

## Adsorption and diffusion of Pt and Au on the stoichiometric and reduced TiO<sub>2</sub> rutile (110) surfaces

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A comparative *ab initio* pseudopotential study of the adsorption and migration profiles of single neutral Pt and Au atoms on the stoichiometric and reduced TiO<sub>2</sub> rutile (110) surfaces is presented. Pt and Au behave similarly with respect to (i) most favorable adsorption sites, (ii) the large increase in their binding energy when the surface is reduced, and (iii) their low migration barrier on the stoichiometric surface. Pt, on the other hand, binds more strongly (by  $\sim 2$  eV) to both surfaces. On the stoichiometric surface, Pt migration pattern is expected to be one dimensional, which is primarily influenced by interactions with O atoms. Au migration is expected to be two dimensional, with Au-Ti interactions playing a more important role. On the reduced surface, the migration barrier of Pt trapped at an O vacancy site is significantly larger compared to that of Au.

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TiO<sub>2</sub> is a widespread catalyst and catalyst support. Because of its fundamental and technological importance, it has been the subject of many experimental and theoretical studies.<sup>1</sup> Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> are two of the most active catalysts for CO oxidation reactions. In extended surfaces, Au is not active, but it turns into a very active catalyst for CO oxidation at low temperatures when highly dispersed on TiO<sub>2</sub> (Refs. 2 and 3). Au/TiO<sub>2</sub>, which is more sensitive to the preparation method than Pt/TiO<sub>2</sub>, presents in some cases a higher activity for heterogeneous CO oxidation.<sup>4</sup> Another fundamentally and technologically important phenomenon which involves the interaction occurring between small metallic particles and TiO<sub>2</sub> surfaces is that of the strong-metal-support interaction (SMSI) (Ref. 5). The SMSI can induce drastic changes in the performance of the catalyst, such as suppression of CO and H<sub>2</sub> chemisorption, and has significant effects on structure-sensitive reactions. Pt/TiO<sub>2</sub> has been the prototype system for SMSI, while Au/TiO<sub>2</sub> does not undergo significant encapsulation under equivalent annealing conditions.<sup>6</sup>

Most of the theoretical work on metal-TiO<sub>2</sub> surface interactions has focused on the Au/TiO<sub>2</sub> interface.<sup>7-16</sup> On the other hand, in spite of being the prototype SMSI system, only three self-consistent-field calculations have been performed for a single Pt atom on TiO<sub>2</sub>, which are also limited due to the small system size and absence of full atomic relaxations.<sup>13,17,18</sup> Furthermore, all studies on Au and Pt/TiO<sub>2</sub> have considered the adsorption of single- or a few-atom metal clusters on some specific sites of the TiO<sub>2</sub> surface. While these studies have provided important information on the structural energetics of a metal/support system, a microscopic understanding of the interaction occurring between the metal particles and the TiO<sub>2</sub> surface also requires calculations for their surface diffusion profiles. Knowledge of the surface diffusion profiles is important in understanding

the growth mode and evolution of the metal particles on these surfaces, as the catalytic activity of Au, for example, was shown to be particularly structure sensitive.<sup>3,4,16,19</sup> The significant differences in the energy barriers between Pt and Au could also help achieve a microscopic understanding for the occurrence of SMSI in the case of Pt but not for Au. Motivated by these observations, in this work we present comparative *ab initio* calculations for the adsorption and diffusion of these two precious metals on the stoichiometric and reduced TiO<sub>2</sub> (110) surfaces.

Our calculations for neutral Pt and Au atoms on the TiO<sub>2</sub> (110) surface were performed using the *ab initio* pseudopotential total-energy method.<sup>20</sup> We used ultrasoft pseudopotentials with a cutoff energy of 300 eV,  $1 \times 2 \times 2$  Monkhorst-Pack  $k$ -point grids, and Perdew and Wang parametrization of the generalized gradient approximation (GGA) (Ref. 21). Increasing the cutoff energy to 400 eV and the  $k$ -point grid to  $2 \times 4 \times 4$  had no appreciable effect on the results. While the binding energies are influenced by the choice of the exchange-correlation functional<sup>22</sup> (for example, there is evidence that the revised Perdew-Burke-Ernzerhof functional gives more accurate binding energies), the central issue in this paper is that of relative energy differences, which are likely to remain unchanged.<sup>23</sup> We made an extensive study of the spin-polarization effects and found them to be negligible for the Pt/TiO<sub>2</sub> system. For the Au/TiO<sub>2</sub> system, including spin polarization reduced the magnitude of the binding energies at different selected sites by a maximum amount of  $\sim 0.13$  eV. However, the changes in the relative energies between different sites were negligible (within 0.05 eV). Hence, the calculations for migration energy profiles were performed without spin polarization.

The surface was modeled with a four-layer slab geometry (4 O-TiO<sub>2</sub>-O units, hence 12 atomic layers), in which the two bottom layers were kept at bulk positions, and a 12-Å

TABLE I. The relative energies (in eV) for Pt (the first three columns) and Au adsorption (the last two columns) above the given specific sites with respect to the most stable (*H1*) site for the stoichiometric  $\text{TiO}_2$  (110) surface as a function of the surface cell size and the number of layers.

Adsorption site	$\Delta E$ (Pt)			$\Delta E$ (Au)	
	$2 \times 1$		$3 \times 2$	$2 \times 1$	$3 \times 2$
	Four layer	Seven layer	Four layer	Four layer	Four layer
Hollow site ( <i>H1</i> )	0.0	0.0	0.0	0.0	0.0
Basal oxygen	0.11	0.12	0.19	0.27	0.29
Hollow site ( <i>H2</i> )	0.13	0.14	0.21	0.20	0.22
Between bridging O ( <i>Ti6c</i> )	0.26	0.24	0.33	0.34	0.32
Bridging oxygen ( <i>O1</i> )	0.70	0.69	0.78	0.17	0.15
Fivefold Ti ( <i>Ti5c</i> )	0.95	0.94	0.98	0.10	0.11

vacuum region. For calculating diffusion profiles of Pt and Au,  $2 \times 1$  (stoichiometric) and  $3 \times 1$  (reduced) surface unit cells were used. To arrive at these model system sizes, we performed extensive convergence tests on larger systems. For example, although even/odd oscillations are observed for many important physical properties of the  $\text{TiO}_2$  (110) surface,<sup>24</sup> the binding energy (BE) of Pt at various sites calculated with the four-layer slab used in the diffusion profiles and a seven-layer slab were found to differ by less than 0.02 eV. We also tested the convergence of surface unit-cell size up to  $3 \times 2$  cells (stoichiometric) and  $4 \times 2$  cells (reduced). Tests performed on several points of the stoichiometric surface with  $3 \times 2$  and  $2 \times 1$  cells revealed a maximum difference (in relative BE) of 0.08 eV for Pt and 0.03 eV for Au. Tests on the reduced surface with  $4 \times 2$  versus  $3 \times 1$  cells resulted in a similar finding with relative BE differing by not more than 0.15 eV for Pt and 0.1 eV for Au. It is important to note that while the absolute values of the BE in some cases change by as much as 0.25 eV upon employing larger surface cells, the energy differences (relevant for diffusion profiles) are much less sensitive to this, converged to  $\sim 0.1$  eV. In addition, as will be shown below, the potential-energy profiles for Pt and Au present significant differences (much larger than 0.1 eV), making it possible for a meaningful cross comparison with the use of  $2 \times 1$  and  $3 \times 1$  surface unit cells. Results from the convergence tests on the stoichiometric surface are displayed in Table I.

We first investigate the binding of a metal atom to the stoichiometric  $\text{TiO}_2$  rutile (110) surface. The various possible sites of adsorption are shown in Fig. 1(a). We find the most favorable position for Pt adsorption as the hollow site *H1* [Fig. 1(b)]. The calculated BE of a Pt atom on the hollow site is 2.51 eV (2.62 eV for  $3 \times 2$  cell). As shown in Table I, the least favorable position for Pt adsorption, by  $\sim 1$  eV compared to *H1*, is the *Ti5c* site. This finding is in contrast with an interpretation from an experimental study,<sup>25</sup> which suggests that Pt atoms at low coverages adsorb preferentially at the *Ti5c* site. However, the experimental study considered only two possible positions based on key assumptions of

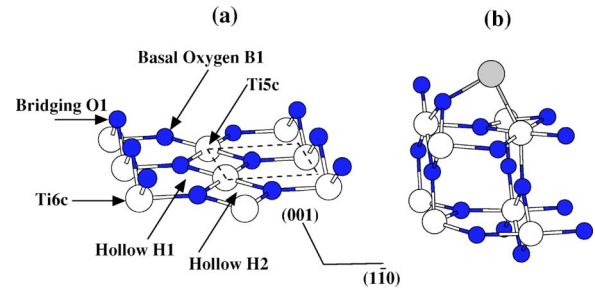


FIG. 1. (Color online) (a) An oblique view of an extended  $\text{TiO}_2$  (110) surface showing the possible sites for metal adsorption above them (listed in Table I). The white and black circles represent Ti and O atoms, respectively. The dashed rectangle shows the region for which the diffusion profiles are plotted in Figs. 2 and 3. (b) Top two-layer view of  $\text{TiO}_2$  (110) surface with a Pt atom (gray circle) adsorbed at the hollow site.

hard-sphere atoms with van der Waals-type interactions. Furthermore, the ratio of the attenuated core-level photoemission intensities of the *Ti5c* atom and in-plane surface O atom, which was used to assign the preferential adsorption on the *Ti5c* site, is *not* inconsistent with our finding of the hollow site as the most favorable site. This is because Pt at *H1* is slightly tilted with respect to its relaxed position directly over the *Ti5c* site [Fig. 1(b)]. Pt creates considerable distortions (though localized mostly to two layers, as found by employing a larger number of layers). For example, in the presence of Pt on the surface, the distance between the bridging oxygen *O1* and the sixfold-coordinated Ti (*Ti6c*) increases to 1.98 Å from its bare surface value of 1.84 Å, as Pt pulls the bridging oxygen significantly toward it at the expense of increasing the surface *Ti6c*-*O1* distance.

The most favorable site for Au adsorption on the stoichiometric surface is also the hollow site *H1*. However, the calculated BE of 0.58 eV (0.60 eV for  $3 \times 2$  cell) is lower by almost 2 eV compared to Pt. This result is in very good agreement with previous calculations,<sup>11,15</sup> which yield BE  $\sim 0.6$  eV. The surface *Ti6c*-*O1* distance, in the presence of Au, is 1.89 Å, only slightly larger than the bare surface value. This means that, in comparison to Pt, Au atoms do not perturb the stoichiometric  $\text{TiO}_2$  (110) surface significantly. The relative stability of various sites for Au adsorption is also different compared to Pt. In particular, the *Ti5c* site (the least favorable site for Pt adsorption) is only 0.1 eV higher in energy compared to *H1*.

In order to achieve a better understanding of the similarities and the differences between Pt and Au adsorption, and to gain insight into the energetics of their diffusion, we calculated the full migration energy profiles of the two metals. On the stoichiometric surface, a rectangular region of dimensions  $c/2$  (along [001]) and  $a/\sqrt{2}$  (along  $[1\bar{1}0]$ ) was divided into a  $4 \times 5$  uniform grid. The metal atom placed at each grid point was allowed to relax only in the direction perpendicular to the surface, along with the Ti and O atoms in the top two layers. The results interpolated to a finer ( $30 \times 30$ ) grid are displayed in Figs. 2(a) and 2(b) for Pt and Au, respectively. For Pt, the energy surface is quite corrugated with a large variation of  $\sim 1$  eV across the entire grid. The barrier to

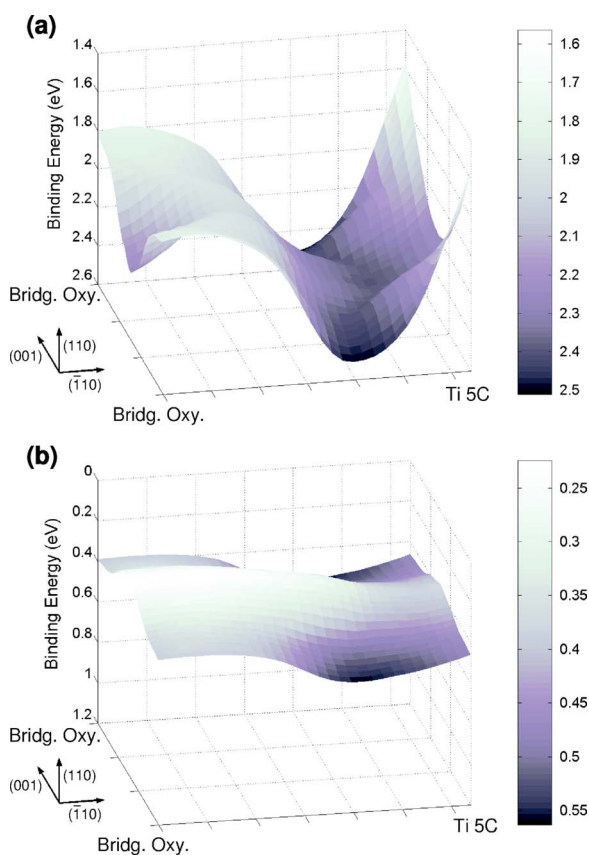


FIG. 2. (Color online) The potential-energy profiles for (a) Pt and (b) Au on the stoichiometric  $\text{TiO}_2$  (110) surface. See Fig. 1 for the atomic structure of the chosen region. The profiles were doubled along the [001] direction (compared to the chosen rectangular grid mentioned in the text) to have the same size as the profiles in the next figure.

migration along the  $[1\bar{1}0]$  direction is 0.95 eV, which is expected to make Pt migration in this direction unlikely, except at high temperatures. In the perpendicular [001] direction, on the other hand, Pt diffusion has a very small barrier of 0.13 eV. From the large difference in the barriers along the  $[1\bar{1}0]$  and [001] directions, we therefore conclude that Pt migration on the stoichiometric  $\text{TiO}_2$  (110) will be strongly one dimensional. The importance of the Pt-O bond in this migration pattern is evident, as Pt can diffuse between hollow sites along the [001] direction easily by bonding to bridging oxygen (at  $H1$ ) and to the basal oxygen at favorable Pt-O distances near 2.01 Å as observed in PtO and  $\text{Pt}_3\text{O}_4$  compounds. This suggests that the structural energetics of Pt on the stoichiometric  $\text{TiO}_2$  (110) surface is primarily influenced by the interaction of the  $p$  bands of the oxygen and the  $d$  orbitals of Pt. The theoretical finding of an easy channel for Pt diffusion is also in good agreement with a scanning tunnel microscopy study of Pt/ $\text{TiO}_2$  (Ref. 26), which suggests that [001] is the preferred orientation for Pt diffusion, based on the elongated shapes of the Pt clusters on  $\text{TiO}_2$  (110).

In contrast to Pt, the potential-energy profile for Au migration [Fig. 2(b)] is quite flat, with energy barriers along any direction not exceeding 0.35 eV, which suggests a two-

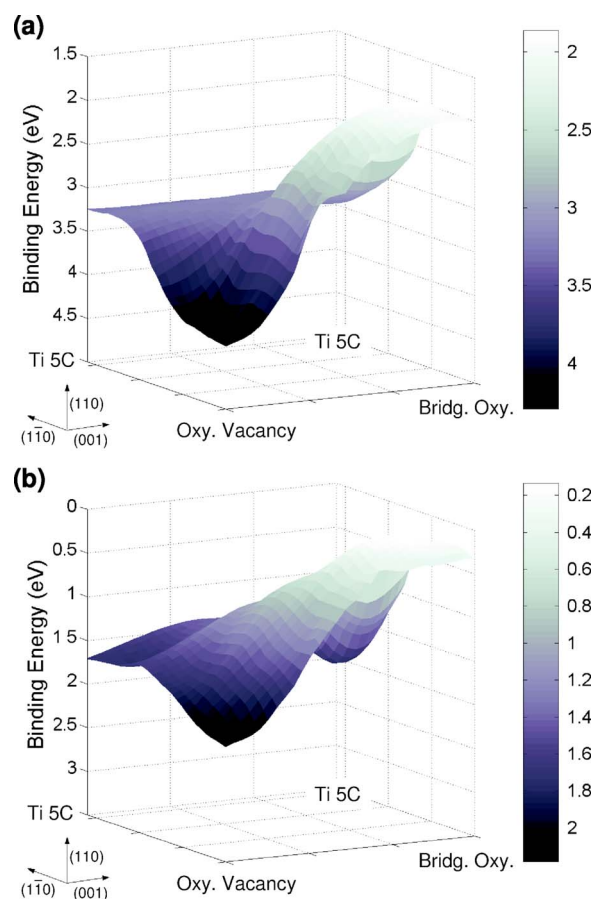


FIG. 3. (Color online) The potential-energy profiles for (a) Pt and (b) Au on the reduced  $\text{TiO}_2$  (110) surface. See Fig. 1 for the atomic structure of the chosen region.

dimensional migration pattern. The calculated barriers of 0.17 and 0.2 eV along  $[1\bar{1}0]$  and  $[110]$ , respectively, indicate that Au can diffuse rather easily on the stoichiometric surface, and could also explain the wide variation in the minimum-energy positions of Au on  $\text{TiO}_2$  (110) reported in the literature.<sup>7</sup> The theoretical values obtained here are also in good agreement with the experimental observation of easy Au diffusion on the oxide surface even at 140 K, as well as the estimates for the BE of 0.5 eV and its small migration barrier of 0.07 eV (Ref. 27). Since Au has a complete  $d$  shell, we expect that the  $p$ - $d$  hybridization will not play as significant a role as in Pt/ $\text{TiO}_2$ . Indeed, the migration profile of Au can be qualitatively understood by considering the Au-Ti bond. The Au-Ti distance at the (lowest energy)  $H1$  site is 2.85 Å, the same as in the AuTi compound. At the  $\text{Ti}5c$  position (which is only 0.1 eV higher compared to  $H1$ ), the Au-Ti distance is 2.78 Å, only slightly shorter than this value. However, as Au gets farther away from Ti, and closer to surface oxygen, the potential-energy profile indicates higher (albeit still less than 0.35 eV) barriers. These observations suggest that the structural energetics of a gold atom is primarily influenced by the interaction of the Au  $s$  orbitals with the Ti  $d$  band.

In spite of the significant differences between the migration profiles of the two metals on the stoichiometric surface,



they both have a small minimum-energy barrier near 0.15 eV. We now move to the reduced surface (with a missing bridging oxygen), where this picture changes considerably. For both Pt and Au, the most favorable adsorption site is the substitutional one (the site of the O vacancy). The binding energies at this site are significantly larger compared to the stoichiometric surface; 4.28 eV for Pt (4.03 eV for the  $4 \times 2$  cell) and 2.18 eV for Au (2.03 eV for the  $4 \times 2$  cell). As in the stoichiometric surface, Pt sits closer to the surface and distorts the underlying lattice more significantly. We calculated the full migration barrier profile of the two metal atoms on the reduced surface. For this case, we chose a rectangular region of dimensions  $c$  (along  $[001]$ ) and  $a/\sqrt{2}$  (along  $[\bar{1}\bar{1}0]$ ) with the substitutional site at one of the corners. As shown in Fig. 3, both metals show a strong preference for adsorption on the substitutional site with similar potential-energy profiles both along the  $[001]$  and  $[\bar{1}\bar{1}0]$  directions. The migration barriers for both metals along the  $[001]$  direction are rather high; 2.3 eV for Pt (2.1 eV with a  $4 \times 2$  cell) and 1.85 eV for Au (1.75 eV with a  $4 \times 2$  cell). This is in contrast to the stoichiometric surface where the  $[001]$  direction has a small energy barrier. The smallest migration barrier on the reduced surface occurs along the  $[\bar{1}\bar{1}0]$  direction, from the substitutional site toward the Ti5c position. In fact, this is where the main difference between Au and Pt is observed. Although the migration barrier for Pt along this direction is still high (1.1 eV for  $3 \times 1$  and 0.95 eV for  $4 \times 2$  cells), the barrier for Au is much smaller (0.6 eV for  $3 \times 1$  and 0.52 eV for  $4 \times 2$  cells). This implies that while O vacancies act as anchoring sites for metal adsorption on the reduced surface, Au is much more likely to

escape from the relatively shallower potential well created by the vacancy compared to Pt, which gets trapped at this site. In addition, Fig. 3(b) shows that in the case of Au, there exists an extra minimum in the potential-energy profile near the diagonal Ti5c site. The energy of this site is only 0.3 eV higher than that of the substitutional site. The existence of this extra minimum at about the same location as the hollow site of the stoichiometric surface shows that the effect of the vacancy for the Au/TiO<sub>2</sub> system is more localized than that for the Pt/TiO<sub>2</sub> system.

In conclusion, we have shown that on the stoichiometric surface, Pt displays a one-dimensional migration pattern on a highly corrugated potential-energy profile, and Au migration is two dimensional with a relatively flat profile. The structural energetics of Pt and Au are primarily influenced by their interactions with O and Ti, respectively. The distortions of the TiO<sub>2</sub> support due to a single-atom adsorbate are much more pronounced for Pt than Au. On the reduced surface, while both Pt and Au are anchored at the substitutional site, Pt binding to O vacancies is considerably stronger compared to Au. From these two observations, we can already infer even at a single-atom level the predisposition of Pt/TiO<sub>2</sub> rather than Au/TiO<sub>2</sub> to undergo encapsulation, which is evidence of SMSI. These findings could also provide a hint for the higher sensitivity of Au catalytic activity to the preparation methods, as Au atom binding to the oxide surface is not only weak but also rather site insensitive (flat profile), making its activity more vulnerable to external effects.

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- <sup>1</sup>For an excellent review, see U. Diebold, *Surf. Sci. Rep.* **48**, 53 (2003), and references therein.
- <sup>2</sup>M. Haruta, *Catal. Today* **36**, 53 (1997).
- <sup>3</sup>M. Valden, X. Lai, and D. W. Goodman, *Science* **281**, 1647 (1998).
- <sup>4</sup>G. R. Bamwenda *et al.*, *Catal. Lett.* **44**, 83 (1997).
- <sup>5</sup>S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.* **100**, 170 (1978).
- <sup>6</sup>L. Zhang, R. Persaud, and T. E. Madey, *Phys. Rev. B* **56**, 10549 (1997).
- <sup>7</sup>N. Lopez and J. K. Nørskov, *Surf. Sci.* **515**, 175 (2002).
- <sup>8</sup>E. Wahlström *et al.*, *Phys. Rev. Lett.* **90**, 026101 (2003).
- <sup>9</sup>A. Vittadini and A. Selloni, *J. Chem. Phys.* **117**, 353 (2002).
- <sup>10</sup>Z. Yang, R. Wu, and D. W. Goodman, *Phys. Rev. B* **61**, 14066 (2000).
- <sup>11</sup>Y. Wang and G. S. Hwang, *Surf. Sci.* **542**, 72 (2003).
- <sup>12</sup>L. Giordano, G. Pacchioni, T. Bredow, and J. F. Sanz, *Surf. Sci.* **471**, 21 (2001).
- <sup>13</sup>L. Thiên-Nga and A. T. Paxton, *Phys. Rev. B* **58**, 13233 (1998).
- <sup>14</sup>K. Okazaki, Y. Morikawa, S. Tanaka, K. Tanaka, and M. Kohyama, *Phys. Rev. B* **69**, 235404 (2004).
- <sup>15</sup>A. Vijay, G. Mills, and H. Metiu, *J. Chem. Phys.* **118**, 6536 (2003).
- <sup>16</sup>M. Mavrikakis, P. Stoltze, and J. K. Nørskov, *Catal. Lett.* **64**, 101 (2000).
- <sup>17</sup>J. A. Horsley, *J. Am. Chem. Soc.* **101**, 2870 (1979).
- <sup>18</sup>X. Wei-xing, K. D. Schierbaum, and W. Goepel, *J. Solid State Chem.* **119**, 237 (1995).
- <sup>19</sup>Y. Xu and M. Mavrikakis, *J. Phys. Chem. B* **107**, 9298 (2003).
- <sup>20</sup>G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- <sup>21</sup>J. P. Perdew *et al.*, *Phys. Rev. B* **46**, 6671 (1992).
- <sup>22</sup>N. Lopez, F. Illas, N. Rösch, and G. Pacchioni, *J. Chem. Phys.* **110**, 4873 (1999).
- <sup>23</sup>B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999), and references therein. Table III of this reference indicates that while the magnitudes of binding energies calculated with PW91 and RPBE functionals differ by  $\sim 0.5$ – $0.6$  eV, the binding-energy differences of a given species between different surfaces are within 0.1 eV of each other.
- <sup>24</sup>S. P. Bates, G. Kresse, and M. J. Gillan, *Surf. Sci.* **385**, 386 (1997); M. Ramamoorthy, R. D. King-Smith, and D. Vanderbilt, *Phys. Rev. B* **49**, 7709 (1994); T. Bredow, L. Giordano, F. Cinquini, and G. Pacchioni, *ibid.* **70**, 035419 (2004).
- <sup>25</sup>K. D. Schierbaum, S. Fischer, M. C. Torquemada, J. L. de Segovia, E. Román, and J. A. Martín-Gago, *Surf. Sci.* **345**, 261 (1996).
- <sup>26</sup>O. Dulub, W. Hebenstreit, and U. Diebold, *Phys. Rev. Lett.* **84**, 3646 (2000).
- <sup>27</sup>S. C. Parker, A. W. Grant, V. A. Bondzie, and C. T. Campbell, *Surf. Sci.* **441**, 10 (1999); C. T. Campbell, S. C. Parker, and D. E. Starr, *Science* **298**, 811 (2002).