



A theoretical understanding on the CO-tolerance mechanism of the WC(0001) supported Pt monolayer: Some improvement strategies

Xilin Zhang^a, Zhansheng Lu^{a,b}, Zongxian Yang^{a,b,*}

^a College of Physics and Materials Science, Henan Normal University, Xinxiang, 453007, China

^b Collaborative Innovation Center of Nano Functional Materials and Applications, Henan Province, China

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ABSTRACT

The deposition of platinum on the tungsten carbide (Pt/WC) have been achieved and proved with high stability, activity and CO-tolerance toward some reactions in experiments. Although a lot of experimental efforts have been focused on understanding the activity, stability and CO-tolerance of Pt/WC, the relevant theoretical works related to the CO-tolerance mechanism are still scarce. In current study, the adsorption and oxidation of CO on the Pt monolayer supported on WC(0001) surface (Pt_{ML}/WC(0001)) are investigated using density functional theory calculations. It is found that the oxidation of CO on Pt_{ML}/WC(0001) proceeds preferably along the Langmuir-Hinshelwood mechanism. The energy barrier of 1.06 eV for the rate-determining step of OOCO formation is almost equal to that (1.05 eV) for CO oxidation by atomic O on Pt(111), while the adsorption energy of 1.59 eV for CO on Pt_{ML}/WC(0001) is smaller than that on Pt(111) (1.85 eV), indicating that the high resistance to CO poisoning of Pt_{ML}/WC(0001) may originate from the weak interaction between them. To further improve the CO tolerance, some probable strategies are proposed based on the relevant kinetics results. The current results are helpful to understanding the origin of the highly resistant to CO poisoning of Pt_{ML}/WC(0001) and rationally designing catalysts to improve the CO oxidation activity.

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1. Introduction

The proton exchange membrane fuel cells (PEMFCs) which can directly convert the O₂ and H₂ into the environmentally friendly product H₂O and produce electricity have attracted a large amount of attention [1,2]. However, the commonly employed Pt-based catalysts in both its cathode and anode suffer from many problems including the high cost, low stability, and high sensitivity to CO [3]. To overcome these barriers, tremendous efforts have been devoted to search for potential replacements with low cost and high resistance to CO.

Tungsten carbide (WC) has been suggested to be promising candidate to replace Pt due to its high stability, good electrical conductivity, and Pt-like properties for some reactions [4–6]. Although the earlier studies demonstrated that WC alone exhibited very low activity towards the reactions [7,8], the inherent high stability of WC make it an outstanding catalyst support [9,10]. As reported by Xiong et al. [4] that the higher electrochemical stability of Pt

supported on WC (Pt/WC) compared to the traditional Pt/C catalysts originated from the high stability of WC support. They also found that the rate constant of oxygen reduction reaction on Pt/WC was twice higher than that on Pt/C, and they ascribed the enhanced activity to the synergetic effect between Pt and WC support. In addition to the inherent stability, the strong interaction of WC support with the supported Pt has positive influences on the stability and activity of Pt/WC too. For example, Esposito and Chen [11] pointed out that the great stability and activity of Pt/WC were likely to arise from the intensive interaction between WC support and Pt, which could alleviate the loss of active Pt surface area and alter the electronic structures of supported Pt.

Besides the exceptional stability and activity, more importantly, the Pt/WC exhibited also highly resistant to CO poisoning. For example, Cui et al. [12] revealed that WC supports would donate the electrons to the supported Pt, which was beneficial to weakening the adsorption of CO. By employing the chronopotentiometry, Fu et al. [13] concluded that Pt/WC exhibited better tolerance to CO than Pt/C since the onset potential for CO electro-oxidation on Pt/WC was more negative than that on Pt/C. Using the temperature-programmed desorption measurement, Mellinger et al. [14] found that the desorption temperature of CO on Pt/WC was lower than that on Pt, indicating the weaker adsorption of CO on Pt/WC than

* Corresponding author at: The College of Physics and Materials Science, Henan Normal University, Xinxiang, 453007, China.

E-mail addresses: yzx@henannu.edu.cn, zongxian.yang@163.com (Z. Yang).

that on Pt. However, although the large amount of experimental efforts were devoted to understanding the CO-tolerance mechanism of Pt/WC, the relevant theoretical studies are still quite scarce up to now. Ma et al. [15] compared the adsorption energies of CO on the Pt monolayer supported on WC(0001) (Pt_{ML}/WC(0001)) with that on pure Pt(111) at different coverage and pointed out that the Pt_{ML}/WC(0001) was much less susceptible to CO poisoning than Pt(111). To weaken the adsorption of CO on catalysts can alleviate the poisoning to some extent, the removal of CO by reacting with oxygen is the fundamental way to solve this problem. Likewise, to the best of our knowledge, the theoretical studies focusing on the CO oxidation over Pt/WC are still lacking now. Although the interaction of CO with OH was mentioned by Sheng et al. [16] when processing the methanol electro-oxidation over the Pt monolayer or bilayer supported on WC(0001), the relevant reaction processes and kinetic data are unexploited. Further, the effect of O₂ which is an important feedstock in PEMFCs on the removal of CO is also unclear.

In present study, we aim to understand the CO-tolerance mechanism by exploring the removal processes of CO by O₂ over the Pt_{ML}/WC(0001) using the first principle methods. Accordingly, the rate-determining step (RDS) along the minimum energy path (MEP) of CO oxidation is identified. The corresponding reaction barrier is calculated and compared with that on the precious metal catalysts. Based on these results, some probable strategies are proposed to further improve the activity and anti-CO-poisoning ability of Pt/WC. The present results are beneficial to understanding the origin of the high tolerance to CO poisoning of Pt/WC and designing the reasonable models to further improve its activity and anti-CO-poisoning ability.

2. Methods and models

The spin-unrestricted density functional theory (DFT) calculations are performed using the Dmol³ code embedded in the Materials Studio software. The generalized gradient approximation with PW91 functional is adopted to describe the exchange-correlation potential [17] based on the existing literatures [15,18] and our previous tests [19]. For the geometry optimization, the convergence tolerances are set to 10⁻⁵ Ha for the energy, 0.002 Ha/Å for the force, and 0.005 Å for the displacement. The electronic self-consistent field tolerance is set to 10⁻⁶ Ha and the smearing value is set to 0.005 Ha to achieve convergence. The valence electronic wave functions are expanded into a set of numerical atomic orbitals by a double-numerical basis with polarization functions (DNP) and the core electrons are described by the DFT semicore pseudopotentials [20]. The reciprocal space is sampled with 5 × 5 × 1 k-points grid generated automatically using the Monkhorst-Pack method [21] for relaxation calculations and transition state (TS) search. The linear synchronous transition/quadratic synchronous transit (LST/QST) tools [22] are employed to locate the saddle points and MEP. It starts with LST maximization, followed by energy minimization in directions conjugate to the reaction pathway. These approximated TS's are then used to perform QST maximization. From that point, another conjugate gradient minimization is performed. The cycle is repeated until a stationary point with only one imaginary frequency is located.

As described in our previous paper [19], the Pt_{ML}/WC(0001) model is constructed to access the CO-tolerance mechanism by exploring CO oxidation processes. A (3 × 3) WC(0001) surface with W termination is selected as the substrate of the Pt ML because the W-terminated WC(0001) surface was previously proved to be thermodynamically more stable and catalytically more active than the C-terminated surface [23]. The supercells are modeled as periodically repeating slabs with three WC bilayers and a vacuum layer of

Table 1

The key adsorption parameters of the probable intermediates on the catalyst substrates. E_{ads} is the adsorption energy and the d_{int} is the intermolecular distance. The h are the adsorption height between the adsorbed molecules and the substrate. Δq stands for the total charge on the adsorbed molecule. The negative and positive numbers represent the loss and gain of electrons, respectively.

Adsorbate	E _{ads} (eV)	h (Å)	d _{int} (Å)	Δq (e)
O ₂	1.55	2.00	1.39	0.42
CO	1.59	1.93	1.16	-0.25
O	4.01	1.53	-	0.55
CO ₂	0.10	2.97	1.17	-0.03

15 Å to eliminate the slab-slab interactions. During optimization, the most bottom four atomic layers of the slabs are constrained at their bulk positions to mimic bulk characteristics, while the remaining layers including the Pt ML and the subsequent adsorbates are allowed to relax freely. It is found that the Pt atoms in the Pt ML are strongly adhered to the hollow sites of WC(0001) surface with C atoms directly beneath them, and the vertical height between the Pt ML and the substrate is calculated to be 2.16 Å, agreeing with the results of Vasić et al. [24]. It is also found that the Pt ML pulls the surface W layer slightly outward by about 0.01 Å with respect to the relaxed WC(0001) surface, while the subsurface C layer is impervious, implying a strong interaction between the first two metal layers. Indeed, the approximate Pt_{ML}/WC(0001) has been prepared successfully and proved with higher stability under the operating condition of fuel cells compared to the traditional Pt/C [11,25]. Additionally, the activity of Pt_{ML}/WC(0001) towards some reactions were experimentally found to be comparable to that of the Pt-based catalysts [26,27], meanwhile, the dosage of Pt loading was dramatically decreased. Additionally, the geometric and electronic properties and the stability as well as the activity of the Pt_{ML}/WC(0001) for the hydrogen evolution and the methanol electro-oxidation were exploited theoretically [15,16,19,24]. The results demonstrated that the strong synergic effect of WC(0001) support with Pt monolayer was beneficial to the enhanced activity and stability. We thus focus mainly on the CO oxidation process on the Pt_{ML}/WC(0001) in present study and the detailed analysis of the geometry and stability as well as the electronic properties are by reference to the previous literatures [19,24].

3. Results and discussions

3.1. The adsorption of the reaction species

The optimized adsorption configuration for a certain reaction species is determined first by comparing the adsorption energies of the reaction gas at different adsorption sites with various adsorption patterns. It is found from Fig. 1a and Table 1 that the CO tends to be vertically adsorbed at the top site of Pt forming a Pt–C bond of 1.93 Å. The calculated adsorption energy is 1.59 eV based on the equation of E_{ads} = E_{Sub} + E_X - E_(X/Sub), where E_(X/Sub) and E_{Sub} are the total energies for the optimized equilibrium configurations of the substrate with and without gas adsorbate (X), respectively, and E_X is the total energy of the corresponding isolated molecule in its ground state. To visualize the charge redistribution, the charge density difference (CDD) map is depicted also in Fig. 1. It is found that the charge accumulate dominantly at the Pt–C bond, while the charge depletion area is located mainly at the C–O bond, resulting in that the CO is positively charged by 0.25 e based on the Mulliken charge analysis (Table 1). The current results are in good agreement with that reported by Ma et al. [15]

The geometric and electronic structures of O₂ and O adsorbed on Pt_{ML}/WC(0001) have been discussed in our previous study [19]. The adsorption strength of O on Pt_{ML}/WC(0001) is found to be much stronger than that of O₂, characterizing with the bigger adsorption

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