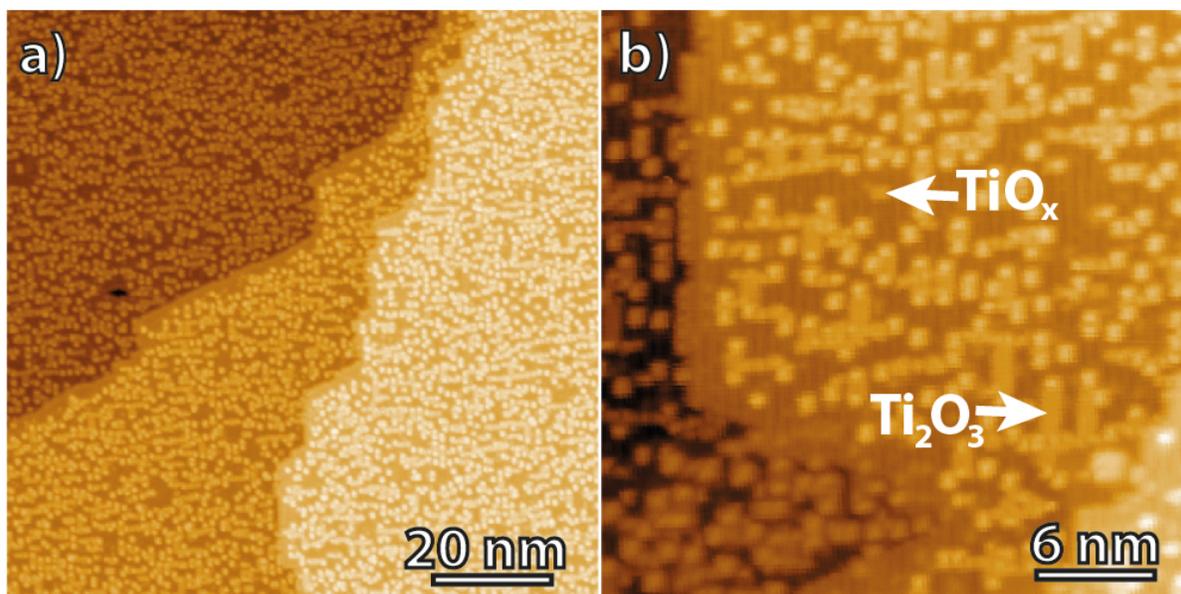


Figure S4: (a,b) STM images of HR-TiO<sub>2</sub>(110)-(1×1) after exposure to alternating CO and O<sub>2</sub> pulses while ramping the temperature from 300 K to 600 K identical to the CO oxidation experiments, however, without Pt clusters on the surface (+1.5V, 0.1 nA, 80 K). TiO<sub>x</sub> (including Ti<sub>2</sub>O<sub>3</sub>) structures analogue to those observed in the presence of Pt clusters (see Figure 3b of the main paper) are formed on the surface due to the reaction of Ti<sup>3+</sup> interstitials with the supplied oxygen.

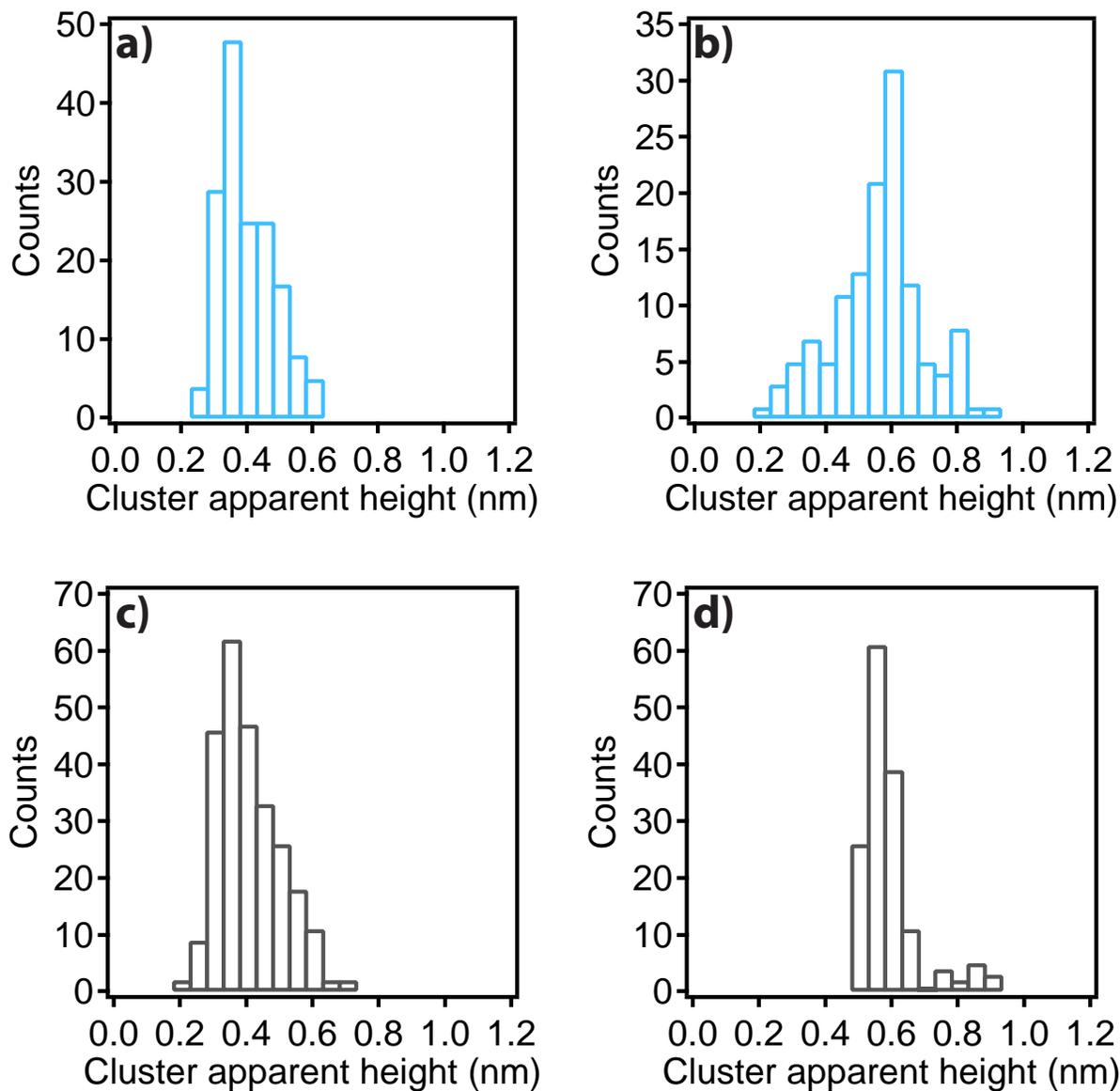


Figure S5: Cluster apparent height histograms before (a) and after (b) the catalytic activity measurement for the Pt/LR-TiO<sub>2</sub> sample and the corresponding histograms for the Pt/HR-TiO<sub>2</sub> sample (c,d). In (d) the clusters having an apparent height below 0.45 nm are not represented because they are hidden by TiO<sub>x</sub>.