Carbon monoxide adsorption on beryllium surfaces

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ABSTRACT

Density functional calculations are here carried out to study the carbon monoxide molecule adsorption on pristine, hydrogenated and hydroxylated beryllium Be (0001) surfaces. The adsorption energies and structures, the activation barriers to molecular adsorption and dissociation are calculated. These reactions are described in terms of potential energy surfaces and electronic density of states. The quantum results are discussed along two directions: the beryllium surface reactivity in the domain of nuclear fusion devices and the possible usage of beryllium as a catalyst of Fischer–Tropsch-type synthesis.

1. Introduction

Carbon monoxide adsorption on solid surface is very often studied because CO is a test model for adsorption on many substrates, besides, adsorption on metals plays a major role in a large number of reactive processes in heterogeneous catalysis and corrosion. These studies are almost always led on transition-metal surfaces and less often on simple metals because these metals are supposed to be less efficient in promoting chemical reactions. Nonetheless, the possible role of alkali-earth metals such as beryllium must not be ignored, whether using the metal by itself or as dopant atoms in transition metal materials [1]. One of the most famous applications of CO reaction catalyzed by metallic surfaces is the Fischer–Tropsch-type synthesis (FTS) [2–4]. FTS converts a mixture of CO and H$_2$, which can be produced from coal or natural gas, to liquid fuels such as gasoline or diesels. One of the key points of such processes is the carbon monoxide dissociation on the metal surface based on the following reaction:

$$CO_{adsorbed} \rightarrow C_{adsorbed} + O_{adsorbed}$$

After dissociation, C$_{adsorbed}$ and/or O$_{adsorbed}$ can react with the other participants of the reaction. Most often the FTS is considered on clean transition metal surfaces [5–8], but studies have also been published on H precovered surfaces [3,9]. The co-reactivity of adsorbed carbon monoxide and hydroxyl groups has also proved to be important in the electro-oxidation processes: CO may be an intermediate in the electro-oxidation reaction of methanol and other organic feedstock, which are used in fuel-cell technology [10,11]. However the toxicity of beryllium cannot be ignored and it can restrict the possible applications of this element [12].

Another area where the couple beryllium/carbon monoxide is very important is that of nuclear fusion reaction in the deuterium/tritium plasma magnetically confined in tokamaks. Beryllium was selected as the main plasma-facing material in the future international experimental fusion reactor (ITER) [13]. One of the benefits of beryllium, besides its power as a neutron multiplier material, is its ability to fix residual gases in the plasma vessel, thus improving the plasma cleanness. Oxygen, water and carbon monoxide are among the main gases poisoning the beryllium surfaces and interfering with hydrogen isotopes retention in the tokamaks.

Tritium is the fuel of the nuclear fusion reaction but it can also get trapped in the tokamak inner walls and this issue is of utmost importance for safety reasons: if the trapped tritium mass exceeds a few hundreds grams, the reactor's operation must be stopped. Hydrogen isotopes can be trapped as atoms adsorbed/absorbed in the beryllium material or as hydrogen isotopes oxides. They can even undergo most complex catalytic reactions with carbon monoxide leading to tritiated substances like aldehydes, alcohols and carboxylic acids [14–16]. It is therefore important to investigate whether beryllium is liable to catalyze such processes whose first steps may be CO adsorption then dissociation by analogy with FTS mechanisms.

In all these areas the chemistry of carbon monoxide in interaction with beryllium involves very complicated reactions and quantum calculations can be of great help in elucidating the underlying mechanisms. Very few articles have already been published on CO interaction with beryllium. However, high level ab initio calculations on Be$_n$ clusters [17] or first-principles plane-wave calculations on Be slabs [18] must be mentioned.

This paper aims to provide a new insight into this system in considering not only the interaction of CO with the clean beryllium surface (Section 3), but also with hydrogenated (Section 4) or hydroxylated surfaces (Section 5).

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2. Computational details

The calculations are performed within the framework of the spin-polarized gradient-corrected (GGA) density functional theory. The exchange as well as the correlation functionals are Perdew-Burke-Ernzerhof (PBE [19]) including a semi-empirical pairwise London damped dispersion correction (PBE-D [20–24]). A plane-wave basis set is used with an energy cutoff of 32 Rydberg (435 eV); the ionic core potential is modeled using Vanderbilt ultra-soft pseudo-potentials. Integration in the first Brillouin zone is performed using the $6 \times 6 \times 1$ points Monkhorst–Pack sampling [25]. Gaussian smearing with a width of 0.10 eV is used.

The working slab includes eleven beryllium p (3×3) Be (0001) (9 atoms) layers, nine of them being active. Such a large system is unavoidable due to the weak cohesion of the beryllium metal [26]. The adsorbed impurity perturbation can be spread over several layers in the slab, and too small a number of layers would confer a non-realistic rigidity to the system.

The stationary state structures are optimized using damped molecular dynamics. All the atoms are included in the optimization procedure, without any geometry or symmetry constraint. All the energy calculations are carried out using the *pwscf* code part of the *Quantum-Espresso* package [27].

The adsorption energies are calculated using Eq. (1):

$$\Delta E_{CO} = E(Be_{slab} + CO) - E(Be_{slab}) - E(CO_{mol}) \qquad (1)$$

where E (Be$_{slab}$ + CO) is the total energy of the full system, E (Be$_{slab}$) and E (CO$_{mol}$) are the total energies of its components.

The potential energy surfaces (PES) describing the various processes investigated in this work are built according to the method largely detailed in our previously published contributions and the reader is invited to refer to these articles [28–30].

3. CO adsorption on pristine beryllium surface

We have already shown [29] that molecular oxygen adsorbs on clean beryllium surfaces with a low but non-zero barrier. In this section we examine the 2D PESs of CO approaching the clean surface above the special symmetry points.

Carbon monoxide takes a special place in general and inorganic chemistry because of its unusual chemical properties and its very special electronic structure which is far from trivial to describe [31]. Linus Pauling, in his prophetic "Nature of Chemical Bond" [32], already described the CO electronic structure as a resonance between three configurations. The first and most often invoked one involves a triple CO bond and two electron lone pairs on C (LPC) and one on O (LPO). The second configuration features a double CO bond, one LPC and two LPOs. The last configuration would combine a single CO bond, one LPC and three LPOs. Of course, DFT is not able to reflect this multi-configuration structure, the important point for chemical reactivity is that all these models involve non-bonding lone pairs of electrons that will take part in the interaction with the solid surface. The CO molecular orbitals are presented in Fig. 1 to illustrate these points. Simply considering the shape of the molecular orbitals (MO) allows us to identify a major contribution of carbon orbitals on the 5σ MO, 1π and 1π′ are the two orthogonal delocalized π systems and 4σ includes the LPOs. The 3σ MO (not shown here) is the CO single bond and it lies much deeper in terms of energy.

According to this molecular scheme, the electronic density of states (DOS) of the monoxide taking the metal Fermi energy as reference somehow reflects this structure in 5 peaks (10 valence electrons) located respectively at −24.2 eV eigenvalue of the 3σ MO, −8.9 eV is 4σ, the −6.7 eV peak is degenerated and corresponds to the two π systems of electrons since it is built only on O and C 2p orbitals (Fig. 1). The contribution to the −3.8 eV (5σ) peak primarily comes from C (2s) and C (2p) and it includes the carbon's lone pair. Symmetrically, the 4σ peak

includes almost only O (2s) and O (2p) contributions, the signature of the oxygen's lone pair. The lowest unoccupied molecular orbitals (LUMO) are located at 2.8 eV above the beryllium Fermi level, they are the 2π* components.

1. CO parallel to the surface (bridge position):
   When approaching the surface, with the molecular axis remaining parallel to the surface plane, the monoxide first finds a very weakly bonded physisorption site whose energy is -0.03 eV, which is not significant at the level of approximation of the PBE-D method. At this point the oxygen atom is located above a superficial Be and the carbon atom is above a tetrahedral hollow site. The adsorbed monoxide is oriented likewise all along the PES surface determination.
   A barrier then occurs 2 Å above the surface (Fig. 2) with a height of 0.62 eV. The C–O distance exhibited in Fig. 2 increases continuously versus the gas phase CO bond length (1.141 Å *pwscf* calculated) thus suggesting that the loss in total energy is mainly ascribable to the adsorbed molecule undergoing the surface potential. This is true down to a distance of about 1.35 Å from the original surface. Beyond this particular point, the total energy starts decreasing without any noticeable evolution in the CO distance. The explanation is that for the CO-surface distances between 1.35 and 1.0 Å, the beryllium surface is able to adjust to the monoxide and re-arranges itself in order to stabilize the total system to some extent. The local minimum (0.06 eV in Fig. 2) shows that almost all the energy lost during the first phase has now been restored to the system. However this adjustment of the surface reaches its limits at 0.5 Å where the local maximum in energy is located (0.32 eV). Beyond this structure, the CO distance increases dramatically and goes to the extent that the bond breaks, resulting in dissociation of the adsorbed molecule and the total reaction energy is −2.56 eV. Therefore this model of dissociation involves a barrier of activation of 0.62 eV and does not include the usual step of stable molecular adsorption.
   The DOS of CO adsorbed on the surface is shown in Fig. 4A. The strong peaks at −6.3 and −7.7 eV result from the splitting of the original 1π CO peak induced by the surface potential, they interact with the substrate 2s and 2p orbitals, the oxygen atom orbitals contribute to a larger extent to these peaks. The molecular 4σ peak is stabilized by mixing with the Be energy levels and now lies at −11.4 eV, it should be considered as the Be–CO chemical bond.
   The peak at energy −2.1 eV mostly involves 2p oxygen energy levels whereas that at −0.2 eV one sees a larger contribution of C (2p). These peaks result from the original 2π* CO virtual orbital which is stabilized through interaction with Be (2s) and Be (2p). It is also worth noting that the CO 5σ energy level does not appear in the valence band of the complex, it is shifted above the Fermi level.
   At this point of the potential energy surface (PES), the electron transfer from the carbon to the surface is only 0.03 e$^-$, whereas the oxygen gains 0.01 e$^-$, on the whole the monoxide accepts 0.06 e$^-$ from the beryllium.
   Last point worth noting on this PES, after another low barrier of 0.32 eV the molecule exothermically dissociates to produce the structure displayed in the insert of Fig. 2, the oxygen and carbon atoms remain relatively close to one another and are incorporated into the surface layer. However, since the adsorbed structure is unstable, we must consider the first maximum (0.62 eV) as the barrier to dissociation.
   The total reaction energy is −2.56 eV, which is not very important for a chemical bond breaking, in fact the newly established O—Be and C—Be bonds are energetically almost equivalent to the original CO bond.
2. CO adsorption above the fcc hollow site
   On this site, carbon monoxide can interact with the beryllium surface according to two models: (i) C down i.e. closer to the surface, (ii) O down. The latter model is quite unreactive since no stationary point is found on the corresponding PES (Fig. 3): the high