

Density functional study of the CO oxidation on a doped rutile TiO₂(110): effect of ionic Au in catalysis

Steeve Chrétien and Horia Metiu*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA

Received 3 October 2005; accepted 13 December 2005

We used density functional theory to examine whether doping oxides makes them better oxidation catalysts. We studied in detail titania doped with Au and used CO oxidation as a test of the oxidizing power of the system. We show that doping with Au, Ag, Cu, Pt, Pd, Ni reduces dramatically the bond of surface oxygen to titania or ceria, making them better oxidation catalysts. These calculations suggest that it is worthwhile to explore doped oxides as oxidation catalysts.

KEY WORDS: density functional theory; TiO₂(110); molecular oxygen; carbon monoxide; CO oxidation; reaction mechanism; doped oxides; Au; Ag; Cu; Ni; Pd; Pt.

1. Introduction

Recent experiments suggest that doped oxides may be a new class of oxidation catalysts. Fu *et al.* [1,2] examined the water–gas shift reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, catalyzed by Au or Pt supported on ceria (CeO₂), and presented evidence that catalysis is performed by Au or Pt positive ions, not the Au or Pt nanoparticles. Other papers show that a catalyst consisting of Au ions on ceria [3,4], magnesia [5], alumina [6], or iron oxide [7], oxidize CO more efficiently than the neutral metal clusters on the same supports. Experiments [8–11] also show that the perovskite LaFe_{0.95}Pd_{0.05}O₃ is a better automotive catalyst than the Pd–metal clusters supported on alumina. X-ray photoelectron spectroscopy measurements indicate that, under oxidative conditions, Pd is present only as Pd²⁺ and Pd³⁺. Several other doped perovskites were shown to have good catalytic activity.

X-ray scattering measurements suggest [2,4,8–11] that the active catalyst is a doped oxide with the chemical formula $\text{M}_{1-x}\text{N}_x\text{O}_y$, where M and N are cations. If this is a general feature, these metal-doped oxides may provide a new class of promising catalysts. First, they contain less metal than catalysts consisting of supported metal clusters; when expensive metals are used, this is a considerable advantage. Second, in some cases, the catalyst resists sintering better than the supported metallic particles [8–11]. Finally, a catalytic center consisting of one ion is likely to be more sensitive to its environment than a metal cluster containing thousands of atoms; it is therefore more likely that its activity can be “tuned” by changing M and N.

Given the complexity of these systems the experimental observations are not absolutely conclusive, even though taken together they provide strong circumstantial evidence. It is therefore useful to use theory to examine the possibility that doped oxides are good oxidation catalysts and to understand the mechanism through which such catalysis proceeds.

We use density functional theory (DFT) to show that doping weakens greatly the bond of surface oxygen to the oxide, making it more reactive. We have examined rutile TiO₂(110) doped with Au, Cu, Ag, Pt, Pd, and Ni and CeO₂(111) doped with gold. We present here the results for Au_xTi_{1-x}O₂, as a model oxide and CO oxidation as a test reaction. CO oxidation by neutral Au particles supported on various oxides was studied extensively both experimentally and theoretically [12–15]. However, we are not aware of any theoretical study of CO oxidation by a doped oxide. We have selected TiO₂(110) because it is a widely used support and we wanted to see if the experimental observations made on ceria are valid for other oxides.

2. Computational details

We have performed periodic spin-unrestricted DFT calculations by using a generalized gradient approximation [16,17] and the VASP program [18–21]. The ionic cores were described by scalar relativistic ultrasoft pseudopotentials [22] allowing 6, 10 and 11 “valence” electrons for O, Ti, and Au atoms, respectively. The cutoff in the plane wave expansion was 396 eV. We sampled the Brillouin zone at the Γ -point only and allowed fractional occupancy of the bands using the Gaussian smearing method and a window of 0.05 eV.

*To whom correspondence should be addressed.

E-mail: metiu@chem.ucsb.edu

Monopole, dipole and quadrupole corrections to the energy were taken into account using a modified version of the method proposed by Makov and Payne [23]. The pure and doped $\text{TiO}_2(110)$ surface were modeled by a $[3 \times 2]$ supercell and a vacuum space of 17 Å. All the structures were completely relaxed except the bottom triple-layer of $\text{TiO}_2(110)$, which was kept fix to the bulk position. Many starting structures, corresponding to the adsorption of O_2 , CO, and CO_2 on a stoichiometric and on a reduced doped rutile $\text{TiO}_2(110)$ surface, have been fully optimized without symmetry constraints by using a conjugated gradient algorithm [24]. The transition states were located using the nudged elastic band method [25].

3. Results and discussion

X-ray diffraction measurements, performed on the gold-doped ceria, have shown that the CeO_2 lattice is slightly expanded, which suggest that Au substitutes a Ce ion [1,2,4]. The same observation holds for Pd-doped LaFeO_3 perovskite [11]. Given this information, we decided to study a system in which a Au atom substitutes a Ti one.

We have calculated the energy of a series of 15 layers (5 triple-layers) $\text{TiO}_2(110)$ slabs with Au substituting a five-coordinated (5c-Ti) or a six-coordinated Ti (6c-Ti) atom in the first, second or third atomic layer. The slab in which Au substitutes a 5c-Ti atom in the surface layer (figure 1a) has the lowest energy; the energy of the others is higher by at least 1.4 eV. Because of this, we have studied only the catalytic activity of the slab in which Au substitutes a 5c-Ti atom in the surface layer of a 12 layers (4 triple-layers) $\text{TiO}_2(110)$ slab [26].

To determine to what extent the oxide becomes a better oxidant when doped with Au, we have calculated the energy (E_{vf}) required for removing one of the oxygen atoms to form a vacancy in the surface layer and half an oxygen molecule in the gas phase. The oxygen atoms 1 and 2 are bridging oxygens and 3 to 6 are in-plane oxygens (see figure 1a). For the Au-doped surface, the values of E_{vf} are 1.57 eV(O1), 1.92 eV(O2), 2.05 eV(O3), 2.43 eV(O4), 2.58 eV(O5), and 2.62 eV(O6). For the stoichiometric, undoped rutile $\text{TiO}_2(110)$, E_{vf} of the bridging oxygen is 3.7 eV and that of the in-plane oxygen is 4.8 eV. Doping weakens dramatically the bond of surface oxygen to the oxide, even when a Ti atom is substituted by Au in the slab sub layer (not shown). We obtained very similar results for $\text{Au}_x\text{Ce}_{1-x}\text{O}_2$ [27]. Moreover, doping TiO_2 with Pt, Pd, Cu, Ni and Ag weakens the bond of the surface oxygen to the oxide even more than doping with Au (see table 1).

It may seem strange that Cu or Ni are capable of weakening the bond of the surface oxygen to the oxide, more than Au, even though the Cu and Ni oxides are more stable than those of Au (Cu and Ni have higher

affinity for oxygen than Au). This happens for several reasons. First, Cu and Ni are not capable of making compounds with the formal charge of 4+ and the oxygen surrounding them (when they are dopants) see an electron deficit, which weakens their ability to bond. In addition, the dopant–oxygen coordination is that of TiO_2 and this is different from that in Ni, Cu or Au oxides. This is likely to affect strongly the manner in which the dopant bonds to the oxygen. Finally, an additional cause for change in the binding energy is the change in the size of the ion, as compared to that of Ti.

Our results suggest that the Au-doped TiO_2 is a stronger oxidant than the pure oxide or the one with a neutral Au cluster on it. On the pure $\text{TiO}_2(110)$ surface, E_{vf} is larger than the exothermicity of the CO_2 formation ($\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$) and the clean $\text{TiO}_2(110)$ surface does not oxidize CO at low temperature [28]. On the other hand, CO oxidation by using any one of the four oxygen atoms of the $\text{Au}_x\text{Ti}_{1-x}\text{O}_2$ surface is exothermic; on this surface CO oxidation is thermodynamically favored.

On the $\text{Au}_x\text{Ti}_{1-x}\text{O}_2(110)$, CO binds most strongly to the oxygen atoms most weakened by the presence of gold, and forms an adsorbed CO_2 molecule (see figure 1b). The desorption energies of the CO_2 formed by CO binding to the oxygens O1, O2, and O3, are 0.2, 0.3, and 0.1 eV, respectively.

While CO adsorption and CO_2 desorption produce the desired product, this reactions is not catalytic because it removes irreversibly oxygen from the surface. To have a catalyst we must find how gas-phase oxygen fills the oxygen vacancies formed by CO_2 desorption. Because of this, we examine oxygen chemistry on the Au-doped TiO_2 next. There are a lot of similarities between the adsorption of O_2 on a pure and Au-doped $\text{TiO}_2(110)$ surface. In both cases, O_2 adsorbs only on the reduced surface (i.e., having oxygen vacancies), prefers to bind at the location of a missing bridging oxygen (see figure 1d), and its dissociation (after adsorption) is endothermic. However, O_2 binds more weakly on an bridging-oxygen vacancy on the Au-doped ($D_e[\text{O}_2] = 0.68$ eV) than on a pure $\text{TiO}_2(110)$ surface ($D_e[\text{O}_2] = 2.80$ eV).

After adsorption, the oxygen molecule reacts with gas-phase CO to form a “carbonate” (figure 1e), with a very substantial release of energy (about 4 eV). This complex decomposes to release CO_2 and leaves behind an oxygen atom that fills the vacancy. This restores the surface to its initial state, which means that this set of reactions is catalytic.

Some experiments find that the doped oxide catalyst is reduced by CO to form neutral gold. Others find that the system is stable [1,2]. The stability of the doped oxide depends on the method of preparation and the composition of the reacting gases [1,2]. Our calculations shed some light on the possible mechanism of Au reduction during the reaction. After the surface oxygen 1 is removed, the surface oxygen 2 can react with CO, to form a CO_2 molecule, which desorbs from the

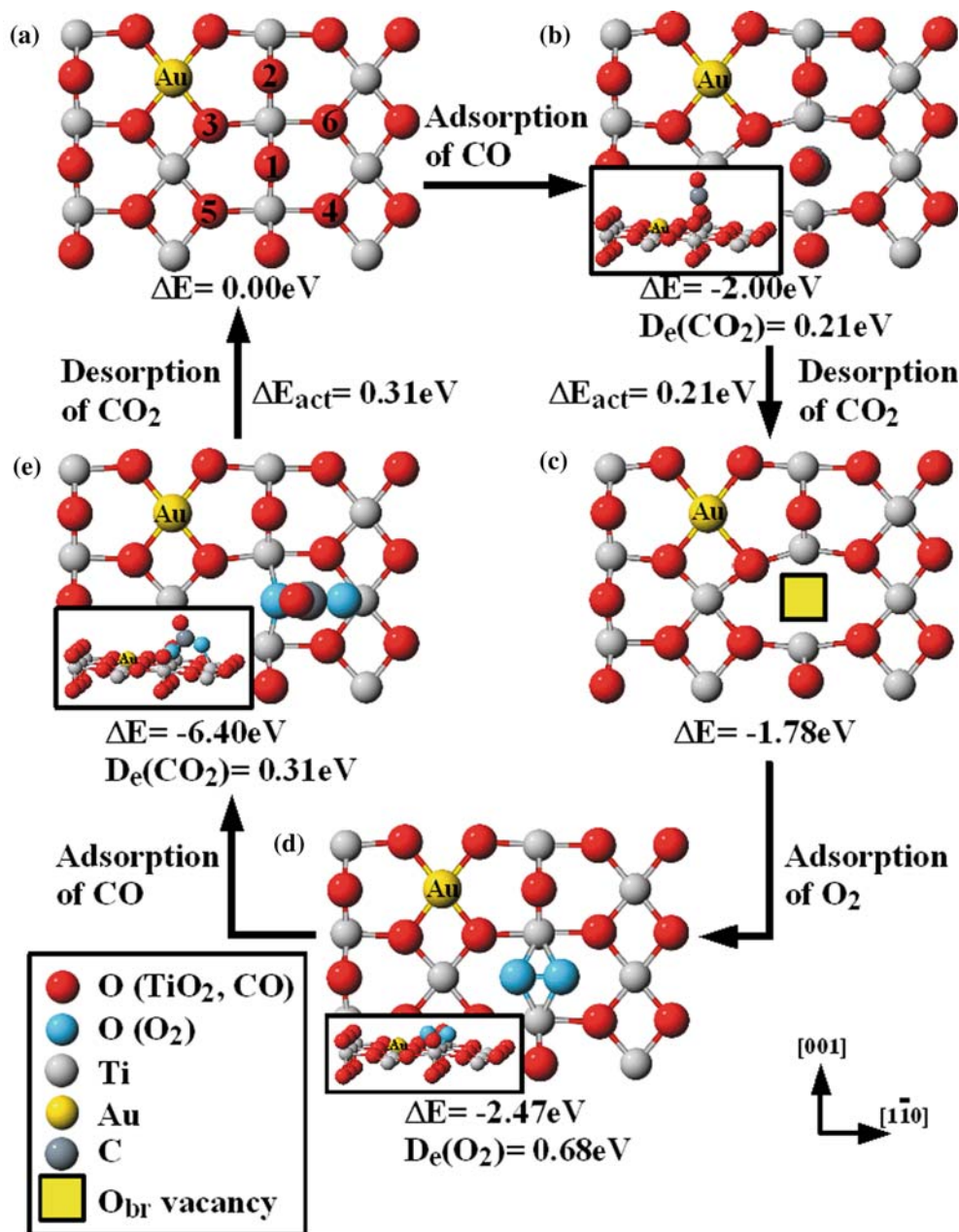


Figure 1. CO oxidation by Au-substituted rutile $\text{TiO}_2(110)$, $\text{Au}_x\text{Ti}_{1-x}\text{O}_2$. D_e and E_{act} are the desorption and the activation energies. The relative energies, ΔE , are computed relative to the sum of the energies of $\text{Au}_x\text{Ti}_{1-x}\text{O}_2$, one O_2 and two CO molecules. Nudge-elastic band calculations [25] indicate that the desorption energy of CO_2 is the only contribution to the activation energies reported here.

surface, leaving behind a second bridging-oxygen vacancy. The latter process is exothermic by 0.79 eV. We propose that removing two oxygen atoms from the surface facilitates the conversion of the ion to a neutral Au atom. Since the neutral atoms on oxide surfaces are mobile, it is likely that they will migrate on the surface and form gold clusters. This suggests that stability is achieved if the annihilation (the oxidation) of the vacancy formed by the removal of oxygen one is faster than the formation of a vacancy by removal of oxygen 2. Experiments show that this balance is achieved when the

water-gas shift reaction [1,2] or CO oxidation [4] is performed on Au-doped ceria.

Table 1 shows that doping titania with copper produces the greatest weakening of the oxygen-oxide bond. This does not necessarily mean that $\text{Cu}_x\text{Ti}_{1-x}\text{O}_2$ is the best oxidation catalyst. A good catalyst in this class must strike a balance between the ability to donate an oxygen atom during oxidation, and that of taking oxygen from the gas phase to heal the oxygen vacancy formed by the oxidation reaction. One may presume that a dopant that makes it very easy to remove oxygen,

Table 1

Energy cost associated with the desorption of lattice oxygen atom, to form half an oxygen molecule in the gas phase, for pure and metal-doped rutile $\text{TiO}_2(110)$ surfaces

	Bridging oxygen (O1)*	In-plane oxygen (O3)*
Pure rutile $\text{TiO}_2(110)$	3.72	4.78
Cu-doped $\text{TiO}_2(110)$	0.64	1.21
Ag-doped $\text{TiO}_2(110)$	0.73	1.23
Au-doped $\text{TiO}_2(110)$	1.57	2.05
Ni-doped $\text{TiO}_2(110)$	1.02	1.53
Pd-doped $\text{TiO}_2(110)$	0.89	1.90
Pt-doped $\text{TiO}_2(110)$	1.26	2.47

*See figure 1a for definition.

will slow down the annihilation of the oxygen vacancy. Moreover, a too rapid removal of the oxygen atoms will compromise the stability of the catalyst, by formation of neutral dopant atoms. A good oxidation catalyst in this class of compounds requires a fine balance between the rate of oxide reduction and oxidation.

We conclude with a note of caution regarding the accuracy of GGA-DFT calculations for oxide chemistry. The essential elements of the oxidation mechanism proposed here involve the weakening, by the dopant, of the bond between the oxygen atoms in the top surface layer and the oxide, and the reactivity of the oxygen vacancy and of the molecules adsorbed at an oxygen vacancy site. It is well known that density functional theory does not describe correctly the electronic structure of transition metal and rare-earth oxides. Theory predicts that these compounds are metals, while experiments show them to be antiferromagnetic Mott insulators. The error is caused by the electron self-interaction in DFT, which favors the delocalization of the electron in the d- or f-bands where the electron should be localized on individual atoms. When an oxygen vacancy is created, two electrons that used to be “tied up” up in the metal–oxygen bond are left behind in the vacancy. If the Kohn-Sham states created by vacancy formation consist of hybrids involving narrow d- or f-bands, it is likely that DFT will spread the electrons left behind around the vacancy, rather than localize them on the metal ion to diminish its charge (e.g., to turn two Ti^{4+} ions into Ti^{3+}). A similar effect is suspected when we replace an ion of the host oxide with an ion of different charge. In the case when the dopant has a lower charge than the ions of the host (e.g., Au^{3+} replacing Ti^{4+} in TiO_2) the oxygen atoms surrounding the dopant “see” an electron deficit (a hole). DFT will tend to spread this hole among several atoms, while a correct theory might tend to localize it on one of the oxygen atoms (forming a system that a chemist would formally describe as $\text{Au}^{3+} - \text{O}^-$). A thorough analysis of a similar situation can be found in an excellent paper by Pacchioni *et al.*[29]. At this time it is not clear whether these errors in the nature of the Kohn-Sham states

cause substantial errors in binding energies. After all, these states are only supposed to provide the correct density and, strictly speaking, were not meant to describe the “electronic structure.” There are many examples in which the Kohn-Sham states give the wrong band gap but describe, nevertheless, adsorbate binding energies correctly. As far as the present study is concerned, we note that our qualitative conclusions will not change even if the numerical values provided by DFT are off by 0.5 eV or more. In spite of the uncertainty surrounding the GGA method, we believe that three of our qualitative conclusions are fairly safe: (1) Doped oxides are an interesting class of oxidation catalyst, worth exploring by experiments; (2) The oxidation takes place by a Mars-van Krevelen mechanism; (3) Conclusions based on energy differences (such as a TiO_2 doped with Cu is easier to reduce than when doped with Au) are likely to be correct. While the accuracy of the DFT for the processes described here deserves further study, we believe that GGA-DFT results can be used for asking qualitative questions that do not rely on obtaining accurate values for the energies.

Acknowledgments

This work was supported by the Air Force Office of Scientific Research through a Defense University Research Initiative on Nanotechnology. Computer resources were provided by the California NanoSystems Institute through an NSF Grant (CHE-0321368). We gratefully acknowledge useful discussions with Ju Chou and Eric McFarland.

References

- [1] Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science* 301 (2003) 935.
- [2] Q. Fu, W. Deng, H. Saltsburg and M. Flytzani-Stephanopoulos, *Appl. Catal. B* 56 (2005) 57.
- [3] J. Guzman, S. Carrettin and A. Corma, *J. Am. Chem. Soc.* 127 (2005) 3286.
- [4] A.M. Venezia, G. Pantaleo, A. Longo, G. Di Carlo, M.P. Casaletto, F.L. Liotta and G. Deganello, *J. Phys. Chem. B* 109 (2005) 2821.
- [5] J. Guzman and B.C. Gates, *J. Am. Chem. Soc.* 126 (2004) 2672.
- [6] J.T. Calla and R.J. Davis, *Catal. Lett.* 99 (2005) 21.
- [7] N.A. Hodge, C.J. Kiely, R. Whyman, M.R.H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram and S.E. Golunski, *Catal. Today* 72 (2002) 133.
- [8] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto and N. Hamada, *Nature* 418 (2002) 164.
- [9] H. Tanaka, N. Mizuno and M. Misono, *Appl. Catal. A* 244 (2003) 371.
- [10] H. Tanaka, I. Tan, M. Uenishi, M. Kimura and K. Dohmae, *Top. Catal.* 16/17 (2001) 63.
- [11] H. Tanaka, M. Taniguchi, N. Kajita, M. Uenishi, I. Tan, N. Sato, K. Narita and M. Kimura, *Top. Catal.* 30/31 (2004) 389.
- [12] G.C. Bond, *Catal. Today* 72 (2002) 5.
- [13] H. Haruta and M. Date, *Appl. Cat. A* 222 (2001) 427.
- [14] M. Haruta, *Gold Bull.* 37 (2004) 27.

- [15] R. Meyer, C. Lemire, S.K. Shaikhutdinor and H.-J. Freund, *Gold Bull.* 37 (2004) 72.
- [16] 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 (1992) 6671.
- [17] J.P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B* 54 (1996) 16533.
- [18] G. Kresse and J. Hafner, *Phys. Rev. B* 47 (1993) 558.
- [19] G. Kresse and J. Hafner, *Phys. Rev. B* 49 (1994) 14251.
- [20] G. Kresse and J. Furthmuller, *Phys. Rev. B* 54 (1996) 11169.
- [21] G. Kresse and J. Furthmuller, *Comput. Mater. Sci.* 6 (1996) 15.
- [22] D. Vanderbilt, *Phys. Rev. B* 41 (1990) 7892.
- [23] G. Makov and M.C. Payne, *Phys. Rev. B* 51 (1995) 4014.
- [24] W.H. Press, S.A. Teukolsky, W.T. Flannery and B.P. Vetterling, *Numerical Recipes in Fortran: The Art of Scientific Computing* (Cambridge University Press, Cambridge, 1992).
- [25] H. Jónsson, G. Mills and K.W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations: Proceedings of the International School of Physics "Computer Simulation of Rare Events and the Dynamics of Classical and Quantum Condensed-Phase Systems"*, B.J. Berne, G. Cicotti and D.F. eds, Coker (World Scientific Publishing Company, Singapore, 1998) ch. 18.
- [26] The results report for the remaining of the paper were obtained on a slab composed of 12 layers (4 triple-layers) in order to reduce the computational cost associated with the 15 layers slab. The energy to form a bridging oxygen vacancy in $\text{Au}_x\text{Ti}_{1-x}\text{O}_2(110)$ oscillates with the slab thickness, as it does for the undoped oxide (see Ref. 28). However, regardless of slab thickness doping produces a dramatic lowering of the energy to form a vacancy and variations due to slab thickness do not alter our qualitative conclusions.
- [27] V. Shapovalov and H. Metiu, In preparation (2005).
- [28] X.Y. Wu, A. Selloni and S.K. Nayak, *J. Chem. Phys.* 120 (2004) 4512.
- [29] G. Pacchioni, F. Frigoli, D. Ricci and J.A. Weil, *Phys. Rev. B* 63 (2001) 054102.