



# Molybdenum carbide catalysed hydrogen production from formic acid – A density functional theory study



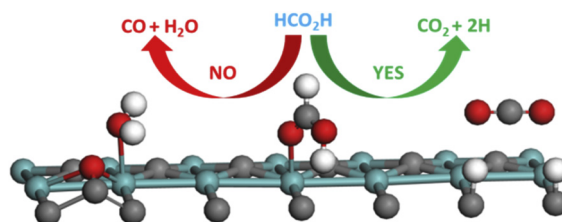
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## HIGHLIGHTS

- HCOOH decomposition on  $\beta$ -Mo<sub>2</sub>C (101) was investigated using First-principles calculations.
- The decomposition mechanisms were compared with those on Pt group metals.
- CO-free hydrogen formation was found via the formate route dissociation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Density functional theory computations have been employed to investigate the decomposition of formic acid (HCO<sub>2</sub>H) into CO<sub>2</sub> and hydrogen on the  $\beta$ -Mo<sub>2</sub>C(101) surface. The adsorption configurations and energies of the surface intermediates (HCO<sub>2</sub>H, CO<sub>2</sub>, CO, H<sub>2</sub>O, HCO<sub>2</sub>, CO<sub>2</sub>H, CHO, OH, O and H) have been systematically characterized. Among the different dissociation steps considered, our results showed the formate route (HCO<sub>2</sub>H → H + HCO<sub>2</sub>; HCO<sub>2</sub> → H + CO<sub>2</sub>) is the minimum energy path for hydrogen formation and CO<sub>2</sub> has very strong chemisorption. The adsorption and dissociation of formic acid on the Mo<sub>2</sub>C(101) surface have been compared with those of Pt group metals.

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## 1. Introduction

Selective and catalytic decomposition of formic acid (FA, HCO<sub>2</sub>H) into H<sub>2</sub> and CO<sub>2</sub> is considered as one of the potential chemical processes to satisfy the increasing energy demand, especially in fuel cell, green and clean technologies [1–3]. For FA selective decomposition both heterogeneous [4–7] and homogeneous [8–12] catalysts have been used. Recently, Flaherty et al. studied FA decomposition on molybdenum carbide and found that

C-modified Mo(110) and C–Mo(110) are up to 15 times more selective than pure Mo(110) for H<sub>2</sub> formation [13]. Koós and Solymosi reported that the highly stable molybdenum carbide (Mo<sub>2</sub>C) catalyst prepared from the reaction of MoO<sub>3</sub> with a multiwall carbon nanotube and carbon Norit can selectively decompose FA into CO-free H<sub>2</sub> at 373–473 K [14]. Cui et al. reported that Pd catalysts supported on Mo<sub>2</sub>C which is supported on multiwall carbon nanotube has much higher electrocatalytic activity and stability for FA electrooxidation than only Mo<sub>2</sub>C catalyst supported on multiwall carbon nanotubes and only Pd catalysts supported on Mo<sub>2</sub>C, and they concluded that Mo<sub>2</sub>C is not only a support but also a co-catalyst [15]. In addition, Mo<sub>2</sub>C is active for hydrogenation and dehydrogenation [16], as well as for low temperature water-gas

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shift (WGS) reaction [17,18]. Transition metal carbides which have the added benefits of lower cost with respect to the Pt group metals, like  $W_2C$  and  $MoC_2$  have been found to have Pt-like reactivity [19,20].

Theoretically, molybdenum carbides have been used to study various reactions. The hydrogenolysis mechanisms of thiophene [21] and indole [22,23] on clean  $\beta$ - $Mo_2C$  have been studied systematically. The chemisorption and decomposition of small molecules [24–29] such as nitrogenous compounds, aromatic hydrocarbons and  $CO_2$  were examined on both  $\alpha$ - $Mo_2C$  and  $\beta$ - $Mo_2C$  phases. Theoretical studies of the chemical properties of methanol [30], methyl iodide [31], CO and the promoting effect of potassium on  $\beta$ - $Mo_2C$  were reported systematically by Pistonesi et al. [32]. Based on their surface experiments; and they found that the incorporation of potassium atoms enhances the dissociation ability of the C–I and C–O bonds in  $CH_3I$  and  $CH_3OH$ , while blocks the dissociation of CO. Tominaga and Nagai built a schematic potential energy surface for WGS reaction and concluded that  $CO_2$  formation from CO oxidation by surface O is the rate-limiting step [33]. The mechanism of CO hydrogenation and the promoter effect of cobalt have also been systematically reported recently [34]. Liu et al. also calculated WGS mechanism and emphasized the importance of oxygen on the  $Mo_2C$  surface [35]. In order to study the intrinsic WGS activities of  $Mo_2C$ , Schweitzer et al. loaded Pt on  $Mo_2C$  and found  $Mo_2C$  to play the role of both support and catalyst [36]. Shi et al. [37] and Han et al. [38] calculated the surface energies of low miller index surfaces of hexagonal  $Mo_2C$  to compare their stabilities and concluded that the (011) facet was the most stable surface. The elementary steps of syngas reaction have been systematically studied by using *ab initio* thermodynamics method by Andrew et al. and  $Mo_2C$  was proved to have similar catalytic properties with noble metals [39]. Recently, Zheng et al. reported  $H_2$  production from ammonia decomposition catalysed by molybdenum carbide both experimentally and theoretically [40].

In this work, we carried out spin-polarized periodic density functional theory computations to study the adsorption and dissociation of FA on the  $Mo_2C(101)$  surface. Our goal is the understanding into the adsorption configurations of FA and its dissociation intermediates on the  $Mo_2C(101)$  surface as well as the dissociation paths. These results are compared with those on the Pt group metals, e.g.; Pd(111) [41–44], Pt(111) [43,45,46], and Ir(100) [47], from recent computational studies.

## 2. Computational details

### 2.1. Model

$Mo_2C$  mainly has two crystalline structures, the orthorhombic  $\alpha$ - $Mo_2C$  phase [48] and the hexagonal  $\beta$ - $Mo_2C$  phase [49,50]. In our work, we used the  $\beta$ -hexagonal  $Mo_2C$  phase with an eclipsed configuration as unit cell [51,52]. The calculated lattice parameter of the cell is  $2a = 6.075 \text{ \AA}$ ,  $2b = 6.069 \text{ \AA}$  and  $c = 4.722 \text{ \AA}$ , in good agreement with the experiment:  $a = b = 3.011 \text{ \AA}$  and  $c = 4.771 \text{ \AA}$  [53]. Among all the surfaces of  $\beta$ - $Mo_2C$ , the (101) surface was reported to be most stable [37,51–55], and there are two types of C atoms and two types of Mo atoms on the exposed surface (Fig. 1). For describing this surface atoms easily, the 4-coordinated (two surface Mo atoms and two bulky phase Mo atoms) C atom is marked as  $C_A$ , the 5-coordinated (four surface Mo atoms and one bulky phase Mo atom) C atom is denoted as  $C_B$ . The 10-coordinated (three surface Mo atoms, three surface C atoms and four bulky phase Mo atoms) and 11-coordinated (three surface Mo atoms, three surface C atoms and five bulky phase Mo atoms) Mo atoms are notated as  $Mo_A$  and  $Mo_B$ , respectively. The total supercell contains a  $Mo_32C_{64}$  unit within a volume of  $15.40 \times 12.11 \times 17.96 \text{ \AA}$ , and

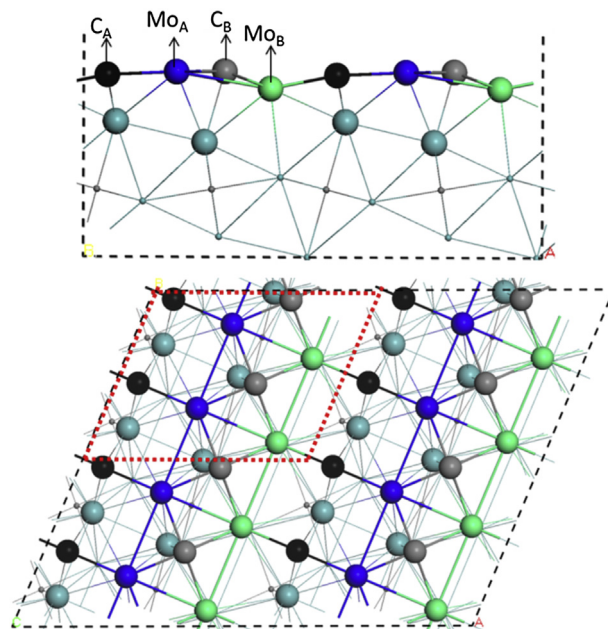


Fig. 1. Side and top views of the  $Mo_2C(101)$  surface.

the exposed surface has 16 Mo atoms and 16 C atoms. In addition, a smaller surface model containing 4 exposed Mo atoms and 4 exposed C atoms within the red region of the surface was also employed to study coverage effect, which is defined as the exposed surface Mo atoms, e.g.; 1/16 ML for the large model and 1/4 ML for the small model (Fig. 1).

### 2.2. Method

All calculations were done using the plane-wave spin-polarized periodic density functional method (DFT) in the Vienna *ab initio* simulation package (VASP) [56–59]. The electron ion interaction was described with the projector augmented wave (PAW) method [60]. The electron exchange and correlation energy was treated within the generalized gradient approximation in the Perdew–Burke–Ernzerhof formalism (GGA-PBE) [61]. For Mo, the core 4p states were also taken into valence region and totally 12 valence electrons were included. The Kohn–Sham one-electron states were expanded in a plane wave with an energy cutoff 400 eV, and the Methfessel–Paxton scheme was used under the electron smearing of  $\sigma = 0.1 \text{ eV}$  [62]. The vacuum zone was set up to 12  $\text{\AA}$  in the z direction to separate the slabs. The geometry optimization was done when force becomes smaller than  $0.02 \text{ eV \AA}^{-1}$  and the energy difference was lower than  $10^{-5} \text{ eV}$ . For bulk optimization, the lattice parameters were obtained by minimizing the total energy of the unit cell using a conjugated-gradient algorithm to relax the ions and a  $5 \times 5 \times 5$  Monkhorst–Pack k-point grid was used for sampling the Brillouin zone [63]. The first Brillouin zone was sampled with  $3 \times 3 \times 1$  k-point grid for investigating the surfaces (1/16 and 1/4 ML). The nudged elastic band (NEB) method was used to locate the minimum energy path [64]. The computed vibrational frequencies were used to characterize a minimum state without imaginary frequencies or an authentic transition state with only one imaginary frequency.

The adsorption energy is defined as in Equation,  $E_{ads} = E_{A/slab} - [E_{slab} + E_A]$ ; where  $E_{A/slab}$  is the total energy of the slab with adsorbates A,  $E_{slab}$  is the total energy of the bare slab, and  $E_A$  is the total energy of free adsorbate A in gas phase; and the more negative the  $E_{ads}$ , the stronger the adsorption. The activation energy is

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