

When reconstruction comes around: Ni, Cu, and Au adatoms on δ -MoC(001)



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ABSTRACT

The interaction of Au, Cu, and Ni metal atoms with the δ -MoC(001) surface was studied using periodic density functional (DF) calculations to analyze adsorption energies and equilibrium geometries, work functions, atomic charges, projected density of states (PDOS), and shifts of the transition metal *d*-band center. The atomic adsorption is found to cause an in-plane distortion of the surface, and, besides, the interaction strength turns to be coverage dependent. A lower coverage allows for a better accommodation of the adsorbate, alongside causing a *d*-band center shift to more negative energies, as shown by plots of the PDOS. Regardless of the coverage, interaction strength diminishes following the order Ni > Cu > Au. Adatom chemical activity can be inferred based on the calculated *d*-band center; Ni being the most active metal, followed by Cu, and then Au for every coverage studied. This result well correlates with experiments on other transition metal carbides. Atomic adsorption also diminishes surface work function.

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1. Introduction

The manifold technological applications of transition metal carbides (TMC) are nowadays well-known, and they have been the subject of several reviews in the last years [1,2]. For instance, such materials are currently widely used as cutting tools or covering materials, due to their extreme hardness. This feature and other important physical properties like their high electric conductivities and refractory melting temperatures have been interpreted by means of the analysis of the covalent, metallic, and ionic contributions to the chemical bonding between the transition metals and the carbon atoms [3]. From the early seventies, some other promising and more exciting possible uses of TMC captured the attention of the scientific community, including their usage as heterogeneous catalysts for industrial reactions: high activities have been found for both TMC single crystals and nanometric powders. In some cases, the TMC catalytic activity has been estimated to be higher than currently used industrial catalysts, as happened for the water gas shift reaction, where density functional (DF) calculations predicted that TiC(001) surface overtake the industrial Cu-based catalyst [4]. In the field of heterogeneous catalysis models, TMC has been explored as well as non-innocent supports for noble and coinage metal catalysts, but also as electrocatalysts in fuel cells [5]. For instance, metal clusters supported on TMC have been used for desulfurization (DeSO_x) reactions [6], hydrogenation of CO₂ to obtain methanol or methane [7], and also for oxidation reactions [8,9].

From earlier theoretical works it is found that the carbide–metal adatom interaction induces an important charge polarization in the latter [10–13], partially reducing the admetal and consequently boosting the activation of small organic or inorganic molecules adsorbed on the system [6–9,14–19]. Polarization of the electron density results in a charge accumulation in the proximity of the adsorbed transition metals, which is considered the key aspect in the enhanced catalytic activity of TMC-supported metal clusters [10]. This background is capitially important when designing new catalysts combining transition metals with TMC, together with the linear relation demonstrated among adsorption and activation energies [20]. In many cases simple computational models well-reproduced *in silico* experimental trends for adsorption energies, adsorbate geometries, and preferred adsorption sites, recovering the experimental data on the activity trends of various TMC–metal nanoparticles composite systems.

In this work we present a detailed analysis of the adsorption of single Au, Cu, and Ni atoms on the (001) surface of δ -MoC as carried out previously on a few metal–TMC combinations [10–13]. In these previous works several transition metals were tested on δ -MoC and similar carbides, such as TiC, yet only a high coverage situation was considered. Furthermore, surface relaxation was not properly taken into account, and, although hardness is a common and important feature of TMCs, it has been shown that adsorption can cause an important distortion of the surface, vital for a proper description of adsorptive processes, as found for the relaxation found when adsorbing CO on TiC(001) [21]. The choice of Ni, Cu, and Au transition metals is also motivated by recent theoretical and experimental work on CO₂ hydrogenation to methanol, catalyzed precisely by Au, Cu, and Ni supported on TiC(001) [6,19].

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Molybdenum carbides display interesting catalytic properties [2] which could be enhanced by the deposition of metals such as Ni, Cu, or Au [1]. Here it will be shown that surface reconstruction and in-plane relaxation happen to be determining when supporting metals on δ -MoC(001). In addition, adsorption energy trends and changes in surface properties such as work function or atomic charges have been identified, and connected to the most stable adsorption configurations. The single atom adsorption provides a first idea of the interactions of a certain metal to the carbide surface and, subsequently, how the support can affect the atoms in a larger cluster.

1.1. Computational details

Adsorption of Cu, Ni, and Au metal atoms has been studied using standard state-of-the-art periodic DF calculations. Four-layered slabs of δ -MoC were cut from the bulk perpendicular to the [001] direction and later on optimized. Atoms include in the uppermost 2 layers plus the adatom were fully allowed to relax whereas the two bottom layers were kept fixed at the previously optimized bulk positions [22]. Interaction between translationally repeated slabs was avoided adding 10 Å of vacuum along the [001] direction. Top image of the pristine relaxed surface is shown in Fig. 1. Note in passing that δ -MoC is a metastable phase compared to the hexagonal form. However, due to the high intrinsic stability of the (001) nonpolar surface, confirmed by its very low surface energy, it can be expected to be partially exposed.

Three different slab models have been used to represent diverse coverages. The smallest cell is a $(\sqrt{2} \times \sqrt{2})R45^\circ$ supercell exposing two Mo and two C surface atoms in a square arrangement, see Fig. 1. This latter cell has been renamed (1×1) for simplicity. The other two employed supercells for each surface are – following the above notation – (2×2) and (3×3) supercells. These permits one to scan metal coverages (θ) from 0.25 to 0.028. Following a previous computational strategy [22], we used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [23], given its suitability in describing molybdenum carbides. Calculations were carried out using the VASP computational package [24]. All calculations were carried out in a spin-polarized fashion. Valence electrons have been described using a plane-wave basis set with an associated maximum kinetic energy of 415 eV. The effect of the core electrons on the valence electron density was described using the Projector Augmented Wave (PAW) method [25]. The electron density was considered converged when subsequent energy minimization steps lead to a maximum difference of 10^{-6} eV. Similarly, structures were optimized until forces

calculated on each relaxed atom were smaller than $0.02 \text{ eV } \text{Å}^{-1}$. For an accurate evaluation of the total energy of the system a Monkhorst–Pack k-point grid of $5 \times 5 \times 1$ was used for the sampling of the first Brillouin zone on all the employed supercells.

The adsorption energy has been calculated as:

$$E_{\text{ads}} = E_{\text{M/TMC}} - E_{\text{M}} - E_{\text{TMC}} \quad (1)$$

where E_{ads} is the adsorption energy, $E_{\text{M/TMC}}$ is the energy of the supercell with the metal adatom, E_{M} is the energy of the metal atom in the vacuum, and, finally, E_{TMC} is the energy of the pristine carbide slab. Within this formalism, the more negative the E_{ads} values, the stronger the interaction. All stable structures have been identified as minima in the potential energy surface by numerical calculation of the Hessian matrix, obtained by finite displacements of the adatom coordinates. Note that a better characterization would include the coupling with the carbide surface atoms. Vacuum atomic energy references were gained by placing the metal atom in a large $9 \times 10 \times 11 \text{ Å}$ asymmetric box and calculating the total energy. Atomic charges for adatoms were estimated applying a Bader analysis [26]. The surface work function was calculated by subtracting the Fermi energy value of the system under study from the electron potential value in the vacuum region. The center of the d -band was obtained by plotting the projected density of states (PDOS) and numerically integrating the density in the d -band region of the total density of states (DOS).

2. Results

Let us begin with the clean δ -MoC(001) surface. One of its main features is the surface rumpling, a process mostly concerning the atoms of the outermost layer of a surface. Atomic relaxation changes the interplanar distance along the axis perpendicular to the surface, to a different extent for anions and cations. This process has been intensively studied in oxides [27] and in the (001) surface of rock-salt materials such as sodium halides [28], and it is found also in the (001) surface of early transition metals carbides [3]. For carbides, it implies an inward relaxation of the metal atoms at the surface, together with a displacement of the carbon atoms towards the vacuum. It is noteworthy that δ -MoC is the TMC where this effect is most pronounced. DFT calculations using PW91 [29] functional predicted an intralayer rumpling displacement of 0.24 Å (0.26 Å calculated at RPBE level) [3]. Recent calculations performed with the PBE functional confirm both results, with a calculated value of 0.25 Å . However, such relaxation does not imply any reconstruction, that is, the relative in-plane positions of the atoms and long range periodicity do not change. As it will be shown below, an important reconstruction occurs as a consequence of metal atoms adsorption.

Along this line we studied the adsorption of Ni, Cu, and Au atoms on the relaxed δ -MoC(001) surface. Due to its surface symmetry, see Fig. 1, six highly-symmetric adsorption sites have been explored; see previous studies for their definition and notation [30]. However, for these metals only two particular sites happen to be energetically competitive: The three-fold hollow site neighboring two surface Mo atoms and one surface C atom (MMC), and a four-fold hollow site, where metal adatoms are simultaneously bridging two Mo and two C surface atoms (Hollow). Energetic, geometric, and estimations of surface-related properties are encompassed in Table 1, connected to the most stable sites found for each particular case. The adsorption energies are of the same order as compared to other studies of metal adatoms on TiC(001) [13]. A comparison with bulk metal environments reveals that the bond strength of the studied metal atoms to the δ -MoC(001) surface is larger for Cu and Ni at lowest coverage, while at medium coverage it does only for Ni. In the case of Au, the Au–Au bonding is *a priori* stronger [31]. Thus, appearance of Au adatoms can only be feasible if aggregation is kinetically inhibited.

From previous studies [13] on similar surfaces, it is expected that Ni prefers to sit on top of surface C and both Cu and Au prefer MMC adsorption sites. Some of these results are confirmed at our highest coverage

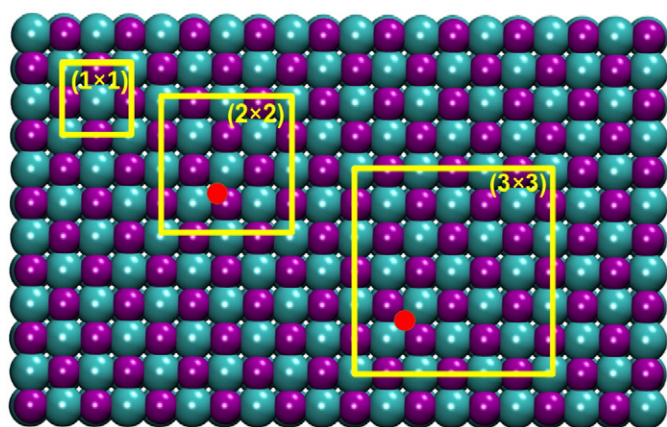


Fig. 1. Top view of the optimized (001) surface of δ -MoC. Yellow lines indicate the vectors of the supercell models used to study adsorption at various coverage θ . The $(\sqrt{2} \times \sqrt{2})R45^\circ$ cell, (1×1) in our notation, exposes 4 atoms in total, 2 Mo and 2 C and represents coverage $\theta = 0.25$. (2×2) and (3×3) supercells represent $\theta = 0.0625$ and $\theta = 0.028$ and expose 16 and 36 atoms respectively. Mo and C atoms are represented by cyan and purple spheres, respectively. In (2×2) and (3×3) supercell sketches the red spots respectively indicate the MMC and Hollow adsorption sites.

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