An ab initio study of CO adsorption on ceria(110)

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Abstract

Hartree–Fock and DFT calculations are reported for the $CO/CeO_2(110)$ surface system. The electron density, electrostatic potential, atomic charges and projected electronic density of states have been calculated from an ECP-and-point-charge-embedded cluster model and is compared with periodic calculations. The agreement between the two surface models is reasonably good. A number of weakly bonding CO adsorption sites were found, with E_{ads} (BSSE-corrected) ranging from 0.01 to 0.22 eV per adsorbed molecule. The two most favourable sites are found in the vicinity of surface cerium ions, with the CO molecule oriented in a tilted fashion, C-end down. The surface-induced CO stretching vibrational frequency shifts on these sites are a redshift of ≈ -30 cm^{-1} and a blueshift of ≈ 25 cm^{-1}, respectively.
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1. Introduction

The adsorption of CO and other small molecules such as NO, CO_2 and methanol on metal oxide surfaces has been the subject of intense research. CO adsorption on MgO and CaO, for example, has been amply investigated both experimentally and theoretically (see, for example [1–4]). For CO on ceria (CeO_2) many experimental studies exist, but few theoretical calculations. The CO/CeO_2 system is interesting in several different contexts. Ceria is an active constituent in today's car catalysts [5–7], both as an oxygen storage component and as a catalytic component, where it assists in the catalytic oxidation reactions of, for example, CO to form carbon dioxide. The oxygen storage capacity and the catalytic activity are both closely connected to the relative ease with which the cerium ions cycle between tri- and tetravalency, while oxygen vacancies form, migrate and annihilate in the material.

Infrared spectroscopy (IR) investigations have shown that CO can physisorb on ceria surfaces with small (up)-shifts of the CO stretching vibrational frequency [8–11]. But chemisorption and large CO frequency downshifts have also been found experimentally [8–15], typical for carbonate and carboxylate species with surface oxygens. An overview over the different surface species found in the CO on ceria system is given in [16].

Adsorption energies of 2.27 eV [17] and 0.22 eV [13], have been reported, suggesting that different types of CO adsorbates were probed in these two experiments. In the former, the heat of adsorption was determined from calorimetric measurements [17], in the latter from a heat of adsorption vs. carbonyl frequency shift correlation [13]. The experimental heats of adsorption in both these references refer to powder measurements and it is difficult to assign such measured heats of adsorption to one special adsorption species on one particular surface and site.

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Recent plane-wave calculations by Yang et al. [18] for CO adsorption on $CeO_2(111)$ and $CeO_2(110)$ found the formation of carbonate complexes on the (110) surface, but not on the (111) surface, where only physisorption was found. Calculated surface–molecule interaction energies for different sites were found in the range from 0.2 to 2.0 eV. As far as we are aware, the paper by Yang et al. is the only quantum-mechanical study of the CO/$CeO_2(110)$ system in the literature.

All in all, unambiguous molecular-level information concerning CO adsorption on ceria surfaces is thus lacking. Therefore, in this paper, we present LCAO-MO quantum-mechanical calculations of the adsorption of CO on an ideally terminated ceria(110) surface, modelled by embedded clusters as well as a periodic slab. The layout of the paper is as follows: First we describe the cluster model used for the clean ceria(110) surface and compare with periodic calculations. Then the CO/$CeO_2(110)$ system will be discussed, focusing on the adsorption structure and energy and on the surface-induced frequency shift of the CO stretching vibration mode.

2. Methods

2.1. Computational methods and basis-sets

The majority of both the periodic and the embedded-cluster calculations presented here were performed at the Hartree–Fock (HF) level. In addition, some density functional theory (DFT) calculations with the B3LYP functional [19,20] were performed to check the influence of electron correlation (at the B3LYP level). All cluster calculations were performed with the GAUSSIAN-03 program [21]. All periodic HF calculations were performed with the CRYSTAL-98 program [22]. For the calculations of adsorption energies, the counterpoise scheme according to Boys and Bernardi [23] was applied to correct for the basis-set superposition error (BSSE).

All cluster calculations were performed with the "*full*" basis-set, except some calculations explicitly aimed at a comparison with the periodic calculations. f functions cannot be used in the CRYSTAL-98 program, and, moreover, diffuse functions would possibly cause convergence problems due to linear dependencies, which easily occur in condensed-matter systems. Therefore, the periodic calculations (and the comparative cluster calculations) were performed with a "*reduced*" version of the *full basis-set*. In the calculations with the *full basis-set*, the $[Kr]4d^{10}$ electrons of the cerium atoms (with total electron configuration $[Kr]5s^24d^{10}5p^66s^24f^15d^1$) were described by the SBKJC [24] effective-core potentials (ECPs), and the remaining electrons were described by the corresponding SBKJC basis-set, consisting of a (6s6p3d7f) Gaussian-type basis-set contracted to [4s4p2d2f]. In the *reduced*

basis-set, the diffuse s and p functions, as well as the f functions, were removed from the full basis-set, similar to what was done by Hill and Catlow [25].

For the oxygen atoms of ceria, all eight electrons were described by a split valence basis-set, namely a (14s6p) basis contracted to [3s2p], as given by Gennard et al. [26]. This basis-set was originally derived by Causà et al. [27] and has been used successfully for bulk and surface studies of different metal oxides [26–28]. For the CO molecule, the 6-31G* basis-set by Hehre, Ditchfield and Pople [29] was used.

2.2. The periodic model

Bulk ceria crystallises in the calcium fluorite structure with a lattice constant of 5.41 Å [30]. The cerium atoms form a cubic face-centred lattice with the oxygen atoms residing in the tetrahedral holes. At the ceria(110) surface, each cerium atom loses two of its eight nearest oxygen neighbours present in the bulk and each oxygen atom loses one of its four cerium neighbours. Two models were used here to study the CO/CeO_2 interactions: a single CO molecule on top of an embedded Ce_6O_{12} cluster and a periodic CO/CeO_2 slab.

The slab model used was truly two dimensionally periodic (in the $\pm x$ and $\pm y$ directions) and finite in the third direction ($\pm z$). Fig. 1 is an illustration of the clean ceria(110) slab system (four unit cells are shown for clarity). The (110) surface and its $(\bar{1}\bar{1}0)$ equivalent are so-called type I surfaces, following Tasker's classification [31], i.e., each layer in the slab is neutral. For the
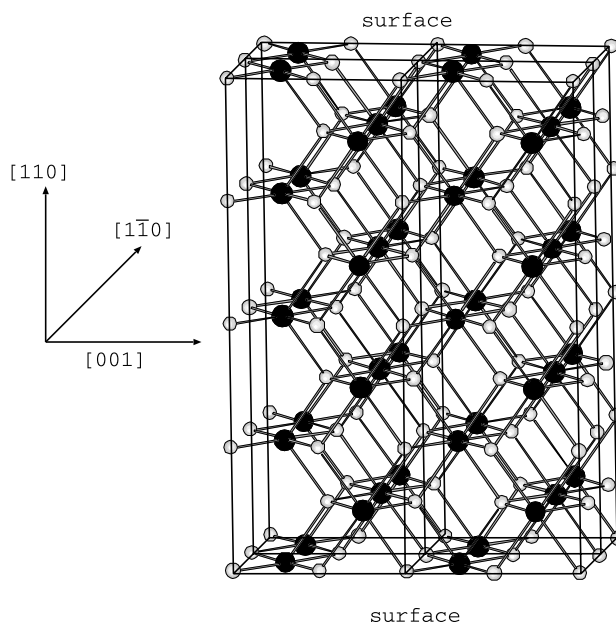

Fig. 1. The slab model used in the periodic calculations. The slab is infinite in the $\pm x$ and $\pm y$ directions with free surfaces in the [110] and $[\bar{1}\bar{1}0]$ directions. The computational cell was one of the four cells shown. The Ce atoms are dark, the O atoms light in colour.