

# Nature of reactive O<sub>2</sub> and slow CO<sub>2</sub> evolution kinetics in CO oxidation by TiO<sub>2</sub> supported Au cluster

Raj Ganesh S. Pala and Feng Liu<sup>a1</sup>

Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

(Received 28 November 2005; accepted 22 August 2006; published online 12 October 2006)

Recent experiments on CO oxidation reaction using seven-atom Au clusters deposited on TiO<sub>2</sub> surface correlate CO<sub>2</sub> formation with oxygen associated with Au clusters. We perform first principles calculations using a seven-atom Au cluster supported on a reduced TiO<sub>2</sub> surface to explore potential candidates for the form of reactive oxygen. These calculations suggest a thermodynamically favorable path for O<sub>2</sub> diffusion along the surface Ti row, resulting in its dissociated state bound to Au cluster and TiO<sub>2</sub> surface. CO can approach along the same path and react with the O<sub>2</sub> so dissociated to form CO<sub>2</sub>. The origin of the slow kinetic evolution of products observed in experiments is also investigated and is attributed to the strong binding of CO<sub>2</sub> simultaneously to the Au cluster and the surface. © 2006 American Institute of Physics. [DOI: 10.1063/1.2355670]

## I. INTRODUCTION

Understanding the catalytic behavior of Au particles supported on TiO<sub>2</sub> has become a major area of experimental and computational research in surface science approach to heterogeneous catalysis.<sup>1-3</sup> The system is particularly interesting as the Au bulk and surfaces are inert<sup>4</sup> and the catalytic properties emerge at the nanoscale, a theme that is central to the science of nanotechnology. In comparison with the transition metals, the relative inertness of Au bulk and surfaces can be rationalized by the relatively high cohesive energy of Au bulk and the filling of the antibonding states during surface adsorption.<sup>4</sup>

The catalytic behavior of Au nanoparticles can be loosely classified into three regimes and it is possible that more than one mechanism may act together in different regimes. The first regime has the largest number of Au atoms in the spherical oxide supported Au nanoparticles which are prepared from the liquid phase.<sup>1-3</sup> This regime is most relevant to industrial catalysis but the preparation method employed offers little chemical and morphological control at the atomistic level of the putative catalytically active centers.<sup>1-3</sup> Even though the overall morphology of particles prepared from different methods may be similar, it is difficult to quantitatively assess the role played by different mechanisms. Different mechanisms have been considered including increased undercoordination of the nanoparticle<sup>5-7</sup> due to increased surface-to-volume ratio and the effect of the support.<sup>1,8,9</sup> Traditionally, the nature of support has been differentiated under two categories, reducible (catalytically active) and irreducible (inactive),<sup>3</sup> but this classification has been questioned by recent experiments.<sup>10</sup>

The second regime is the planar oxide supported Au films that are vapor deposited on to an oxide surface.<sup>11,12</sup> The films may grow via Volmer-Weber or Stranski-Krastanov

mode and the extent of control on the film thickness and particle size is determined by self-assembly characteristics of the metal particle and the oxide interface.<sup>13</sup> This regime gives a better chemical control compared to the first regime, although some contaminants such as hydroxyl groups cannot be easily removed even in high vacuum conditions.<sup>14</sup> One main mechanism that may contribute here is the quantum size effect,<sup>11,12</sup> whereby a bilayer Au film has been suggested to be most active. Other effects such as undercoordination<sup>1,5,6,8,15-17</sup> and strain<sup>17,18</sup> may also play a role.

The third regime is comprised of very small nonmetallic particles, resulting from the effort to decrease coverage so as to reduce cost and enhance performance.<sup>19-21</sup> In this regime, the catalytic activity seems to persist even when the particle contains as few as one to ten atoms depending on the metal investigated.<sup>19-21</sup> A useful experimental method for analyzing such small nonmetallic particles is by depositing size selected metal clusters on the oxide support, a technique pioneered by Heiz and co-workers.<sup>22</sup> This method has been extended to the Au-TiO<sub>2</sub> system by Anderson and co-workers<sup>21,23,24</sup> and by Tong *et al.*,<sup>25</sup> which showed the Au clusters to exhibit strong size-dependent catalytic properties.<sup>21,23,24</sup> The main focus towards the underlying mechanisms in this regime is on the undercoordination in the cluster,<sup>26</sup> nature of the defects,<sup>6,27,28</sup> cluster charge,<sup>15,27,29</sup> cluster fluxionality,<sup>30</sup> and role played by the support.<sup>7</sup>

The present computational study is concerned with the analysis of the experiments performed in the third regime. Previous computational studies have focused on establishing the role of defects and cluster charge,<sup>20</sup> nonmetallic to metallic transition of the cluster,<sup>31</sup> cluster fluxionality<sup>30</sup> and undercoordination,<sup>6,7</sup> support effects,<sup>32</sup> and presence of more than one channel for the reaction.<sup>32</sup> As the Au particle size is the smallest in this regime making it very fluxional, it is most likely that more than one mechanism may play a role in catalysis. Moreover, due to the small particle size, the dis-

<sup>a1</sup>Electronic mail: [fliu@eng.utah.edu](mailto:fliu@eng.utah.edu)

tion between active site arising due to fluxionality, Au/oxide interface, and cluster undercoordination/steps is harder to make. Here, we investigate two aspects of experiments performed using size selected Au clusters containing seven Au atoms that show the highest catalytic activity for CO<sub>2</sub> oxidation reaction, among the clusters deposited.<sup>21,23,24</sup> In contrast to the previous experiments which used atomic oxygen,<sup>33</sup> these experiments used molecular oxygen and yet observed the formation of CO<sub>2</sub>. These experimental studies suggest that the source of all the oxygen contributing to the formation of CO<sub>2</sub> originates from a form of reactive oxygen associated with the Au clusters after the molecular oxygen exposure.<sup>21,23,24</sup> Furthermore, the nature of different modes of activated oxygen is of general interest in Au catalysis.<sup>34</sup> Therefore, as the first objective, we explore a possible candidate for the reactive form of oxygen indicated by these new experiments.<sup>21,24</sup> Another intriguing feature of the experimental results is that the active Au clusters show a 300 ms delay in CO<sub>2</sub> evolution.<sup>21,24</sup> Different factors that may contribute towards such a delay have been previously hypothesized.<sup>24</sup> Here, as the second objective, we investigate computationally the possible origin behind the slow product evolution kinetics observed in these experiments.<sup>21,24</sup>

The present study suggests that there exists a thermodynamically favorable diffusion-reaction path for O<sub>2</sub> to approach the seven-atom Au cluster (Au<sub>7</sub>) along the surface Ti row leading to a dissociated state of oxygen. The O<sub>2</sub> so dissociated has one oxygen atom in between the cluster and surface, bonding simultaneously to one Au atom in the cluster and one surface Ti atom, and the other oxygen atom above the cluster, bonding to the same Au atom in the cluster. As the dissociated O<sub>2</sub> is anchored to the cluster, CO can approach the O<sub>2</sub>-cluster complex along the same surface Ti row, leading to a thermodynamically favorable reaction path for CO<sub>2</sub> formation. The present results may have wider applicability in the context of interpreting other experiments that also observe formation of CO<sub>2</sub> via oxidized Au intermediate even when molecular oxygen is employed.<sup>35</sup> Moreover, the CO<sub>2</sub> so formed is found to have a binding affinity of 0.73 eV to the Au cluster, which may be responsible for the experimentally observed 300 ms delay in CO<sub>2</sub> evolution.

## II. COMPUTATIONAL METHODOLOGY AND ATOMISTIC MODEL OF THE SYSTEM

The calculations are performed using the pseudopotential<sup>36</sup> plane-wave total energy method,<sup>37</sup> as being commonly used for surface adsorption and surface cluster calculations. All atoms were allowed to relax in all the calculations. Exchange-correlation energy was calculated using the PW-91 generalized gradient approximation (GGA) functional.<sup>38</sup> The relaxation of electronic degrees of freedom was converged to within 10<sup>-4</sup> eV per supercell and the ionic positions were optimized with the energy-convergence criterion of 10<sup>-3</sup> eV of the total energy of the system. Test calculations carried out using Perdew-Burke-Ernzerhof (PBE) functional<sup>39</sup> did not affect the general conclusions. Spin polarization effects were also tested and did not contribute appreciably to total energies. Results for the bulk and smaller

surface unit cells were benchmarked with a previous study.<sup>40</sup> The bulk lattice parameters obtained in the present study is  $a=4.649$  Å with  $c/a=0.64$ , in good agreement with those obtained in previous experimental and computational studies.<sup>40,41</sup> The formation enthalpy obtained in the present study is  $-10.29$  eV, which is in reasonable agreement with the experimental value of  $-9.78$  eV.<sup>42</sup>

The characteristic structural features of the TiO<sub>2</sub> (110) surface are the “bridging” oxygen atoms that are twofold coordinated to the titanium atoms. There are two types of surface titanium atoms—fivefold coordinated (5-c) and sixfold coordinated (6-c). The twofold coordinated bridging oxygen atoms and the 5-c Ti atoms are more undercoordinated than other surface atoms and hence are the common reactive sites in the TiO<sub>2</sub> (110) surface.<sup>43</sup> Single point defects are easily created on the surface by the removal of bridging oxygen atoms, where the Au cluster prefer to nucleate.<sup>44</sup> The TiO<sub>2</sub> (110) surface with a single point oxygen defect was represented using a 2 × 4 supercell and by a three-layer slab containing a total of 48 Ti atoms and 95 oxygen atoms stacked together parallel to the  $[\bar{1}10]$  plane and separated by a vacuum layer of 16.5 Å in between slabs. The supercell was sampled with a 2 × 2 × 1 special point mesh generated in the  $K$  space using Monkhorst-Pack technique,<sup>37</sup> and a plane-wave basis set with a cutoff of 420 eV was used for expansion of the wave function.

We chose a seven-atom Au (Au<sub>7</sub>) cluster as it has been observed to exhibit the highest activity for CO oxidation in the experiment.<sup>21,24</sup> The cluster is placed above a missing bridging oxygen point defect as the defect sites has been implicated to be the nucleation centers for Au clusters<sup>44</sup> and also because of the importance of single point defects in catalytic activity.<sup>20,32</sup> The clusters used in the mass selected cluster deposition experiments<sup>20,21,45</sup> are smaller than the clusters used in the metal vapor deposition experiments.<sup>1,3,11</sup> These relatively small clusters may be anticipated to be susceptible to structural changes in response to adsorption of reactants, and such a dynamical fluxionality of cluster has been shown to be important for catalytic activity.<sup>30</sup> But it remains largely unknown *a priori* what form of structure of the cluster would be most *catalytically* active. Computationally, it is also too demanding to exhaust all the possible structures and their associated catalytic activities for the Au<sub>7</sub> cluster on the TiO<sub>2</sub> surface. (Note that it is not necessarily true that the cluster of minimum-energy structure will have the highest reactivity.) Thus, we have opted to limit our investigations to a starting Au<sub>7</sub> cluster with a planar geometry, which was subsequently optimized before and after the molecular adsorption. This choice was partly made because the planar Au cluster was shown to have high stability in the gas phase.<sup>46</sup> Upon adsorption/reaction, the cluster was found to transform into a buckled structure. We note that the results we have so obtained will provide one particular form of reactive Au<sub>7</sub> cluster, without excluding other possible reactive cluster structures. The underlying mechanism we reveal from this particular choice may or may not be generally applicable to other cluster sizes and structures.

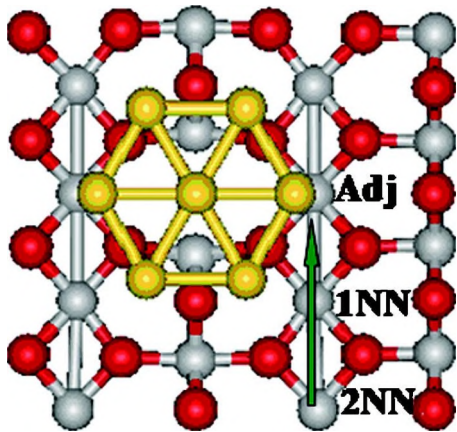


FIG. 1. (Top view) Diffusion-reaction path for reactants O<sub>2</sub> and CO along the surface 5-c Ti row of atoms. Adj, 1NN, and 2NN denote the Ti atoms over which geometry optimization were performed.

### III. RESULTS AND DISCUSSION

In experiments,<sup>21,24</sup> the TiO<sub>2</sub> supported Au<sub>7</sub> clusters are first dosed with excess of molecular oxygen and a part of O<sub>2</sub> is associated with the Au cluster. It is implicated that all the oxygen contributing to CO<sub>2</sub> formation originates from those associated with the Au cluster.<sup>24</sup> Hence, our first objective is to identify a potential candidate for the reactive form of the oxygen associated with the Au cluster. Energy minimizations were performed for a surface diffusion-reaction path along the row of 5-c Ti atoms, as indicated by an arrow in Fig. 1. This path is structurally less corrugated and is expected to be the diffusion path with the least barrier.<sup>47</sup> A set of O<sub>2</sub> structures was optimized by placing O<sub>2</sub> perpendicular to the surface on top/around three Ti atoms (2NN, 1NN, and Adj) along the path next to the Au<sub>7</sub> cluster, as indicated in Fig. 1. As the O<sub>2</sub> approaches the Au<sub>7</sub> cluster, the structure of cluster was also optimized simultaneously along with all other atoms. However, because these calculations are computationally very intensive, we obtained only a restricted phase space for O<sub>2</sub> diffusion (i.e., involving only three positions: 2NN, 1NN, and Adj), without mapping all the energy barriers and transition states along the diffusion path. Among many different geometries tested, the optimized structures with their corresponding energies at three positions are shown in Fig. 2. The energies are reported in reference to O<sub>2</sub> binding to a clean surface (which is  $\sim 0.23$  eV relative to vacuum) as we are considering the driving force of O<sub>2</sub> diffusing towards the Au<sub>7</sub> cluster. Since the energy decreases considerably as the O<sub>2</sub> approaches the cluster (Fig. 2), it indicates an effective attractive interaction between the O<sub>2</sub> molecule and the Au<sub>7</sub> cluster. Most importantly, at the Adj position, the lowest en-

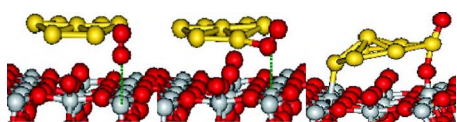


FIG. 2. (Side view) Structure (energy in eV with respect to O<sub>2</sub> adsorbed on a clean surface) of O<sub>2</sub> diffusing towards and reacting with the Au<sub>7</sub> cluster. Green lines mark the coordination of the O<sub>2</sub> to 5-c Ti. In leftmost structure (0.1), middle structure (1.27), and rightmost structure (8.37), the reactant is binding to 5-c Ti atom denoted as Adj, 2Au, and 3Au in Fig. 1, respectively.

ergy structure of O<sub>2</sub> is found in a dissociated form. It has one oxygen atom above the cluster bonding to a Au atom and the other oxygen atom in between the cluster bonding simultaneously to a Au atom in the cluster and a surface 5-c Ti atom (Fig. 2, right panel). Thus, these structural intermediates in Fig. 2 would represent local minima in the potential energy surface for the entire diffusion-reaction channel of O<sub>2</sub> diffusing towards the Au<sub>7</sub> cluster and dissociatively adsorbing with one O atom in between the cluster and the TiO<sub>2</sub> surface. Although we have not computed barriers for this reaction-diffusion channel (which is a challenging problem requiring a more detailed study), the present calculations indicate that there exists a strong thermodynamic driving force for this process to take place. The O<sub>2</sub> driven to the cluster may then provide a source for activated oxygen reactants. The strong binding affinity of O<sub>2</sub> to the cluster may also lead to greater residence time for the active oxygen in the system and such a scenario has been observed in experiments.<sup>9</sup>

To qualitatively understand the dissociation of O<sub>2</sub> in terms of bonding energies, we performed a set of calculations with reactants and Au<sub>7</sub> cluster without the oxide support, but using the same atomic positions as obtained above on the oxide supported. We found that without oxide support, Au<sub>7</sub> cluster alone cannot dissociate O<sub>2</sub> molecule, the energy is higher by 1.34 eV in the dissociated state than in the undissociated state due to the large O<sub>2</sub> binding energy of 5.93 eV. This indicates that the oxide support plays a critical role in dissociating O<sub>2</sub> at the Adj position to the Au<sub>7</sub> cluster. The large binding energy of 8.14 eV for the dissociated O<sub>2</sub> to the Au<sub>7</sub> cluster on the oxide surface comes partly from two additional bond interactions as compared to the bare cluster: the O atom below the cluster bonding with a 5-c surface Ti atom ( $\sim 1.7$  eV as estimated from the formation enthalpy of TiO<sub>2</sub>) and a Au atom bonding with a 5-c surface Ti atom on the other side of the cluster [see Fig. 2 right panel,  $\sim 1.4$  eV as obtained from Au surface adsorption energy on TiO<sub>2</sub> (Ref. 48)]. However, we caution that the absolute value of the large binding energy of 8.37 we obtain here has contributions from bonding changes occurring in the slab and also possible overestimation by density functional theory. One correction that can be possible is to use a much thicker slab, which is unfortunately impractical at present due to limited computational resources. Nevertheless, we expect that the main conclusion of the existence of thermodynamic driving force for O<sub>2</sub> dissociation by TiO<sub>2</sub> supported Au<sub>7</sub> cluster will not be qualitatively affected by these possible sources of errors.

In experiments,<sup>21,24</sup> the excess O<sub>2</sub> is purged and then is followed by pulse of CO. To simulate such a scenario, with the O<sub>2</sub> dissociated on the Au<sub>7</sub> cluster in the Adj position, as shown in Fig. 2 (right panel), CO is introduced along the 5-c Ti row of atoms. Far away from the cluster, CO binds to the surface Ti atoms predominantly via the C atom. As CO diffuses towards the cluster, it can bind to two possible under-coordinated binding sites: surface Ti atom and/or the edge sites of Au<sub>7</sub> cluster (Fig. 3). The tilted geometry of CO observed in the central panel of Fig. 3 (1NN position) is a result of C shifting from binding predominantly to the surface Ti atom to that of binding predominantly to the edge atom of the Au<sub>7</sub> cluster. We find that this diffusion-reaction path for

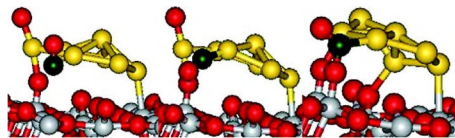


FIG. 3. (Perspective view) The structure (energy in eV with respect to CO adsorbed on a clean surface) of  $O_2$  dissociated on the cluster as CO approaches the cluster to form  $CO_2$ . Left figure (0.05) and middle figure (2.24) denotes CO in 2NN and 1NN positions, respectively. The right (6.19) figure denotes the final structure after  $CO_2$  has been formed.

CO is also energetically downhill (energies are in reference to the CO adsorption energy on a clean  $TiO_2$  which is 0.27 eV relative to vacuum).

The adsorption energies of CO binding to the clean surface via C (as discussed above) versus O are 0.27 and  $\sim 0$  eV, respectively. Hence, far away from the clusters, the possibility of CO binding to surface via O is negligible. However, as the CO with C binding to the surface 5-c Ti diffuses towards the vicinity of the cluster, the C moves up to bind with Au while O flips down below the C, as shown in the central panel of Fig. 3. Finally,  $CO_2$  forms by C forming another bond with the O in the dissociated oxygen anchored above the cluster, and in the meantime the flipped-down O in the CO forming a bond with surface Ti, as shown in the central panel of Fig. 3. We have also performed additional calculations to enforce a CO, with O binding to surface Ti, to diffuse towards the cluster. The energy is also found downhill, eventually leading to the same final stable structures in the vicinity of the cluster, but this pathway has a higher energy state *a priori* to the reaction.

Thus, our calculated dissociated state of  $O_2$ , as shown in Fig. 2 (right panel), provides a potential candidate for the reactive form of  $O_2$  molecule implicated in the experiments. It is interesting to consider these results in the context of experiments that deposit neutral Au atoms onto multilayer of molecular oxygen, which lead to the formation of oxidized Au intermediate and further production of  $CO_2$  at temperatures as low as 35 K.<sup>35</sup> The spectroscopic signature of dissociated molecular  $O_2$  at the Adj position might be similar to the oxidized Au observed in these experiments.

Another interesting experimental observation is that  $CO_2$  evolves only after  $\sim 300$  ms of the CO pulse. So, our second objective is to shed some light on the possible cause for such slow kinetics of reaction product  $CO_2$  evolution. Two hypotheses were suggested,<sup>24</sup> which are partially assessed by our calculations. First, the slow kinetics could be caused by the existence of high-energy barriers for the reactants to approach the cluster. However, the restricted energy landscape for both  $O_2$  and CO as calculated does not provide evidence for such a scenario. Second, the slow kinetics could result from a larger binding affinity of the product, i.e.,  $CO_2$  to the cluster or surface. Indeed, this seems to be consistent with our calculations, which show the binding energy of the  $CO_2$  as formed above in Fig. 3 (right panel) is 0.73 eV lower than that of a  $CO_2$  in the clean surface. This makes it relatively difficult for the  $CO_2$  to dissociate from the cluster and diffuse away from the cluster before eventual desorption from the surface. The observed 300 ms delay of product evolution corresponds to a barrier of  $\sim 0.8$  eV. The calculated binding

energy of 0.73 eV seemed to agree surprisingly well with the measured barrier of 0.8 eV, but we must caution that such a quantitative agreement might not be as reliable considering the known error in binding energy calculated by density functional method. Nevertheless, more importantly, the calculation provides at least qualitatively a possible explanation for the observed slow kinetics of  $CO_2$  removal from the catalytically active site.

The relatively high binding energy of  $CO_2$  can be rationalized by the binding geometry of  $CO_2$  to the  $Au_7$  cluster and the surface simultaneously. The  $CO_2$  forms two bonds, one to the surface via the O atom and a second bond between the C atom and the undercoordinated Au atom at the  $Au_7$  cluster edge. An interesting question is if this particular mode of binding of  $CO_2$  results from the specific diffusion-reaction pathway that we have revealed here on  $TiO_2$  surface and may not be generally available when  $CO_2$  is absorbed on to a  $Au_7$  cluster. In such a scenario, there might be different binding affinities of  $CO_2$  than what we found here, and the possible conversion among different  $CO_2$  adsorption states will be an interesting subject of study. Furthermore, it is also important to note that the present calculation suggests only a thermodynamic driving force for  $O_2$  diffusion and  $CO_2$  formation but it does not address the nature of activation barriers that may be present in such a process. Such a study to obtain the kinetic barrier will be computationally more formidable due to the large system size and the complex nature of transition states for diffusion-reaction pathway.

#### IV. CONCLUSIONS

Using a model  $Au_7$  cluster, we demonstrate a potential pathway for diffusion-dissociation of  $O_2$  along a row of surface Ti atoms towards the cluster. This form of oxygen may be a candidate for the reactive form of oxygen observed in experiments. Our computational results suggest that there exist a thermodynamic driving force for CO to approach along the Ti row of atoms to react with the dissociated  $O_2$  to form  $CO_2$ . Furthermore, a relatively high binding energy of  $CO_2$  to the  $Au_7$  cluster may provide a possible explanation for the observed slow kinetics of reaction product ( $CO_2$ ) evolution. We believe that the two mechanistic findings from our computational studies of the  $Au_7$  cluster may have some general implications in the catalytic activity of Au clusters on oxide surfaces.

#### ACKNOWLEDGMENTS

We thank Scott Anderson for useful discussions and for communicating their experimental results prior to publication. We acknowledge the National Science Foundation for supporting this work (Grant No. DMR-0307000) and the Center for High Performance Computing, University of Utah for providing the computational resources.

<sup>1</sup>M. Haruta, *Encyclopedia of Nanoscience and Nanotechnology*, 1, 655 (American Scientific Publishers, USA, 2004).

<sup>2</sup>T. V. Choudhary and D. W. Goodman, *Top. Catal.* **21**, 25 (2002); C. T. Campbell, A. W. Grant, D. E. Starr, S. C. Parker, and V. A. Bondzie, *ibid.* **14**, 43 (2001).

<sup>3</sup>R. Meyer, C. Lemire, S. K. Shaikhutdinov, and H. J. Freund, *Gold Bull.*

37. 72 (2004).
- <sup>4</sup> B. Hammer and J. K. Nørskov. *Nature (London)* **376**, 238 (1995).
- <sup>5</sup> G. Mills, M. S. Gordon, and H. Metiu. *J. Chem. Phys.* **118**, 4198 (2003).
- <sup>6</sup> N. Lopez, T. V. W. Janssens, B. S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, and J. K. Nørskov. *J. Catal.* **223**, 232 (2004).
- <sup>7</sup> I. N. Remediakis, N. Lopez, and J. K. Nørskov. *Angew. Chem., Int. Ed.* **44**, 1824 (2005).
- <sup>8</sup> Z.-P. Liu, X.-Q. Gong, J. Kohanoff, C. Sanchez, and P. Hu. *Phys. Rev. Lett.* **91**, 266102 (2003).
- <sup>9</sup> J. T. Calla, M. T. Bore, A. K. Datye, and R. J. Davis. *J. Catal.* **238**, 458 (2006).
- <sup>10</sup> M. Comotti, W. C. Li, B. Spliethoff, and F. Schuth. *J. Am. Chem. Soc.* **128**, 917 (2005).
- <sup>11</sup> M. Valden, X. Lai, and D. W. Goodman. *Science* **281**, 1647 (1998).
- <sup>12</sup> M. S. Chen and D. W. Goodman. *Science* **306**, 252 (2004).
- <sup>13</sup> F. Liu. *Phys. Rev. Lett.* **89**, 246105 (2002).
- <sup>14</sup> S. Wendt, R. Schaub, J. Matthiesen *et al.*. *Surf. Sci.* **598**, 226 (2005).
- <sup>15</sup> L. M. Molina, M. D. Rasmussen, and B. Hammer. *J. Chem. Phys.* **120**, 7673 (2004).
- <sup>16</sup> Z.-P. Liu, P. Hu, and A. Alavi. *J. Am. Chem. Soc.* **124**, 14770 (2002).
- <sup>17</sup> M. Mavrikakis, P. Stoltze, and J. K. Nørskov. *Catal. Lett.* **64**, 101 (2000).
- <sup>18</sup> R. G. S. Pala and F. Liu. *J. Chem. Phys.* **120**, 7720 (2004).
- <sup>19</sup> Q. Fu, H. Saltsburg, and M. Flytzani-Stephanopoulos. *Science* **301**, 935 (2003); R. J. Davis. *ibid.* **301**, 926 (2003).
- <sup>20</sup> B. Yoon, H. Häkkinen, U. Landman, A. Z. Wörz, J. M. Antonietti, S. Abbet, K. Judai, and U. Heiz. *Science* **307**, 403 (2005).
- <sup>21</sup> S. Lee, C. Fan, T. Wu, and S. L. Anderson. *J. Am. Chem. Soc.* **126**, 5682 (2004).
- <sup>22</sup> S. Abbet and U. Heiz. *Encyclopedia of Nanoscience and Nanotechnology*, 6, 161 (American Scientific Publishers, USA, 2004).
- <sup>23</sup> S. Lee, C. Fan, T. Wu, and S. L. Anderson. *Surf. Sci.* **578**, 5 (2005).
- <sup>24</sup> S. Lee, C. Fan, T. Wu, and S. L. Anderson. *J. Chem. Phys.* **123**, 124710 (2005).
- <sup>25</sup> X. Tong, L. Benz, P. Kemper, H. Metiu, M. T. Bowers, and S. K. Buratto. *J. Am. Chem. Soc.* **127**, 13516 (2005).
- <sup>26</sup> I. N. Remediakis, N. Lopez, and J. K. Nørskov. *Appl. Catal., A* **291**, 13 (2005).
- <sup>27</sup> B. Yoon, H. Häkkinen, U. Landman, A. S. Wörz, J. M. Antonietti, S. Abbet, K. Judai, and U. Heiz. *Science* **307**, 403 (2005).
- <sup>28</sup> X. Wu, A. Selloni, and S. K. Nayak. *J. Chem. Phys.* **120**, 4512 (2004).
- <sup>29</sup> Q. Sun, P. Jena, Y. D. Kim, M. Fischer, and G. Gantefor. *J. Chem. Phys.* **120**, 6510 (2004); X. Wu, L. Senapati, S. K. Nayak, A. Selloni, and M. Hajaligol. *ibid.* **117**, 4010 (2002); A. Vijay, G. Mills, and H. Metiu. *ibid.* **118**, 6536 (2003).
- <sup>30</sup> H. Häkkinen, S. Abbet, A. Sanchez, U. Heiz, and U. Landman. *Angew. Chem., Int. Ed.* **42**, 1297 (2003).
- <sup>31</sup> L. M. Molina and B. Hammer. *J. Chem. Phys.* **123**, 161104 (2005).
- <sup>32</sup> N. Lopez, J. K. Nørskov, T. V. W. Janssens, A. Carlsson, A. P. Molina, B. S. Clausen, and J. D. Grunwaldt. *J. Catal.* **225**, 86 (2004).
- <sup>33</sup> T. S. Kim, J. D. Stiehl, C. T. Reeves, R. J. Meyer, and C. B. Mullins. *J. Am. Chem. Soc.* **125**, 2018 (2003); V. A. Bondzie, S. C. Parker, and C. T. Campbell. *J. Vac. Sci. Technol. A* **17**, 1717 (1999); J. D. Stiehl, T. S. Kim, C. T. Reeves, R. J. Meyer, and C. B. Mullins. *J. Phys. Chem. B* **108**, 7917 (2004).
- <sup>34</sup> B. Grzybowska-Swierkosz. *Catal. Today* **112**, 3 (2006).
- <sup>35</sup> J. Kim, Z. Dohnalek, and B. D. Kay. *J. Am. Chem. Soc.* **127**, 14592 (2005).
- <sup>36</sup> D. Vanderbilt. *Phys. Rev. B* **41**, 7892 (1990); F. Liu, S. H. Garofalini, R. D. King-Smith, and D. Vanderbilt. *Phys. Rev. Lett.* **70**, 2750 (1993).
- <sup>37</sup> M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos. *Rev. Mod. Phys.* **64**, 1045 (1992).
- <sup>38</sup> J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais. *Phys. Rev. B* **46**, 6671 (1992).
- <sup>39</sup> J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>40</sup> S. P. Bates, G. Kresse, and M. J. Gillan. *Surf. Sci.* **385**, 386 (1997).
- <sup>41</sup> R. W. G. Wyckoff. *Crystal Structures* (Wiley, New York, 1963); M. Ramamoorthy, D. Vanderbilt, and R. D. Kingsmith. *Phys. Rev. B* **49**, 16721 (1994).
- <sup>42</sup> J. D. Cox, D. D. Wagman, and V. A. Medvedev. *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1984).
- <sup>43</sup> H. Idriss and M. A. Barteau. *Adv. Catal.* **45**, 261 (2000).
- <sup>44</sup> E. Wahlstrom, N. Lopez, R. Schaub, P. Thostrup, A. Ronnau, C. Africh, E. Laegsgaard, J. K. Nørskov, and F. Besenbacher. *Phys. Rev. Lett.* **90**, 026101 (2003).
- <sup>45</sup> U. Diebold. *Surf. Sci.* **578**, 1 (2005).
- <sup>46</sup> H. Häkkinen, M. Moseler, and U. Landman. *Phys. Rev. Lett.* **89**, 033401 (2002); Y.-K. Han. *J. Chem. Phys.* **124**, 024316 (2006).
- <sup>47</sup> D. Pillay and G. S. Hwang. *Phys. Rev. B* **72**, 205422 (2005).
- <sup>48</sup> R. G. S. Pala, T. N. Truong, and F. Liu. in *Clusters and Nano-Assemblies*, edited by P. Jena, S. N. Khanna, and B. K. Roa, 135 (World Scientific, Singapore, 2005).