



Theoretical study on the reactivity of the surface of pure oxides: The Influence of the support and oxygen vacancies

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ABSTRACT

The surface reactivity of three oxides widely used as heterogeneous catalysts, CeO₂ (ceria), Ga₂O₃ (gallia), and ZnO, with CO, CO₂, and H₂ was investigated. The most stable perfect (dehydroxylated) oxide surfaces, surfaces that contain oxygen vacancies, and monolayers of Ga₂O₃ and ZnO epitaxially grown over CeO₂(111) were investigated using DFT calculations. As expected, CO₂ exhibited the highest adsorption energies on almost every surface. The only observed exceptions were the ZnO surfaces, viz., the ZnO(0001) perfect surface and a ZnO monolayer grown on ceria, with which the CO molecule interacts more strongly and generates CO₂ species. In contrast, H₂ interacts weakly with the majority of the surfaces, with the exception of gallia/ceria, where this molecule dissociates. The oxides become considerably more reactive when oxygen vacancies are present on the surface. The reactivity of the CeO₂(111) and Ga₂O₃(100) surfaces that contain oxygen vacancies increases up to ten-times with respect to the perfect surfaces. In addition, both Ga₂O₃ and ZnO also exhibit an important increase of their reactivity when they are supported on ceria. Thin films of these oxides that are epitaxially grown onto ceria surfaces have shown to be highly suitable catalysts for oxidizing CO and CO₂ molecules and for dissociating the H₂ molecule.

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1. Introduction

The last UN Climate Change Conferences have confirmed that conventional fossil fuels (petroleum, carbon, and natural gas) will remain as the predominant source of energy used by mankind during this century [1]. These conferences have clearly indicated that the atmospheric accumulation of CO₂ and the consequent greenhouse effect are crucial issues that require immediate action. In this respect, the signing countries have pledged to reduce CO₂ emissions and to search for new alternatives to mitigate the impacts from the combustion of fuels.

The capturing and recycling of CO₂ via chemical processes to create to carbon-neutral liquid fuel derivatives or hydrogen vectors, such as methanol and dimethyl ether, has now become a viable alternative [2,3]. Methanol reforming is particularly suitable for supplying this ubiquitous feedstock to fuel cells [4].

These processes demand novel, multifunctional catalytic materials. Precious metals supported on medium to high-surface area oxides (with or without added promoters) remain the preferred choices. To synthesize methanol from carbon oxides, such

as CO and/or CO₂, Baltanás and co-workers developed ultra-disperse Pd/silica-promoted catalysts capable of hydrogenating CO/H₂ (Ca–Pd/silica) or CO₂/H₂ (Ga–Pd/silica) mixtures [5–8]. These developments followed the finding by Fujitani et al. that palladium deposited on gallium oxide (Pd/Ga₂O₃) was 20 times more active for producing methanol from CO₂/H₂ than the traditional Cu/ZnO catalyst [9]. Indeed, the actual role of Ga₂O₃ (usually known as ‘gallia’, which is a reducible oxide) in the process subsequently became of the utmost interest [10].

Likewise, the excellent properties of CeO₂ (common name ‘ceria’) for transporting oxygen and its redox ability to easily inter-change between the Ce⁴⁺ and Ce³⁺ oxidation states have been known for several decades [11,12]. Ceria is currently used in several electronic applications, such as gate dielectrics and photovoltaic cells [13,14], and it is used as a component of ion conducting films in fuel cells [15]. Ceria is also recognized as a versatile material in modern heterogeneous catalysis, notably as a key component of the three-way catalysts (TWCs), in which this oxide has proven to be highly effective for the conversion of noxious car exhaust gases [16]. The epitaxial coverage of ceria with gallia, for instance, could lead to novel catalytic materials that have unique selectivity and/or activity in processes where carbon oxides are involved.

Considering that the generation of methanol from CO, CO₂ and H₂ molecules first requires the adsorption of the molecule(s) onto

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the surface of the catalyst, we have performed a systematic analysis of the interactions of these molecules with different ceria, gallia and ZnO surfaces. Specifically, with the objective of obtaining a broad database to gain in-depth knowledge about the surface adsorptive properties of these materials, we have focused on the molecular interactions of these gaseous reactants with the $\text{CeO}_2(111)$, $\text{CeO}_2(331)$, $\text{Ga}_2\text{O}_3(100)$ and $\text{ZnO}(0001)$ dehydroxylated surfaces that exhibit the most stable faces [17,18] using DFT calculations. The influence of surface oxygen vacancies on the reactivity and the interaction of the same molecules on epitaxial grown gallium and zinc oxides on the $\text{CeO}_2(111)$ surface were also investigated.

2. Computational details

Self-consistent density functional theory (DFT) calculations using periodic slab models were conducted to investigate the adsorption of CO, H_2 and CO_2 molecules onto the regular surfaces of $\text{CeO}_2(111)$, $\text{CeO}_2(331)$, $\text{Ga}_2\text{O}_3(100)$ and $\text{ZnO}(0001)$. The surfaces of ceria and gallia that contained an oxygen vacancy, which are subsequently designated as $\text{CeO}_2(111)$ vacO and $\text{Ga}_2\text{O}_3(100)$ vacO, respectively, were also investigated. The calculations were performed using the VASP code [19,20], in which one-electron wavefunctions are expanded on the basis of periodic plane-waves.

The PAW method [21,22] was used to represent the inner cores, and one electron states were expanded on a plane-wave basis. The kinetic energy cutoff and k -point grid values were chosen after a systematic study of the geometries and energy convergence with the k -points grid and cutoff energies for the adsorptions of CO, CO_2 and H_2 onto every investigated surface. These test calculations revealed that a kinetic cut-off energy of 415 eV was sufficient to achieve convergence for all the calculations performed in this work. Different Monkhorst–Pack grids of special k -points were employed for every case [23].

Both the local density approximation of the Vosko–Wilk–Nusair (VWN) type [24] and the PW91 [25,26] form of the generalized gradient approximation were employed. Because both the local density (LDA) and generalized gradient (GGA) approximations fail to describe the strong localization of the $4f$ electrons of Ce^{3+} , all the calculations on ceria were performed using the LDA + U and GGA + U approaches. In these cases, the Hubbard parameter (U) penalizes the double occupation of the $4f$ orbital [27,28].

The mentioned failure of DFT also could be overcome by employing hybrid functionals. Hybrid density functional calculations on CeO_2 and Ce_2O_3 led to an accurate description of both systems [29,30], but present a lot of computational problems. Among others, these calculations carried out on relatively small unit cells of slab models are computationally expensive [31,32]. A way of avoiding these difficulties is the use of LDA and GGA exchange-correlated potentials correcting the self-interaction error by means of a Hubbard-like term by explicit inclusion of an effective local two-electron one-center repulsion term, U [27,33,34]. The selection of U is not easy and the best value may depend on the studied properties, and the optimum U values for LDA and GGA can be different [35]. Loschen et al. have found that for GGA + U calculations a value of $U = 3$ eV provides a balanced description of CeO_2 and Ce_2O_3 while for LDA + U calculations a larger value of $U = 5$ eV is recommended instead [36]. Besides, for simple oxides and metals, both LDA and GGA predict lattice parameters very close to the experimental data. However, for more complex oxides or for transition metals involving heavy atoms, GGA overestimates interatomic distances; whereas LDA predicts values that are still close to experiment. In recent studies of stepped ceria surfaces [37], ceria nanoparticles [38–40], and the adsorption of Au on ceria [41], some of us suggested using the LDA + U ($U = 5$ eV) geometry while employing GGA + U ($U = 3$ eV) to obtain the energy and the electron

density. This option could present difficulties in the calculation of properties where the stress plays an important role. In addition, the employment of different approaches to the calculation of geometry and electronic properties also could be problematic in systems where they are highly related. Taking into account that the goal of this work is the study of the influence that the oxygen vacancies and the support could have on the surface reactivity and not to discuss the better methodology choice, LDA + U ($U = 5$ eV) was used to perform the geometric optimization and then single-point calculations using GGA + U ($U = 3$ eV) were performed to obtain the electronic properties of the systems.

Slab models simulate the surface from a unit cell of the atom set with periodical conditions. The size of this cell depends on the size and shape of the molecule to be adsorbed and on the surface coverage to be studied.

Periodic boundary conditions imposed on the electrostatic potential of an asymmetric slab could give rise to an artificial electric field across the slab. Therefore, because the slabs analyzed in this work are not symmetric, we conducted single-point calculations using the dipole correction to analyze possible changes in the adsorption energy values [42,43].

The total energy tolerance defining the self-consistency of the electron density was 10^{-4} eV. The structures were optimized until the maximum forces acting on each atom became less than 0.01 eV/Å.

The perfect surface of $\text{CeO}_2(111)$ and the one that contained oxygen vacancies were represented by slabs (2×2) with nine atomic layers. The perfect surface of $\text{CeO}_2(331)$ was represented by slabs (2×1) with 18 atomic layers. Stoichiometric slabs (2×2) of $\text{Ga}_2\text{O}_3(100)$ and $\text{ZnO}(0001)$ with ten and eight atomic layers, respectively, were used to simulate the perfect surfaces and the surface that contained oxygen vacancies of gallia. Finally, slabs with one layer of Ga_2O_3 and ZnO over the slab of $\text{CeO}_2(111)$ were constructed to represent gallia and ZnO epitaxially grown onto ceria. These mono-layers of Ga_2O_3 and ZnO together with the top ceria layer were fully relaxed. All the slab models were separated by more than 10 Å vacuum widths.

For the geometrical optimization, the joint relaxation of the CO, CO_2 and H_2 molecules and the top layers of the oxides was allowed.

3. Results and discussion

3.1. Reactivity of $\text{CeO}_2(111)$ and $\text{CeO}_2(331)$; $\text{Ga}_2\text{O}_3(100)$ and $\text{ZnO}(0001)$ perfect surfaces

The energies for the adsorption of CO, CO_2 and H_2 onto each of the surfaces investigated in this work are shown in Table 1. The calculated energy values for the adsorption of CO onto almost every surface without defects are very small, with the only exception of $\text{ZnO}(0001)$. For the latter case, the energy value is -1.96 eV using the LDA approach and -1.28 eV using the GGA approach. This large adsorption energy can be attributed to the formation of a CO_2 molecule due to the reaction of CO with a surface oxygen atom (see Fig. 1).

Table 2 presents the Voronoi atomic charges for each atom of the molecules after the adsorption process. On the ceria and gallia surfaces, the CO interaction is only electrostatic, and this interaction changes the charge polarity from that of the free CO; the C atom becomes positive and the O atom becomes negative. The CO molecule adopts a negative charge, and this charge is placed on the O atom (see Table 2). However, when the adsorption of CO occurs on ZnO, the charges corresponding to the formed CO_2 tend to be similar to the ones on the CO_2 free molecule (see the atomic charge values at the bottom of Table 2).

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