Structure-sensitivity of ethane hydrogenolysis over molybdenum carbides: A density functional theory study

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ABSTRACT

The adsorption and hydrogenolysis of ethane on fcc-Mo_2C (1 0 0) and hcp-Mo_2C (1 0 1) has been studied using density functional theory calculations with the periodic slab model. We found that the reaction mechanism for ethane hydrogenolysis are basically the same on both fcc and hcp phase Mo_2C catalysts, that is, C_2H_6 (a) → C_2H_5 (a) → CH_2 (a) → CH_3 (a) → CH_4. For the rate-controlling step (C_2H_5 → CH_2 + CH_3), the activation energy on hcp-Mo_2C (1 0 1) (1.53 eV) is lower than that on fcc-Mo_2C (1 0 0) (1.81 eV), which indicated that the hcp-Mo_2C (1 0 1) shows higher reactivity than that of fcc-Mo_2C (1 0 0). The possible reason may form the fact that the hcp-Mo_2C (1 0 1) is more open and corrugated than fcc-Mo_2C (1 0 0), which results in the interaction (mainly the repulsion effect) between CH_2 and CH_3 at transition state is relatively weak on hcp-Mo_2C (1 0 1), and thus the higher reactivity on hcp-Mo_2C (101) can be expected. Moreover, it was found that the pre-adsorbed hydrogen atom can effectively reduce the barrier of C_2H_5 → CH_2 + CH_3 on Mo_2C catalysts.

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1. Introduction

Molybdenum carbide (Mo_2C) is an active catalyst for a wide variety of reactions with catalytic activity comparable to those of noble metals, accompanied by resistance to sulfur poisoning, and may be used as a cheaper substitute of catalysts [1,2]. It is of great practical interest to replace expensive noble metals showing unique catalytic activity for heterogeneous reactions in the gas or liquid phase by these cheaper but active metal carbides. The interesting catalytic properties of Mo_2C were first reported by Sinfelt and Yates [3]. They discovered that the ethane hydrogenolysis reactivity over supported molybdenum increases 60-fold over the course of 5 h. Subsequent examination of catalyst indicated that a Mo_2C phase had formed and extended appreciably into the bulk. Later, many experiments showed that Mo_2C catalysts have exhibited excellent activities towards different reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), Fischer-Tropsch synthesis, CO hydrogenation and alkane hydrogenolysis [4–9]. In particular, Mo_2C catalysts demonstrate high activity towards hydrogenolysis reaction of ethane. There are two main crystalline structures Mo_2C, i.e., the orthorhombic phase (fcc-Mo_2C) and the hexagonal phase (hcp-Mo_2C). Ranhotra et al. [9] revealed that both fcc and hcp phases of Mo_2C are active for ethane hydrogenolysis

and the main product is methane. More significantly, the specific reactivity of hcp-Mo_2C is 200-fold higher than fcc-Mo_2C, for comparable duration under reaction conditions. Additionally, Li et al. [10] found that Mo_2C exhibits excellent catalytic behaviors for the dehydrogenation of butane, which activity is similar to those of more expensive Pt-group metals. Neylon et al. [11] demonstrated that Mo_2C has better catalytic dehydrogenation ability to butane than other transition metal carbides such as tungsten carbide and vanadium carbide. Mo_2C is also active for synthesis gas conversion, yielding light hydrocarbons at atmospheric pressure [12]. For instance, Woo et al. [13] and Xiang et al. [14] reported that unsupported Mo_2C produced CO_2 and hydrocarbons from synthesis gas. Addition of K to the Mo_2C decreased conversion and increased selectivity to alcohols, especially methanol and ethanol.

Ethane hydrogenolysis is widely accepted as a probe reaction for studying the catalytic activities of various catalysts [15]. So far, hydrogenolysis of ethane has been investigated extensively by using experimental and theoretical techniques [16,17]. However, the exact mechanism of ethane hydrogenolysis is still unclear. More importantly, the physical nature why the hcp-Mo_2C is much higher than that of fcc-Mo_2C needs to be explored from theoretical side. On the basis of the kinetic scheme originally proposed by Cimino et al. [18], the Sinfelt-Taylor mechanism involves C_2 dehydrogenation to some extent on metal catalyst, followed by C—C cleavage and C_1 hydrogenation to form methane. Recently, Watwe et al. [19] studied of C—C bond breaking reactions over Pt and suggested that more highly hydrogenated C_2 adsorbates are more active for C—C bond cleavage. Their theoretical results showed that the primary reaction

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pathway for C—C bond cleavage takes place through activated C_2H_5 species. In addition, Sinfelt [20] analyzed the proposed mechanism of ethane hydrogenolysis on various transition metals supported by SiO_2 and suggested that the number of hydrogen atoms in the C_2H_x fragments affects the C—C bond cleavage on different surfaces.

Previous studies of the ethane hydrogenolysis give great insight into the reaction mechanisms on Pt-group metals, however, there are few theoretical studies on C—C or C—H cleavage over Mo_2C catalysts were reported, and the nature of the hydrogenolysis of ethane on Mo_2C surfaces is still unclear. In this work, we perform a comprehensive density functional theory (DFT) calculation to investigate some reaction intermediates and some pivotal transition states in ethane hydrogenolysis, in order to identify and compare the most favorable pathways during ethane hydrogenolysis on fcc-Mo_2C (1 0 0) and hcp-Mo_2C (1 0 1), respectively. Furthermore, we also perform electronic structure analysis to probe whether the C_2H_6 hydrogenolysis is sensitive to the catalyst structure. This paper is organized as follows. In Section 2, we describe calculation details. Sections 3 and 4 present DFT results and discussion, respectively. Conclusions are summarized in the Section 5.

2. Computational method and models

All the calculations are performed by using the plane-wave DFT Vienna ab initio simulation package (VASP) [21,22]. The exchange-correlation energy and potential are described by generalized gradient approximation (GGA-PW91) [23]. The electron-ion interaction is described by the projector-augmented wave scheme [24,25], and the electronic wave functions are expanded by plane waves up to a kinetic energy of 350 eV. The surface Brillouin zone is sampled using a $4 \times 4 \times 1$ Monkhorst–Pack mesh [26]. The fcc-Mo_2C (1 0 0) surface was modeled by a four-layer Mo_2C slab using the lattice constants of $a = 6.109$ Å, $b = 4.827$ Å, and $c = 5.224$ Å, and the hcp-Mo_2C (1 0 1) surface was modeled by a four-layer Mo_2C slab using the lattice constants of $a = 3.003$ Å, $b = 3.003$ Å and $c = 4.729$ Å. Our DFT-optimized lattice constants for fcc and hcp Mo_2C phases are in good agreement with the experimental results [27,28]. The selectivity of surface model is based on that the dominant planes exposed by fcc and hcp Mo_2C are (1 0 0) and (1 0 1) respectively (Fig. 1) [9,10,29,30]. With the development of the nanotechnology, it can be achieved to synthesize that either fcc Mo_2C exposed (1 0 0) or hcp Mo_2C exposed (1 0 1) [31,32]. Recent theoretical results verified the configuration with a Mo—C—Mo—C stacking mode to be the most stable [33]. Therefore, our focus is the Mo-terminated surface, while the C-terminated surface is not considered in this work. The vacuum region is 15 Å between slabs to make sure that there are no interactions between slabs. In order to evaluate the effect of the slab size on the reaction of ethane hydrogenolysis, the adsorption and C—C cleavage of C_2H_5 on (4×4) and (2×2) Mo_2C surfaces were both calculated. C_2H_5 owns a relative large volume comparing with other possible intermediates, thus we choose C_2H_5 for this test. Comparing the adsorption energy of C_2H_5 on
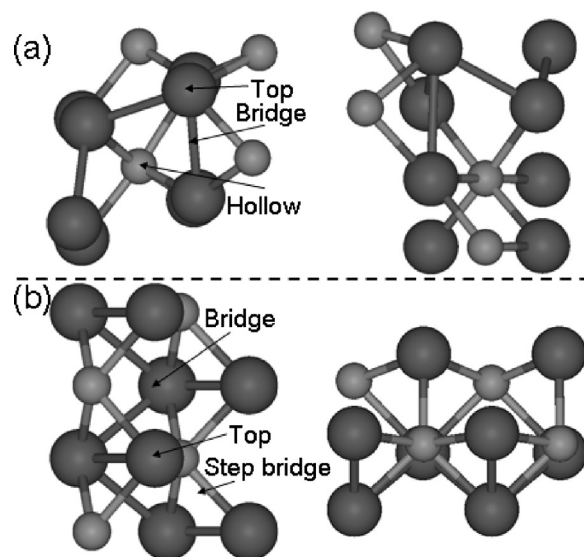

Fig. 1. Top and side views of (a) fcc-Mo_2C (1 0 0) and (b) hcp-Mo_2C (1 0 1) periodic slab models, the large black balls for Mo atoms and the gray ones for C atoms respectively.

Table 1
Adsorption energy for possible species on fcc-Mo_2C (1 0 0) and hcp-Mo_2C (1 0 1) surfaces (unit: eV).

Adsorption species	fcc (1 0 0)		hcp (1 0 1)	
	Adsorption site	E_{ads}	Adsorption site	E_{ads}
C_2H_6	Bridge	−0.10	Bridge	−0.15
C_2H_5	Bridge	−3.17	Bridge	−3.20
CH_4	Bridge	−0.15	Top	−0.10
CH_3	Hollow	−3.55	Bridge	−3.27
CH_2	Top	−5.77	Bridge	−5.46
H	Hollow	−3.44	Step bridge	−3.21

the Mo_2C surface using (4×4) and (2×2) slabs, the difference is within 0.10 eV, which can be neglected (see Table S1 in Supporting Information and Table 1). The activation energies of C—C cleavage of C_2H_5 on the two slab models are almost the same (see Table S2 in Supporting Information and Table 2). In order to save computational time, the (2×2) slab surface was adopted in this work, and the corresponding coverage is 1/4 ML. During the calculation, the top two layers and the adsorbed species are allowed to relax while the bottom layer Mo and C atoms are fixed. The molecules in the gas phase have been calculated using a $15 \times 15 \times 15$ Å^3 cubic unit cell. Spin-polarized calculations were performed when needed.

The adsorption energy (E_{ads}) is calculated based on the equation of $E_{ads} = E_{A/M} - E_M - E_A$. Here $E_{A/M}$, E_M, and E_A represent the calculated energy of adsorption system, substrate, and adsorbate, respectively. The nudged elastic band (NEB) method was employed

Table 2
DFT calculated activation energy (E_a), reaction energy (ΔH), and imaginary frequency (ν_i) of the TS.

Step	fcc (1 0 0)			hcp (1 0 1)		
	E_a (eV)	ΔH (eV)	ν_i (cm^{-1})	E_a (eV)	ΔH (eV)	ν_i (cm^{-1})
$C_2H_6 \rightarrow CH_3 + CH_3$	2.68 (2.50)	0.09	657	1.99 (1.89)	0.78	476
$C_2H_6 \rightarrow C_2H_5 + H$	0.93 (0.79)	−0.67	894	0.56 (0.53)	−0.47	768
$C_2H_5 \rightarrow CH_3 + CH_2$	1.81 (1.85)	0.89	456	1.53 (1.52)	0.45	432
$C_2H_5 + H \rightarrow CH_3 + CH_2 + H$	1.70 (1.71)	0.69	480	1.37 (1.32)	0.24	481
$CH_2 + H \rightarrow CH_3$	0.42 (0.40)	−0.46	828	1.15 (1.12)	−0.37	934
$CH_3 + H \rightarrow CH_4$	0.84 (0.80)	0.47	1030	1.20 (1.09)	0.47	875

Note: activation energies with ZPE correction are given in parenthesis.