

INVESTIGATION OF MOLYBDENUM CARBIDES AS CATALYST FOR HYDROGEN EVOLUTION IN PH UNIVERSAL ENVIRONMENT USING DENSITY FUNCTIONAL THEORY SIMULATION

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Preliminary Note – Prethodno priopćenje

Transition metal carbides (TMC) have intriguing physical and chemical properties, especially when structured down to nanoscale. The temperature and chemical resilience of this family of materials made it ideal candidate for electrochemical applications in harsh environment. Among the TMC family, molybdenum carbide has been demonstrated as efficient catalyst for hydrogen evolution reactions (HER). This paper will use density function theory to investigate the efficiency of molybdenum and tungsten carbide as catalyst for HER in neutral and alkane environment.

Key words: molybdenum carbide; crystal structure; hydrogen evolution reaction; catalysis; simulation method

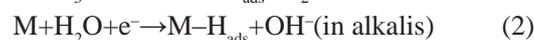
INTRODUCTION

Refractory transition metal carbides (WC, MoC, TaC, HfC, ZrC and etc) exhibit exceptional strong mechanical properties such as high melting temperature [1], high strength, large harness and wear resistance, and become ideal candidate for structures and devices working in harsh environment such as aerospace engine and waste nozzle [2,3]. Among all the refractory transition metal carbide, molybdenum carbide has also recently been widely studied for their exceptional catalytical activities in their nano/micro architectures [4]. The clean combustion of hydrogen has presented an attractive alternative to fossil fuel use. [1] Considerable improvements in hydrogen fuel-cell technology and solid-state hydrogen storage have made significant strides in recent years. Electrocatalytic hydrogen evolution using sustainably produced electricity has promised a carbon free production of a chemical fuel. [1] However, most commercial hydrogen is still produced via steam reforming of methane because there are few scalable base-metal replacements for platinum at the scales required for electrocatalysis. Nano structured transition metal carbides (Mo₂C, WC, etc) have shown excellence of catalytical for hydrogen evolution reactions (HER) in acidic environmental. In this work, it will be systematically investigate the HER efficiency in neutral and alkane environmental by simulation methods [1].

RESULTS AND DISCUSSION

Hydrogen evolution reaction (HER) in alkaline medium is currently a point of focus for sustainable devel-

opment of hydrogen as an alternative clean fuel for various energy systems, but suffers from sluggish reaction kinetics due to additional water dissociation step. So, the state of the art catalysts performing well in acidic media lose considerable catalytic performance in alkaline media. The HER pathway normally starts from a Volmer step followed by a Heyrovsky step or a Tafel step [2, 3]. The Volmer step is different according to various environments:



In an acidic environment, the H* can be easily pursued by the reduction of H₃O⁺. But in an alkaline medium, the catalyst requires extra energy to break the strong covalent H–O–H bonds prior to the adsorption of H*. Hence, the catalytic activity is over one order of magnitude lower in alkaline environments than in acidic media, even for the best performing material of Pt. [4] The key to the efficient bifunctional electrocatalysts is to build effective heterostructures, for which the co-catalysts (or sites) dissociate water efficiently to provide sufficient protons (H⁺) for the adjacent HER active catalysts to produce hydrogen molecules. [4-7].

Our first-principle calculations were conducted based on density functional theory (DFT) using the generalized gradient approximation (GGA) known as PBE [8], implemented in the *Vienna ab initio simulation package* (VASP) code. [9] The projected augmented wave (PAW) method [10, 11] with a plane-wave basis set was used. The van der Waals (vdW, D3 method) [12] interaction between different layers was included in our calculation. Periodic boundary conditions is applied with a vacuum space of 20 Å in order to avoid interactions between the layers in nearest-neighbor unit cells. All of the structures were relaxed using the conjugated gradient method without any symmetric constraints.

W. Zang, email: wlzangkd@gmail.com, University of Science and Technology Liaoning, Anshan, Liaoning, China.

The energy cutoff and convergence criteria for energy and force is set to be 400 eV, 10^{-6} eV, and 0,05 eV/Å, respectively. The free energy of OH⁻ was obtained from $G(\text{OH}^-) = G(\text{H}_2\text{O}) - G(\text{H}^+)$ by assuming $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ was in equilibrium.[13-15] $G(\text{H}^+)$ was equal to half the free energy of a hydrogen molecule.[13, 14]

Thermodynamic free energy was calculated using the following equation:

$$G = E_{\text{DFT}} + E_{\text{ZPE}} - TS$$

where E_{DFT} was the total energy from DFT calculation, E_{ZPE} was the zero-point energy based on a harmonic approximation taking the vibration frequencies (ν_i) from DFT calculation and E_{ZPE} was calculated using the following equation:

$$E_{\text{ZPE}} = \frac{1}{2} \sum_i h\nu_i$$

h is the plank's constant, ν_i is the vibration frequencies of i state.

The entropy for molecules was taken from the previous report, the vibrational entropy for adsorbed species was calculated by[15]:

$$S = k_B \left[\sum_i \ln \left(\frac{1}{1 - e^{-h\nu_i/k_B T}} \right) + \sum_i \frac{h\nu_i}{k_B T} \left(\frac{1}{e^{h\nu_i/k_B T} - 1} \right) + 1 \right]$$

k_B is the Boltzmann constant, h is the plank's constant, ν_i is the vibration frequencies of i state.

In this paper, it is focused on two phases of molybdenum carbide α -MoC and β -Mo₂C, structures of which are illustrated in Figure 1. β -Mo₂C has been reported as excellent catalyst for HER in acidic solution, while the α -MoC has not been well investigated due to the synthesis difficulty. The $3 \times 3 \times 3$ generated structures were relaxed using the Vienna Ab Initio Simulation Package to ensure all the forces on the ions were smaller than 0,01 eV Å⁻¹. All surface geometries were optimized before placing any adsorbate. The initial guesses for adsorbate geometries were obtained by placing the adsorbate at different sites. Such optimized geometries were characterized as minima on the potential energy surface by appropriate frequency analysis involving diagonalization of the corresponding block of the Hessian matrix with elements obtained through finite differences of analytic gradients of 0,03 Å length. The necessary numerical integrations in the reciprocal space were carried out using an optimal $3 \times 3 \times 1$ k-point mesh se-

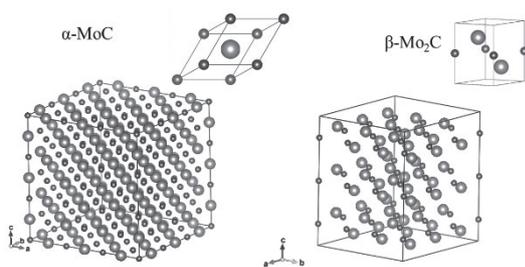


Figure 1 Structure of α -MoC and β -Mo₂C, primitive cell and 3x3 cluster.

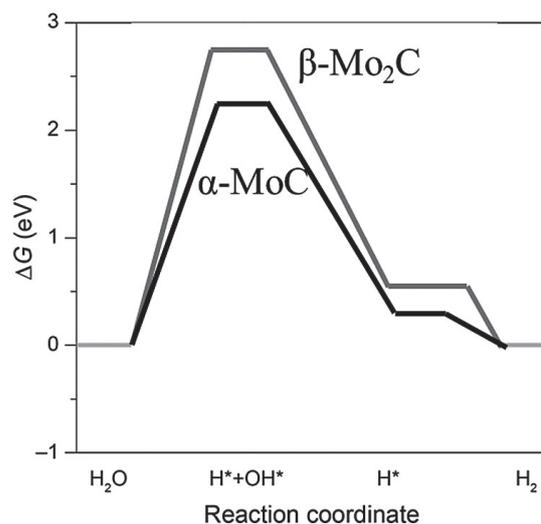


Figure 2 Free energy diagram for HER on the investigated carbide. Inset shows the optimized structures during HER reaction

lected following the Monkhorst-Pack scheme for the α -MoC and β -Mo₂C.

Results are summarized in Figure 2 and Table 1. α -MoC has large energy barriers of 2,51 eV for water dissociation ($\Delta G_{\text{H}_2\text{O}}$), 0,014 for hydrogen dissociation, respectively. β -Mo₂C has large energy barriers of 2,71 eV and 0,75 eV for water dissociation ($\Delta G_{\text{H}_2\text{O}}$), respectively. Also, the ΔG_{OH} of -2,71 eV is close to the optimal value ($\sim -2,5$ eV) for the alkaline HER process, demonstrating that the carbides have a good balance between facilitating water dissociation and preventing the blocking of active sites by the strongly adsorbed hydroxyls.[5, 6]

Table 1. Calculated energy barriers of water dissociation for generating H* and OH* intermediates ($\Delta G_{\text{H}_2\text{O}}$), hydrogen generation (ΔG_{H}), and chemisorption energies of hydroxyl (ΔG_{OH}) on nanostructured carbides.

Reaction site	$\Delta G_{\text{H}_2\text{O}}$ (eV)	ΔG_{H} (eV)	ΔG_{OH} (eV)
α -MoC	0,012	- 0,14	- 2,52
β -Mo ₂ C	0,37	0,75	- 2,71

CONCLUSION

The results indicate that the dissociation energy of H* and OH* on α -MoC is smaller than that on β -Mo₂C. In future, a method to enhance the HER activity in alkalis is to combine an HER active catalyst (in acids) with a co-catalyst, which allows the catalytic hybrid to work in a bifunctional architecture [4, 5], such like incorporating $\text{M}(\text{OH})_2$, where M denoted some transition metals, and is currently successfully applied to other earth abundant catalysts. In future all the HER mechanism in alkaline electrolyte needs to be clarified using both theoretical studies and experimental results. The DFT calculations can be employed to see how the different surfaces affect the HER catalysis as well as what kind of relation exists

among the adsorption/desorption energies of water, proton, and hydroxyl ions and how these affect the final reaction rate. Then to verify these theoretical studies, in situ microscopic, structural, and compositional characterization should be employed, to see how the various surfaces are behaving during the HER catalysis under practical conditions and what factors are controlling the releasing of hydrogen from catalyst surface.

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Note: The responsible translator for language English is associate professor W, Zang - University of Science and Technology LiaoNing, China.