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Stable surface terminations of orthorhombic Mo_2C catalysts and their CO activation mechanisms

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ABSTRACT

The structure and stability of all twenty-two terminations of the seven low-Miller index orthorhombic Mo_2C surfaces have been systematically investigated on the basis of the computed surface energies from periodic density functional theory. With the increase of the carbon chemical potential (μ_C), the most stable surface structure and composition change from the metallic (1 1 0)-Mo and (1 0 0)-Mo terminations to the mixed (1 1 1)-Mo/C and strongly reconstructed (1 1 0)-Mo/C terminations. The calculated stability order and surface area proportions of the (1 0 0), (1 1 0) and (1 1 1) surfaces agree very well with the available X-ray diffraction data. In addition, CO adsorption and dissociation on these surfaces have been computed and micro-kinetic analysis reveals that CO dissociation is rate-determining on the metallic termination, and CO adsorption is rate-determining on the mixed Mo/C-termination. This might explain the observed catalytic differences of orthorhombic Mo_2C catalysts prepared from different ways.

1. Introduction

On the basis of their extreme hardness and brittleness, high melting points and electrical or thermal conductivities [1–3], transition metal carbides (TMC) have found wide applications as cutting tools [4] and hard-coating materials [5]. TMC also exhibit excellent catalytic activities [6], e.g., in hydrogenation [7–10], dehydrogenation [11], hydrogenolysis [12] and Fischer–Tropsch synthesis [13–17]. As a representative member of TMC, molybdenum carbide (Mo_2C) has been intensively studied experimentally and theoretically. Mo_2C mainly has two crystalline phases with slight distinctions; the orthorhombic [18] and the hexagonal [19] phases.

Mo_2C and WC have been reported to have similar catalytic activities as noble metals [20,21]. The catalytic activities of Mo_2C in water–gas shift (WGS, $CO + H_2O = CO_2 + H_2$) reaction [22,23], alcohol synthesis from CO hydrogenation [24–26], hydrodesulfurization (HDS) [27] and hydrodenitrogenation (HDN) [28] in petroleum refining, hydro-treating [29,30] and hydrogen production [31] as well as the unique catalytic behaviors in the aromatization of CH_4 [32,33] have been widely investigated experimentally. The adsorption and decomposition of small molecules [34–38], like nitrogenous compounds, aromatic hydrocarbons and CO, have been studied on both orthorhombic and hexagonal Mo_2C phases. Liu et al., [39–41] found that surface carbon in Mo_2C plays a key role in the dissociation of sulfur-containing molecules, and emphasized the importance of surface oxygen on Mo_2C in WGS reaction [42]. The hydrogenolysis of thiophene [43] and indole [44] on the clean hexagonal Mo_2C surface was also computed systematically. Pistonesi et al., discussed the chemical properties of methanol [45], methyl iodide [46] and potassium promoting effect on orthorhombic Mo_2C [47] and found that the incorporation of potassium atoms promotes the dissociation ability of the C—I and C—O bonds. Tominaga and Nagai [48] studied the potential energy surface of WGS reaction and concluded that the formation of CO_2 is rate-determining. In order to study the intrinsic WGS activity of Mo_2C, Schweitzer et al., [49] loaded Pt on Mo_2C and found Mo_2C to play the roles of both support and catalyst. Study of the thermodynamics of elementary steps of synthesis gas reactions on Mo_2C(0 0 1) [50] indicates that the Mo-termination exhibits similar activity with transition metals such as Ru and Ir in carbon related reactions. Tominaga et al., [51] studied CO hydrogenation on both clean and cobalt doped hexagonal Mo_2C(1 0 0) surface and they ruled out the possible formation of CH_3OH, and these results are supported by their experimental findings. The

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mechanism of CO hydrogenation into CH_4 on both orthorhombic Mo_2C(1 0 0) and hexagonal Mo_2C(1 0 1) surfaces was reported by Qi et al., [52] and the orthorhombic Mo_2C(1 0 0) surface was proved to have higher activity in CH_4 formation. A combined experimental and density functional theory (DFT) study showed very high catalytic activity of hexagonal Mo_2C in ammonia dehydrogenation [53]. A recent formic acid decomposition mechanism study [54] revealed that Mo_2C is a promising catalyst for CO-free hydrogen production.

Theoretical attentions have been paid to the adsorptions of simple molecules and reaction mechanisms on hexagonal Mo_2C(0 0 1) and orthorhombic Mo_2C(1 0 0) surfaces, but discussions about other Mo_2C surfaces are less known. Shi et al., [55] and Han et al., [56] calculated the surface energies of the low Miller index surfaces of hexagonal Mo_2C and found the (0 1 1) facet to be most stable. However, calculations of surface free energies of low and high Miller index surfaces of hexagonal Mo_2C using atomistic thermodynamics under the consideration of carburization conditions showed the (1 0 1) surface to be most stable and representative [57], in good agreement with the available X-ray diffraction (XRD) [58,59] and high resolution transmission electron microscopy (HRTEM) [60] results. Recently, dos Santos Politi et al., [61] computed the atomic and electronic structures of the bulk and low Miller-index surfaces of three molybdenum carbide phases (α-MoC, β-Mo_2C and δ-MoC) and found that the Perdew–Burke–Ernzerhof (PBE) functional is particularly suited to study molybdenum carbide and the β-Mo_2C phase has strong metallic character.

The adsorption and activation of CO is of particular importance for understanding the initial steps in many practical industry applications, such as Fischer–Tropsch synthesis [62], alcohol synthesis [63], water–gas sift reaction [64], fuel-cell technology and environment protection [65]. Since the orthorhombic molybdenum carbide has been proposed as potential substitute for the commercially used Cu-based catalysts for WGS reaction [66], it is essential to study the interaction of CO with Mo_2C. Despite of its importance, only few theoretical studies about CO adsorption and activation on Mo_2C were reported. Shi et al., [67] calculated CO adsorption on the hexagonal Mo_2C(0 0 1) surface and found that the Mo-termination can activate CO more strongly than the C-termination. On the basis of the computed Gibbs free energies, we studied the relationship among temperature, CO equilibrium coverage and CO partial pressure on the hexagonal Mo_2C surfaces [68], and found good agreement between the predicated and the experimentally recorded spectra of temperature programmed CO desorption. Our results provide useful information not only for adjusting the equilibrium between temperature and CO partial pressure for stable CO coverage but also for identifying the active surfaces and the initial states under given conditions. Ren et al., [69] calculated CO adsorption on the orthorhombic Mo_2C(1 0 0) surface and found CO preferring the Mo-termination over the C-termination. Pistonesi et al., [70] studied CO adsorption and dissociation on the clean and K-doped orthorhombic Mo_2C(0 0 1) surfaces and found that the incorporation of K strengthens CO adsorption but increases CO dissociation barrier. Apart from the (1 0 0) surface, to the best of our knowledge, the stability of the other low Miller-index surfaces of the orthorhombic Mo_2C phase as well as CO adsorption and dissociation on these surfaces have not been systematically studied. Furthermore, atomistic thermodynamics method [71–74] facilitates the discussion of the relationship of reaction conditions with surface stability and adsorption properties. In this method, the effects of reaction conditions (temperature, pressure and gas contents) can be reflected by the values of chemical potential. In particular, the effect of carbon chemical potential on the stability and composition of different surface terminations is of great relevance in investigating the properties of transition metal carbides for practical applications [75,76].

In this work we present a systematic study on the stability of the (0 0 1), (0 1 0), (0 1 1), (1 0 0), (1 0 1), (1 1 0) and (1 1 1) surfaces of the orthorhombic Mo_2C phase on the basis of periodic DFT calculations. We also present CO adsorption and dissociation properties on those surfaces from the thermodynamic and kinetic points of view. Our goal is to discuss the effect of carbon chemical potential on the stability of different surface terminations and also to build the relationships among surface stability as well as CO adsorption and activation properties.

2. Computational model and method

2.1. Method

All calculations were done by using the plane-wave based periodic DFT method implemented in the Vienna *ab initio* simulation package (VASP) [77,78]. The electron ion interaction is described with the projector augmented wave (PAW) method [79,80]. The electron exchange and correlation energy is treated within the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof formalism (PBE) [81]. Although DFT + U_{eff} is required to clearly describe the properties of Mo oxides [82,83], GGA-PBE is proved to be particularly suitable to describe the properties of Mo_2C catalyst [61]. Moreover, we also tested the effect of different U_{eff} values on the structural parameters. In comparison with the bulk structural parameters from experiment, the best agreement is found for $U_{\text{eff}} = 0$; and the larger the U_{eff}, and the worse the agreement (Table S1). To have the energies with errors less than 1 meV per atom, cutoff energy of 400 eV and Gaussian electron smearing method with $\sigma = 0.05$ eV were used. For the bulk optimization, the lattice parameters for orthorhombic Mo_2C were determined by minimizing the total energy of the unit cell on the basis of a conjugated-gradient algorithm to relax the ions, and a 5 × 5 × 5 Monkhorst–Pack *k*-point grid was used for sampling the Brillouin zone. The geometry optimization was done when force difference became smaller than 0.02 eV/Å and the energy difference was lower than 10^{-4} eV. (The test of this parameter is given in Table S2) Adsorption energy (E_{ads}) is calculated by subtracting the energies of gas phase species and the clean surface from the total energy of the adsorbed system; $E_{\text{ads}} = E(\text{adsorbate/slab}) - [E(\text{adsorbate}) + E(\text{slab})]$, and a more negative E_{ads} indicates a more stable adsorption. For evaluating the energy barrier, the transitional state (TS) was located using the nudged elastic band (NEB) method [84]. The TS configurations were verified by vibration analyses, and in all cases, only one imaginary frequency is found. The barrier (E_a) and reaction energy (ΔE_r) are calculated according to $E_a = E_{\text{TS}} - E_{\text{IS}}$ and $\Delta E_r = E_{\text{FS}} - E_{\text{IS}}$, where E_{IS}, E_{FS} and E_{TS} are the energies of the corresponding initial state (IS), final state (FS) and transition state (TS), respectively. The description of the method for the calculation of surface energy is included in Supporting information.

2.2. Model

We used the orthorhombic Mo_2C phase as unit cell. The calculated lattice parameters for Mo_2C bulk are $a = 4.751$ Å, $b = 6.065$ Å, $c = 5.237$ Å, very close to the experimental values ($a = 4.732$ Å, $b = 6.037$ Å and $c = 5.204$ Å) [85]. When calculating the surface energies, all applied slabs are equivalent in both sides and all the atoms were allowed to fully relax. The slab thickness of different terminations is in the range of 9–14 Å, thick enough to avoid significant influence on the surface energies from our tests in Supporting information. For example (Table S3), the calculated surface energies are 3.11 and 3.08 J/m^2 for 9-layer (1 0 0)-Mo (9.55 Å) and (1 0 0)-C (9.50 Å) slabs, as well as for 17-layer (1 0 0)-Mo (19.05 Å) and (1 0 0)-C (19.00 Å) slabs, respectively. A vacuum layer of 10 Å was set to