Abstract

We have calculated the adsorption energy of carbon monoxide on a monolayer of copper adsorbed on the (111) face of cubic zirconia. We investigate the structural parameters of three phases of bulk zirconia (cubic, tetragonal, and monoclinic) and find excellent agreement with experiment. We have also analyzed the structural relaxation of both the stoichiometric and reduced (111) surfaces of cubic zirconia (c-ZrO$_2$). For adsorption of copper on c-ZrO$_2$, we find that the preferred binding site is atop the terminal oxygen atom, favored by 0.3 eV over other high symmetry sites. We compare CO adsorption on zirconia-supported copper to the results of carbon monoxide on copper (100) (S. P. Lewis and A. M. Rappe, J. Chem. Phys. 110, 4619, (1999).) and show
that adsorption on oxide-supported copper is over 0.2 eV more stable than adsorption on the bare surface.

82.65.My, 71.15.Mb, 82.65.Jv
I. INTRODUCTION

Oxide-supported transition metals have received much attention due to their utility in automotive catalysis and other catalytic processes. Use of an oxide as a support material for transition metals has clear economic benefits because this reduces the amount of costly noble metals (e.g., Rh, Pt) that need to be used in functioning catalysts. Moreover, the ability of the support material to contribute oxygen to chemical reactions can significantly enhance many catalytic mechanisms. Zirconium dioxide (or zirconia) is a technologically important catalytic support medium. This material has many other applications, as well, including gas sensors, solid fuel cells, and high durability coatings.

Copper has recently been identified as an important catalytic agent for NO reduction and CO oxidation. For instance, Cu-ion exchanged zeolites such as Cu/ZSM-5, alumina-supported CuO and ZrO$_2$-supported copper all exhibit high activity for the catalytic promotion of NO$_x$ reduction by CO (forming N$_2$ and CO$_2$). An attractive quality of the Cu/ZrO$_2$ system is its unusually high catalytic activity for the NO-CO reaction at very low temperatures (100-200°C).

Because of the interest in Cu/ZrO$_2$ as a part of the next generation of automotive catalysts, we have performed a series of ab initio calculations to study the energetics of molecular adsorption on this surface. Although there have been previous theoretical studies of bulk ZrO$_2$ and a recent thorough investigation of ZrO$_2$ surfaces, this investigation is the first to study molecular adsorption onto metal films on this surface. To the best of our knowledge, this is also the first ab initio study of oxide-supported metal chemisorption. A monolayer of copper was chosen for several reasons. The monolayer geometry can be conveniently determined theoretically, and we believe that it can be reproducibly prepared experimentally. Adsorption onto a monolayer of copper also forms the starting point for systematic studies of clusters of atoms on surfaces. Furthermore, interactions of molecules with individual atoms in a copper monolayer makes contact with zeolite systems. To aid in interpretation, we also make a direct comparison between adsorption onto Cu/ZrO$_2$
and onto the bare Cu(100) surface.\textsuperscript{17}

\section*{II. METHOD}

All calculations in this study use density functional theory\textsuperscript{18,19} (DFT) within the plane-wave pseudopotential\textsuperscript{20} method to determine all structural parameters and energies. Optimized pseudopotentials\textsuperscript{21} for all elements were constructed to be well converged for a 50 Ry plane wave cut-off energy.

For structural parameters, the local density approximation (LDA)\textsuperscript{22} of DFT gives highly accurate results for most bulk and surface systems. Typically, the optimal computed parameters are within 1\% of the experimental values. However, for adsorption energies, the generalized gradient approximation (GGA)\textsuperscript{23} typical yields significantly more accurate results. To obtain GGA results for the adsorption energies of copper and carbon monoxide on the substrate we take a hybrid approach. First, the structure is fully relaxed within the LDA (i.e., the atoms are moved until all atomic forces are less than 0.01 eV/Å). Second, the GGA energy of the optimal configuration is obtained from the ground-state charge density of the LDA calculation. This hybrid approach yields significantly more accurate adsorption energies than LDA calculations alone; for most systems, this approach gives results very close to fully self-consistent GGA calculations\textsuperscript{24}.

For bulk systems, Monkhorst-Pack\textsuperscript{25} special $k$-point sets were used for Brillouin zone integrations. For the bulk cubic system, calculations using 10 irreducible $k$-points gave convergence error of less than 1 meV per unit cell. Similar convergence criteria were used for the other bulk systems. For calculations involving the (111) surface unit cell, we used the Ramírez-Böhm\textsuperscript{26} $k$-point sampling method and found that convergence was obtained with 3 irreducible $k$-points.

\section*{III. RESULTS AND DISCUSSION}
A. Bulk Zirconia

The ground-state phase of zirconia—baddeleyite—has a very complex monoclinic structure ($m$-$ZrO_2$) with nine internal degrees of freedom and four formula units per primitive cell. Each Zr cation is 7-fold coordinated by oxygen in the monoclinic phase. The structure can be viewed as alternating layers of Zr and O with the coordination of the O atoms alternating between 3 and 4 from one oxygen layer to the next.

At about 1400 K, a first-order martensitic phase transition occurs, yielding the tetragonal phase ($t$-$ZrO_2$). The tetragonal form of zirconia can be viewed as a simple distortion of the cubic fluorite structure, with alternating columns of oxygen atoms along one crystallographic axis shifting upward or downward by an amount $d_z$. This structure is described by two lattice constants, $a$ and $c$, and it has two formula units per unit cell.

Above about 2650 K, zirconia assumes the cubic fluorite structure ($c$-$ZrO_2$). In this phase there are only two degrees of freedom: the lattice constant, $a$, and an internal coordinate, $u$, reflecting the positions of the oxygen atoms along the body diagonal of the cubic cell. For the ideal fluorite structure, the value of this coordinate is 0.25. The cubic structure can be stabilized at room temperature by incorporation of a few percent of $Y_2O_3$. Addition of cation impurities also improves the thermochemical properties substantially, giving the cubic phase extremely high strength and thermal-shock resistance.

Table 1 shows the optimized structural parameters for the monoclinic, tetragonal and the cubic phase of bulk zirconia (see Fig. 1). All computed values are in excellent agreement with experiment.

B. Cubic Zirconia (111) Surface

Table 2 shows the relaxation data for two (111) surfaces of $c$-$ZrO_2$: the stoichiometric and the fully reduced (i.e., top layer of oxygen removed) surfaces. The stoichiometric surface shows an outward relaxation of the top oxygen-zirconium spacing and a significant reduction
in the oxygen-oxygen interlayer spacing between the two outermost layers of ZrO₂ formula units. For the reduced surface, removal of the top layer of oxygen changes these relaxations dramatically. We predict a huge (24.4%) inward relaxation of the top zirconium-oxygen spacing and a reversal in the relaxation of the oxygen-oxygen spacing between the top two layers of formula units. Our calculations show a large energetic cost of 9.4 eV/atom for completely reducing the (111) surface. The possibility of surface reconstructions has not been considered in this study. A detailed study of many zirconia surfaces can be found in reference 16.

C. Copper on α-Zirconia

Before investigating the chemisorption of CO on zirconia supported copper, we first determine the preferred binding site for copper on (111) c-ZrO₂. There are three high-symmetry positions on this surface: the top oxygen site (O1), the three-fold hollow site directly above the zirconium atom (Zr), and the hollow site above the subsurface oxygen atom in the top ZrO₂ formula unit (O2). Table 3 shows the GGA binding energies for a monolayer of copper centered on each of these three sites. As shown in the table, the O1 site is preferred by about 0.3 eV/atom over the other possible sites.

It is important to compare the binding energy of copper on the c-ZrO₂ surface with the cohesive energy of bulk copper. Since the cohesive energy is nearly twice the adsorption energy of copper on c-ZrO₂, the oxide-supported copper monolayer is, at best, a metastable configuration. Annealing this monolayer would result in the formation of copper particles on the oxide surface.

D. CO on Cu on ZrO₂(111) with comparison to CO on Cu(100)

With the preferred binding site of copper determined, the binding energy of carbon monoxide on the oxide-supported monolayer of copper can now be calculated. Table 4 shows the GGA binding energy and the relaxed structural parameters of carbon monoxide
on the oxide supported copper monolayer. It is illustrative to compare the binding energy of carbon monoxide on zirconia-supported copper to the binding energy of a half monolayer of carbon monoxide on the Cu(100) surface\textsuperscript{17}. As seen in Table 4, the nearest-neighbor distance of CO molecules is very similar for these systems.

Our computations reveal that the binding energy of CO on zirconia-supported copper is nearly 0.2 eV greater than that of CO on the Cu (100) surface. This is most likely due to charge transfer from the copper atoms to the zirconia substrate. It has been shown experimentally\textsuperscript{28} that the Cu-CO chemisorption bond is dative, resulting from charge transfer from the weakly anti-bonding $5\sigma$ orbital of the CO molecule to the metal conduction bands. This process is therefore enhanced due to the presence of the strongly electronegative oxide substrate.

**IV. CONCLUSIONS**

We have computed the bulk parameters of monoclinic, tetragonal and cubic zirconia which are in excellent agreement with experiment. Our surface relaxation data for the stoichiometric (111) $c$-ZrO$_2$ surface shows an outward relaxation of the top layer of oxygen. This may be related to the propensity of the ZrO$_2$ top-site oxygen atoms to participate in surface chemical reactions. Furthermore, we have found that the preferred binding site for copper on the $c$-ZrO$_2$ (111) surface, by 0.3 eV/atom, is atop the surface oxygen atom. We have calculated the adsorption energy of CO on an oxide-supported monolayer of copper. Comparing our results to that of CO on Cu (100), we find that the presence of the support increases the binding energy by over 0.2 eV/molecule.

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FIG. 1. Unit cells for cubic, tetragonal monoclinic ZrO$_2$. Oxygen atoms are white, zirconium atoms are grey.

FIG. 2. Top and side view of the (111) $c$-ZrO$_2$ surface. Copper atoms were adsorbed to the sites listed (O1, O2 and Zr).
| Parameter | This Work | Experiment\textsuperscript{a} |
|-----------|-----------|-----------------------------|
| \textbf{Cubic} | | |
| $a$ | 5.043 | 5.090 |
| $u$ | 0.260 | 0.275 |
| \textbf{Tetragonal} | | |
| $a$ | 5.047 | 5.050 |
| $c$ | 5.127 | 5.182 |
| $d_z$ | 0.043 | 0.0574 |
| \textbf{Monoclinic} | | |
| $a$ | 5.226 | 5.317 |
| $b$ | 5.082 | 5.150 |
| $c$ | 5.229 | 5.212 |
| $\theta$ | 99.18° | 99.23° |
| $x_{Zr}$ | 0.2107 | 0.2083 |
| $y_{Zr}$ | 0.2778 | 0.2754 |
| $z_{Zr}$ | 0.0417 | 0.0395 |
| $x_{O1}$ | 0.3303 | 0.3317 |
| $y_{O1}$ | 0.0771 | 0.0700 |
| $z_{O1}$ | 0.3500 | 0.3447 |
| $x_{O2}$ | 0.4824 | 0.4792 |
| $y_{O2}$ | 0.4477 | 0.4496 |
| $z_{O2}$ | 0.7588 | 0.7569 |

\textsuperscript{a}Reference 27
TABLE II. Relaxation data for the (111) surface of cubic zirconia, stoichiometric and reduced. Data are listed as the percent deviation from the bulk terminated interlayer spacing.

| Spacing    | Stoichiometric | Reduced |
|------------|----------------|---------|
| $\Delta_{O-Zr}$ | +5.89          | —       |
| $\Delta_{Zr-O}$ | -0.03          | -24.4   |
| $\Delta_{O-O}$ | -3.88          | +4.70   |
| $\Delta_{O-Zr}$ | +1.14          | +0.70   |
| $\Delta_{Zr-O}$ | +0.62          | -1.63   |
| $\Delta_{O-O}$ | -0.12          | +0.08   |

TABLE III. Binding energies of copper at various sites on the (111) surface of cubic zirconia

| Site  | Binding Energy(eV/atom) |
|-------|-------------------------|
| O1    | 1.8                     |
| Zr    | 1.5                     |
| O2    | 1.3                     |
| Bulk Cu | 3.5                  |

TABLE IV. Structural data and binding energies of CO on Cu (100) and zirconia supported copper

| Parameter               | CO-Cu-ZrO$_2$ | CO-Cu(100) |
|-------------------------|---------------|------------|
| Binding energy(eV)      | 0.86          | 0.65       |
| CO-CO distance (Å)      | 3.61          | 3.56       |
| C-O bond length (Å)     | 1.140         | 1.139      |
| Cu-CO bond length (Å)   | 1.801         | 1.852      |