

# Trends in the chemical properties of early transition metal carbide surfaces: A density functional study

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## Abstract

In this paper we present density functional theory (DFT) investigations of the physical, chemical and electronic structure properties of several close-packed surfaces of early transition metal carbides, including  $\beta$ -Mo<sub>2</sub>C(0 0 0 1), and the (1 1 1) surfaces of TiC, VC, NbC, and TaC. The results are in excellent agreement with experimental values of lattice constants and bulk moduli. The adsorption of atomic hydrogen is used as a probe to compare the chemical properties of various carbide surfaces. Hydrogen adsorbs more strongly to the metal-terminated carbide surfaces than to the corresponding closest-packed pure metal surfaces, due to the tensile strain induced in the carbide surfaces upon incorporation of carbon into the lattice. Hydrogen atoms were found to adsorb more weakly on carbide surfaces than on the corresponding closest-packed pure metal surfaces only when there were surface carbon atoms present, and in some cases very stable C–H species were formed. The DFT results indicated that the hydrogen adsorption energy could be correlated to the d-band center of the carbide surfaces, although the correlation was not as good as our previous studies on bimetallic surfaces.

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## 1. Introduction

Early transition metal carbides and nitrides are among the hardest and most refractory materials known [1]. They have also gathered attention as potential catalysts since their “platinum-like behavior” was reported by Levy and Boudart [2]. In that work, “platinum-like behavior” referred specifically to three types of catalytic activity that are unique to Pt-group metals: (1) the oxidation of H<sub>2</sub> to form water, (2) the reduction of WO<sub>3</sub> by moist hydrogen, and (3) the isomerization of 2,2-dimethylpropane to 2-methylbutane. It was suggested in this seminal paper that carbon must change the electron distribution of the tungsten atoms in a manner that makes them more platinum-like. Since then, many studies and reviews have been reported on the electronic and structural properties of carbide surfaces [3] and their catalytic properties [4–6].

The purpose of the present work is to investigate the electronic structure of early transition metal carbide

surfaces, in particular how their electronic structures are modified compared to those of the parent metal surfaces, and how these changes affect the chemical properties of these surfaces. The paper begins with a density functional theory (DFT) investigation of bulk  $\beta$ -Mo<sub>2</sub>C and  $\beta$ -Mo<sub>2</sub>C(0 0 0 1) surfaces. This is followed by the results of a DFT study of the electronic and chemical properties of the (1 1 1) surfaces of TiC, VC, NbC, and TaC.

## 2. Theoretical studies of $\beta$ -Mo<sub>2</sub>C

### 2.1. Bulk properties

Below 1500 K, mixtures of Mo- and C exist in the following phases: Mo,  $\alpha$ -Mo<sub>2</sub>C,  $\beta$ -Mo<sub>2</sub>C and C, depending on the relative amounts of the two components [7]. We chose  $\beta$ -Mo<sub>2</sub>C as a representative carbide phase for this work. The  $\beta$ -Mo<sub>2</sub>C phase has an orthorhombic crystal structure, with  $a = 6.022 \text{ \AA}$ ,  $b = 4.725 \text{ \AA}$ , and  $c = 5.195 \text{ \AA}$  [8]. The (1 0 0) surface corresponds to the closest-packed surface, and it can

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Table 1  
Lattice constants for  $\beta$ -Mo<sub>2</sub>C

Lattice parameter	Experimental [8]	Calculated	Difference (%)
<i>a</i>	6.022	6.129	1.8
<i>b</i>	4.725	4.805	1.7
<i>c</i>	5.204	5.298	1.8

be either Mo or C-terminated. Although the crystal structure is orthorhombic, the arrangement of Mo atoms is only slightly distorted from an hcp arrangement. Thus, the crystal structure can be loosely described as an hcp arrangement of Mo atoms, with carbon atoms occupying one-half of the octahedral interstitial sites. This has resulted in many reports referring to the closest-packed surface as the (0 0 0 1) surface. Although it is incorrect, it is convenient to keep this notation for consistency with the literature.

The DFT lattice parameters for  $\beta$ -Mo<sub>2</sub>C were determined by minimizing the total energy of the unit cell with respect to the length of the lattice vectors using a Newton–Raphson scheme developed for that purpose. The experimentally known crystal structure was used as the initial starting point for the optimization. Complete internal relaxation was allowed at each step. DACAPO [9], which uses planewaves and ultrasoft pseudopotentials, was used for all calculations in this paper. A planewave cutoff of 350 eV, a  $4 \times 4 \times 4$  Monkhorst Pack k-point grid, and the PW91 exchange-correlation functional were used in the optimization. The results are listed in Table 1. Each of the lattice parameters was overestimated by 1.5–2%. This is consistent with errors for pure transition metals; the calculated lattice constants for Mo and Pt were larger by 1.3 and 2.3%, respectively. Liu et al. recently determined the lattice constants of  $\alpha$ -Mo<sub>2</sub>C using DMol<sup>3</sup> [10], which uses a localized basis set rather than planewaves. Their results are also within  $\pm 2\%$  of the experimental values. The bulk  $\beta$ -Mo<sub>2</sub>C lattice parameters were determined for later use in investigations of surface properties, described in the next section.

## 2.2. Surface properties

The  $\beta$ -Mo<sub>2</sub>C(0 0 0 1) was chosen as a model surface for a close-packed  $\beta$ -Mo<sub>2</sub>C substrate. The surfaces were modeled by slabs separated by vacuum, using the DFT lattice parameters listed in Table 1. Each slab was two unit cells thick (four layers of Mo atoms and four layers of C atoms). Two of the layers were allowed to fully relax, and the other two layers were frozen at the bulk lattice parameters. A  $4 \times 4 \times 1$  Monkhorst-Pack k-point setup was used. The planewave cutoff was set at 350 eV, and the PW91 exchange-correlation functional was used. The slabs were separated by three unit cells of vacuum and were further decoupled by use of a dipole correction scheme. Atom-projected densities of states (DOS) were calculated by projection of the one-electron states onto spherical harmonic atomic orbitals centered on atomic sites. Two projections were obtained, one with a cutoff radius at 1 Å to minimize

contributions from neighboring sites, hereafter referred to as the short cutoff radius. The other result used no cutoff radius, hereafter referred to as the infinite cutoff radius. It has not been important to differentiate between these two radii in previous works examining electronic structures of metals and bimetallic surfaces in our research groups, but in this work it was found to be important, as will be discussed later.

The calculated electronic d-band structures of  $\beta$ -Mo<sub>2</sub>C(0 0 0 1) surfaces were compared with those of Mo(1 1 0) and Pt(1 1 1), shown in Fig. 1. The surface d-band of both C- and Mo-terminated carbide surfaces appears broader than that of Mo(1 1 0). There are several new features in the Mo d-band structure of the carbide surface. Most obviously, there is a new peak around  $-12$  eV in both the Mo- and C-terminated surfaces, and a second peak around  $-10$  eV on the C-terminated surface. Both carbide d-bands show a shoulder between about  $-7$  and  $-5$  eV that is absent for the Mo(1 1 0) surface. These new features can be associated directly with hybridization between the d-orbitals and the carbon sp-orbitals. More specifically, the peak near  $-12$  eV can be attributed to interactions between the surface Mo atoms and subsurface C atoms. This is illustrated in Fig. 2, where the s and p-bands of C atoms in the second layer are compared with the surface Mo atom d-band. The overlap of the peaks clearly identifies the feature near  $-12$  eV as an interaction between the C s-orbitals and Mo d-orbitals. An interaction between the Mo d-orbitals and the subsurface carbon p-orbitals is responsible for the broadened shoulder between  $-5$  and  $-7$  eV. Fig. 2 shows the results of the atom-projected DOS for the infinite cutoff radius. The same conclusions were reached for the short cutoff radius results.

The second peak in the C-terminated surface at  $-10$  eV is due to interactions between the surface Mo d-orbitals and the s-orbitals of the carbon atoms on the surface. The surface C s and p-bands closely resemble the subsurface C s and p-bands, but they are higher in energy due to their lower coordination compared to carbon in the bulk. Consequently, all of the resonances with the surface d-band are shifted to higher energy, as illustrated in Fig. 3. The same conclusions were reached if the short cutoff radius was used.

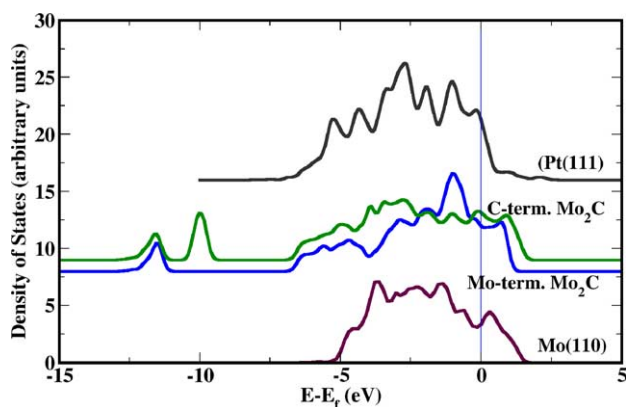


Fig. 1. Comparison of d-band structures of Pt(1 1 1),  $\beta$ -Mo<sub>2</sub>C surfaces and Mo(1 1 0).

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