

**CO oxidation on fully oxygen covered Ru(0001): Role of step edges**

Željko Šljivančanin and Bjørk Hammer

*Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark*

(Received 5 February 2010; published 18 March 2010)

We present a reaction mechanism for CO oxidation at the Ru(0001)-(1×1) surface. By means of density-functional theory studies, we compare the reactivity of flat and stepped regions of the Ru(0001). We find that at saturation oxygen coverage, where the flat parts are unreactive toward CO adsorption an intricate reaction pathway for CO adsorption and CO<sub>2</sub> formation exists at the monatomic Ru step. By suggesting an efficient mechanism for CO oxidation on nonoxidic Ru, our results offer an explanation for the controversy in the experimental literature regarding how nonoxidic Ru may be as active in CO oxidation as oxidic rutile RuO<sub>2</sub>.

DOI: [10.1103/PhysRevB.81.121413](https://doi.org/10.1103/PhysRevB.81.121413)

PACS number(s): 68.35.Md, 68.43.Fg, 82.45.Jn, 82.65.+r

The study of elementary chemical reactions taking place at surfaces of real catalysts is an enormously difficult task due to their complex structure and chemical composition. The surface science approach relies on modeling real catalysts by simpler systems, usually plane surfaces, and on combining a variety of experimental and theoretical techniques to achieve an atomic scale description of the elementary reaction steps taking place at them.<sup>1–3</sup> The model studies are usually carried out under ultrahigh vacuum (UHV) conditions. Since this approach introduces the so-called pressure and material gap, it is not clear if the catalytic properties of simple model systems determined under UHV conditions are transferable to realistic catalysts operating at ambient or higher pressures.

One of the well-known manifestations of the pressure gap is the CO oxidation over Ru.<sup>4</sup> Although under UHV conditions Ru shows the lowest catalytic activity among late transition metals,<sup>5</sup> it becomes superior to Pt, Rh, and Pd when exposed to higher oxygen pressures.<sup>6</sup> The high catalytic activity was initially attributed to the well-ordered (1×1)-O overlayer on Ru(0001) surface as it contains less strongly bound O atoms, not present under UHV conditions.<sup>4,7</sup>

The density-functional theory (DFT) calculations challenged this picture by showing that CO does not adsorb on the flat Ru(0001)-(1×1)-O surface.<sup>8</sup> Furthermore, it was shown that CO can adsorb into O vacancies on a defected Ru(0001)-(1×1)-O surface, but the rate of the CO oxidation would, however, be very low due to a high activation energy of 1.5 eV.<sup>9</sup> By combining several experimental techniques together with the DFT calculations Over *et al.* revealed a microscopic mechanism for CO adsorption and oxidation on the RuO<sub>2</sub>(110) surface.<sup>10,11</sup> It was demonstrated that the RuO<sub>2</sub> is a remarkably efficient oxidation catalyst, and it was proposed that at near-atmospheric pressures and at typical reaction temperatures the oxide is the active phase of Ru catalysts.

This interpretation of the pressure gap observed for Ru catalysts was recently questioned by Goodman and co-workers.<sup>12</sup> Their earlier experiments on Ru(0001) samples<sup>4</sup> showed high catalytic activity of the surface even under reaction conditions when RuO<sub>2</sub> does not form. More indications that the RuO<sub>2</sub> might not be the only active phase of Ru exposed to high oxygen pressures has appeared recently. Blume *et al.*<sup>13</sup> reported on the formation of a so-

called transient surface oxide, a catalytically active phase at temperatures below 500 K and Flege *et al.*<sup>14</sup> reported on a tri-layer-like surface oxide after large doses of NO<sub>2</sub> at 790 K. Recently Over *et al.* suggested the presence of a nonoxidic Ru phase, in addition to the RuO<sub>2</sub>(110), as the catalytically active at the oxygen pressures in the mbar range and at temperatures lower than 520 K.<sup>15,16</sup> The microscopic structures of the surface oxides and the nonoxidic phase are unknown.

All previous studies of the catalytic activity of Ru(0001)-(1×1)-O were focused on flat surfaces, including the DFT studies of the CO adsorption and oxidation.<sup>8</sup> Scanning tunneling microscopy studies have, however, revealed the presence of monatomic steps on Ru(0001)-(1×1)-O regions under operating conditions.<sup>17</sup> Such monatomic steps have further been observed to bunch together in regions that show higher activity for oxide formation.<sup>18</sup> While steps have been demonstrated to exhibit enhanced catalytic activity under low-coverage UHV conditions,<sup>19–23</sup> no studies exist addressing the possible role of steps under high coverage conditions. Naively, it might be speculated that stronger chemisorption at steps would pollute the steps entirely under such conditions. However, in this Rapid Communication we provide evidence that the role of atomic step edges as special active sites at metal surfaces indeed goes beyond the UHV conditions. Our DFT calculations show that the CO oxidation at the Ru(0001) surface exposed to high oxygen pressures occurs at the step edges even under reaction condition when no oxidic phase exists. These findings demonstrate that in an oxygen rich environment the metal phase of Ru with a chemisorbed O layer can sustain a catalytic activity comparable to that of the rutile oxide structure due to the presence of special active sites at the monatomic steps.

All calculations presented here are performed with DACAPO computer code.<sup>24</sup> We described the electronic structure using the spin-dependent generalized gradient approximation (GGA) based revised Perdew-Burke-Ernzerhof (GGA-RPBE) exchange-correlation functional.<sup>24</sup> Only valence wave functions were treated explicitly and valence-core interactions were described by ultrasoft pseudopotentials. The electron wave functions and the augmented electron density were expanded in plane waves with cut-off energies of 25 and 140 Ry, respectively. Converged energies are obtained by sampling the Brillouin zone with a (2×2) **k**-point mesh. We used a supercell slab geometry with a Ru(0001) vicinal

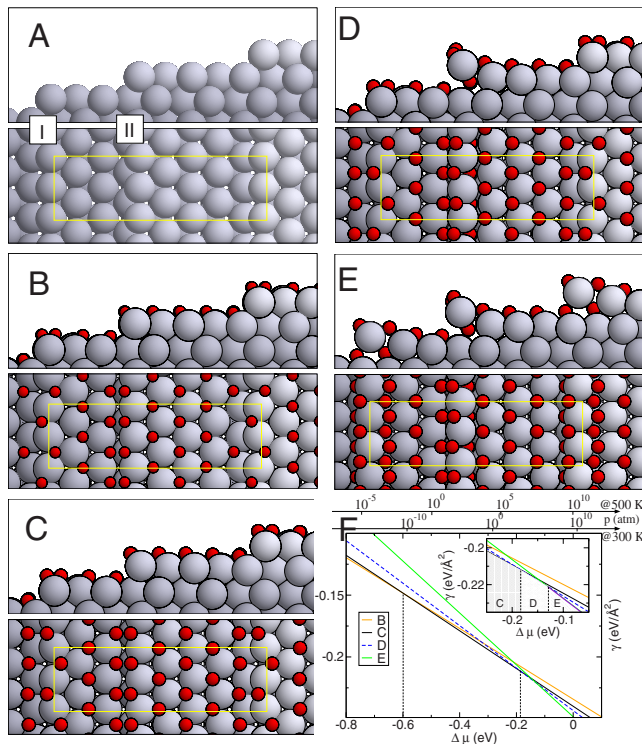


FIG. 1. (Color online) (A) Ru(0001) surface with two types of monatomic steps, marked as “I” and “II;” [(B)–(E)] the most stable configurations of O on stepped Ru(0001) at increasing O coverages; (F) the corresponding phase diagram.

made up by five hexagonal layers. Periodically repeated slabs are separated by at least 13 Å of vacuum. The positions of the atoms were always fully relaxed, except those of the three bottom Ru layers which were held in ideal bulk positions. The O adsorption energies are referred to half the energy of the gas-phase  $O_2$  molecule.

The Ru(0001) vicinal has two kinds of steps, denoted “I” and “II” in Fig. 1(A). These monatomic steps have been observed experimentally and are known to bind atomic O differently in the low coverage limit.<sup>19</sup> Our first objective was to identify the equilibrium state of this stepped Ru(0001) surface in an oxygen atmosphere. An extensive search for the most stable structures at different O coverages led to the geometries shown in Figs. 1(B)–1(E). Following the procedure described in Ref. 25 the surface-free energy of adsorption was constructed as a function of the oxygen chemical potential. The result is shown in Fig. 1(F) where the chemical potential is further related to the oxygen pressure at two different gas temperatures.

Generally, we find that the Ru terraces are covered by a  $(1 \times 1)$  pattern of O atoms in hcp sites. At the steps, deviations from this structure occurs with the appearance of O vacancies at the foot of step I [Fig. 1(B)], O in fcc-sites at the top of step I [Fig. 1(C)], and O in subsurface sites at either steps [Figs. 1(D) and 1(E)]. The structure being predicted to be the most stable one at any reasonable oxygen pressure is the one in Fig. 1(C). The equilibrium conditions for this structure range in pressure from  $10^{-11}$  to 1000 atm at 300 K. At lower pressures the O vacancies form, at higher pressures the subsurface O atoms occur. At 500 K the corresponding

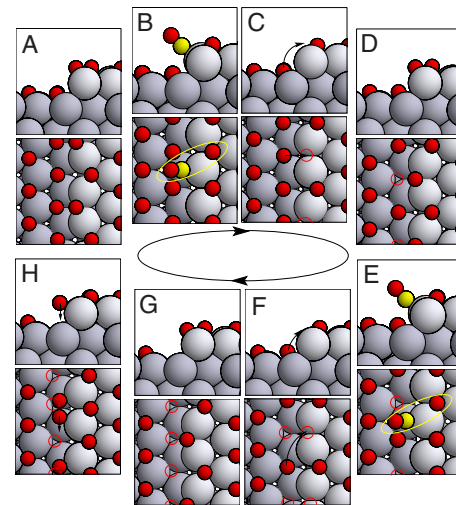


FIG. 2. (Color online) Catalytic cycle for  $CO_2$  formation on stepped Ru(0001), including sequential adsorption and oxidation of two CO molecules (the small ellipses highlight the interacting species), diffusion of O atoms to the upper terrace (indicated by the arrows), and dissociative adsorption of an  $O_2$  molecule.

pressure range is from  $10^{-2}$  to  $3 \times 10^6$  atm.<sup>26</sup>

Having identified the structure in Fig. 1(C) as the thermodynamically most stable one a search was done for the possible CO adsorption sites on this surface. The most stable CO adsorption site found was an on-top site at step I. The local structure before and after the CO adsorption is depicted in Figs. 2(A) and 2(B) from which it is seen that the O in the fcc-site at the top of the step relocates upon the CO adsorption to the hcp site behind the step leaving room for the CO at the very step edge. The energetics of the CO adsorption process is sketched as the initial part of Fig. 3. It is seen that CO adsorption is activated by a small barrier of 0.25 eV and that CO binds to the surface with 0.69 eV. This is a remarkable result. The stepped Ru(0001) surface is fully covered with O and adsorption of more O would require abnormal oxygen partial pressures. Yet, CO can adsorb and bind strongly at the steps.

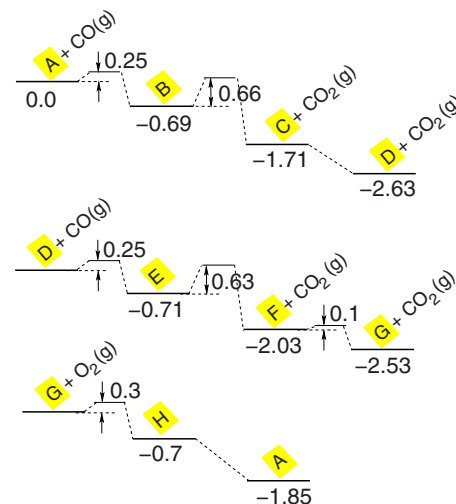


FIG. 3. (Color online) Potential-energy diagram corresponding to the configurations shown in Fig. 2. All energies are given in eV.

A search for possible CO oxidation pathways revealed that the adsorbed CO may react with adsorbed O at the upper side of the step. The reacting species are pointed out in Fig. 2(B). The barrier for the CO<sub>2</sub> formation was found to be 0.66 eV which is considerably lower than the barrier for CO desorption,  $0.94(=0.25+0.69)$  eV. After desorption of the CO<sub>2</sub>, an O vacancy is formed at the upper terrace, cf. Fig. 2(C). Adsorption of CO in this vacancy would seem likely and we calculate a barrier of 1.0 eV for CO<sub>2</sub> formation from such a CO species. However, since the diffusion of an O atom from the lower terrace in to the vacancy experiences no barrier, this is by far more likely to happen, resulting in the configuration [Fig. 2(D)], which is identical to the thermodynamically most stable state of the surface at low O coverage [Fig. 1(B)].

Following the CO oxidation we studied the possibility of O<sub>2</sub> adsorption and dissociation on the surface of Fig. 2(D). However, no likely pathways were found. Rather, we found that a second CO may adsorb [Fig. 2(E)] and react with step bound O to form a second CO<sub>2</sub>. As evidenced by Fig. 3, the energetics of this second CO reaction step is very similar to the first reaction step; 0.25 eV barrier for adsorption, 0.71 eV CO adsorption bond strength, and 0.63 eV barrier for CO<sub>2</sub> formation. After the CO<sub>2</sub> desorption [Fig. 2(F)] an O from the lower terrace diffuses to the top of the step facing a very low barrier,  $\sim 0.1$  eV. The resulting configuration, depicted in Fig. 2(G), now contains adjacent O vacancies at the foot of the step.<sup>27</sup>

The initial adsorption configuration [Fig. 2(A)] may subsequently be restored by dissociative adsorption of an O<sub>2</sub> molecule in the O-vacancies at the foot of the step. A barrier of 0.3 eV was found for the molecular adsorption [Fig. 2(H)]. Once adsorbed, the O<sub>2</sub> molecule dissociates spontaneously and the catalytic cycle is closed. With a view at the entire cycle, it is seen to be downhill in energy throughout with none of the energy barriers exceeding 0.66 eV. This renders the present microscopic reaction mechanism a likely candidate to explain the observed high activity of a nonoxidic phase of Ru.<sup>12,15</sup>

The results in Figs. 2 and 3 testify that it is possible to catalytically oxidize CO at the fully O covered monatomic steps of Ru(0001). This is unlike the situation computed for the flat Ru(0001)-(1×1)-O surface.<sup>8</sup> For such surfaces, O vacancies must be introduced to provide adsorption sites for CO.<sup>9</sup> However, the barrier for CO<sub>2</sub> formation from this adsorption site is large (1.5 eV), which is much higher than the 0.63–0.66 eV barriers calculated for the step-bound CO, cf. Fig. 3. That our proposed activity of step-bound CO further compares with that of CO bound to oxidic ruthenium, RuO<sub>2</sub>(110), can be deduced by considering the CO oxidation barrier of 0.74 eV (71 kJ/mol)<sup>11</sup> calculated by Seitsonen and Over. At, e.g., room temperature, this barrier difference of  $\sim 0.1$  eV would (using an Arrhenius rate expression) translate to about two orders of magnitude higher reaction rate per site for step-bound CO. Such step sites thus need not be very abundant to dominate the overall activity of a partially oxidized Ru surface.

A qualitative explanation for the enhanced activity of the fully oxygen covered step compared to the flat (1×1) surface may be given simply in terms of the O-coordination of

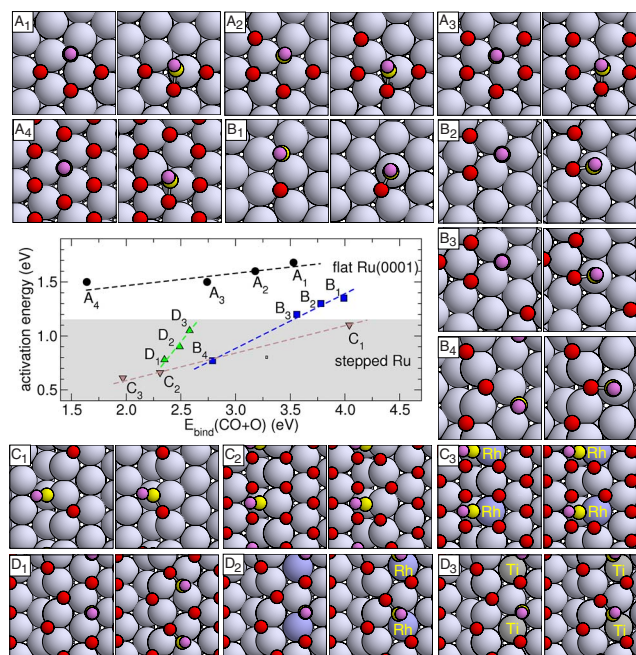


FIG. 4. (Color online) The correlations between the activation energy for CO<sub>2</sub> formation and the combined binding energy of the interacting species for four series of distinctive reaction geometries. The shaded area highlights systems involving steps; The structure plots show the initial and transition state geometries of the corresponding structures. A<sub>4</sub> represents the CO oxidation from CO adsorbed in an O vacancy on the flat Ru(0001)-(1×1)-O. C<sub>2</sub> represents CO oxidation on the stepped Ru as in Figs. 2 and 3.

the Ru atoms. On the flat Ru surface, every Ru coordinates to three O atoms, while at the step, the Ru atoms only coordinate to two O atoms.

A more quantitative explanation can be built on the universality concept introduced by Nørskov and co-workers.<sup>28,29</sup> This concept states that the activation energies for formation or dissociation of small molecules on metal surfaces correlates with the binding energies of the interacting species or the final products. Correlation diagrams—so-called Brønsted-Evans-Polanyi (BEP) plots—reveal that weaker bound adsorbates generally react with lower activation energies. Yet, the energy barriers are very sensitive to the nature of the initial and the transition states and the BEP plots are applicable only to reaction pathways with similar geometries.

To produce BEP plots we broadened our computational study beyond finding the most favorable pathways on the equilibrium surfaces. Four series of calculations were done. For each series, the geometries of the initial and the transition states (TSs) of the reacting CO+O adsorbates were kept fixed while their surroundings were varied. The systems are shown in Fig. 4. In series A, the O coverage on the flat Ru(0001) surface was varied and TSs in which the CO passes a plane perpendicular to the surface, containing two nearby O atoms was studied. The proximity of the O atoms causes the CO to be off-center the Ru atom when in the TS. In series B, a lower O coverage was used so that the CO may migrate via the Ru atop site in the transition state. This series contains three data point for flat Ru(0001) and one for



stepped Ru. In series C we studied the most favorable reaction pathway at the stepped Ru [configuration  $C_2$  = Fig. 2(B)] and compared to either lower O coverage or the influence of changing the chemical identity of one step edge atom from Ru to Rh. Finally, in series D, an alternative pathway at the step was studied in which the CO was adsorbed on the upper terrace in an O vacancy. The substitution of a Ru atom with either Rh or Ti atoms was studied.

The correlation plot in Fig. 4 nicely shows that for each of the four series of reaction pathways considered, a linear relation exists between the sum of the binding energies of the CO and the O and the activation energy for the formation of the  $CO_2$  molecule. This is the electronic effect. Viewing all data points for flat Ru surfaces,  $A_1$ – $A_4$  and  $B_1$ – $B_3$ , it is seen that the electronic effect is too weak to significantly lower the energy barrier on the flat surfaces. Only with data point  $B_4$ , where the transition state structure of the flat surfaces is used at the upper side of a step edge, we find a significant lowering of the energy barrier.

Considering instead the data points of series C and D, it is seen that the reaction pathways made possible at stepped

surfaces immediately give small reaction barriers. We consequently conclude that structural effects are more important than electronic effects in setting up reactive sites at fully O covered Ru steps. With this general understanding of our results, we expect structural effects to cause low-barrier pathways on corrugated O-saturated Ru surfaces in general.

In conclusion, by modeling the O adsorption on stepped Ru(0001) we identified a chemisorption phase which is stable at realistic  $O_2$  pressures and temperatures. The chemisorption phase is a perturbed  $(1 \times 1)$ -O structure, i.e., a non-oxidic phase. The calculated microscopic mechanism for the CO oxidation on the Ru steps reveals barriers that are comparable or lower than those reported for the CO oxidation on the rutile  $RuO_2(110)$  oxide surface rendering the presently identified pathway a possible explanation for the observed high activity of nonoxidic Ru.<sup>4,12</sup>

We thank Stefan Wendt for a critical reading of the Rapid Communication. The calculations were performed at the Danish Center for Scientific Computing (DCSC).

- <sup>1</sup>J. H. Sinfelt, *Surf. Sci.* **500**, 923 (2002).
- <sup>2</sup>G. Ertl, *Angew. Chem., Int. Ed.* **47**, 3524 (2008).
- <sup>3</sup>K. W. Kolasinski, *Surface Science: Foundations of Catalysis and Nanoscience* (John Wiley & Sons, New York, 2002).
- <sup>4</sup>C. H. F. Peden and D. W. Goodman, *J. Phys. Chem.* **90**, 1360 (1986).
- <sup>5</sup>A. Böttcher, H. Niehus, S. Schwegmann, H. Over, and G. Ertl, *J. Phys. Chem. B* **101**, 11185 (1997).
- <sup>6</sup>N. W. Cant, P. C. Hicks, and B. S. Lennon, *J. Catal.* **54**, 372 (1978).
- <sup>7</sup>C. Stampfl, S. Schwegmann, H. Over, M. Scheffler, and G. Ertl, *Phys. Rev. Lett.* **77**, 3371 (1996).
- <sup>8</sup>C. Stampfl and M. Scheffler, *Phys. Rev. Lett.* **78**, 1500 (1997).
- <sup>9</sup>C. Stampfl and M. Scheffler, *Surf. Sci.* **433-435**, 119 (1999).
- <sup>10</sup>H. Over, Y. D. Kim, A. P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, and G. Ertl, *Science* **287**, 1474 (2000).
- <sup>11</sup>A. P. Seitsonen and H. Over, *Surf. Sci.* **603**, 1717 (2009).
- <sup>12</sup>D. W. Goodman, C. H. F. Peden, and M. S. Chen, *Surf. Sci.* **601**, L124 (2007).
- <sup>13</sup>R. Blume, M. Hävecker, S. Zafeirotos, D. Teschner, E. Kleimenov, A. Knop-Gericke, R. Schlögl, A. Barinov, P. Dudin, and M. Kiskinova, *J. Catal.* **239**, 354 (2006).
- <sup>14</sup>J. I. Flege, J. Hrbek, and P. Sutter, *Phys. Rev. B* **78**, 165407 (2008).
- <sup>15</sup>H. Over, O. Balmes, and E. Lundgren, *Catal. Today* **145**, 236 (2009).
- <sup>16</sup>H. Over, O. Balmes, and E. Lundgren, *Surf. Sci.* **603**, 298 (2009).
- <sup>17</sup>H. Over, A. P. Seitsonen, E. Lundgren, M. Schmid, and P. Varga, *Surf. Sci.* **515**, 143 (2002).
- <sup>18</sup>P. Dudin, A. Barinov, M. Dalmiglio, L. Gregoratti, M. Kiskinova, A. Goriachko, and H. Over, *J. Electron Spectrosc. Relat. Phenom.* **166-167**, 89 (2008).
- <sup>19</sup>T. Zambelli, J. Winterlin, J. Trost, and G. Ertl, *Science* **273**, 1688 (1996).
- <sup>20</sup>S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, *Phys. Rev. Lett.* **83**, 1814 (1999).
- <sup>21</sup>B. Hammer, *Phys. Rev. Lett.* **83**, 3681 (1999).
- <sup>22</sup>P. Gambardella, Ž. Šljivančanin, B. Hammer, M. Blanc, K. Kuhnke, and K. Kern, *Phys. Rev. Lett.* **87**, 056103 (2001).
- <sup>23</sup>Y. K. Kim, G. A. Morgan, and J. T. Yates, *J. Phys. Chem. C* **111**, 3366 (2007).
- <sup>24</sup>B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
- <sup>25</sup>K. Reuter and M. Scheffler, *Phys. Rev. B* **65**, 035406 (2001).
- <sup>26</sup>The  $RuO_2$  strips forming along the step edges would be stabilized if strain relieve was allowed. This would lower the calculated transition pressures.
- <sup>27</sup>Since the periodicity along the step edge is two in our calculations we obtain rows of O vacancies.
- <sup>28</sup>J. K. Nørskov *et al.*, *J. Catal.* **209**, 275 (2002).
- <sup>29</sup>X.-Q. Gong, Z.-P. Liu, R. Raval, and P. Hu, *J. Am. Chem. Soc.* **126**, 8 (2004).