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Zongtang Fang, Lucun Wang, Yixiao Wang, Rebecca R Fushimi



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**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

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Article

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Pt-Assisted Carbon Remediation of Mo₂C Materials for CO Disproportionation

Zongtang Fang,^a LuCun Wang,^a Yixiao Wang,^a Ember Sikorski,^{b,c} Shuai Tan,^{c,d} Dongmei
(Katie) Li-Oakey,^{c,d} Lan (Samantha) Li,^{b,c} Gregory Yablonsky,^e David A. Dixon^f, Rebecca
Fushimi^{a,*}

^a Biological and Chemical Science and Technology, Idaho National Laboratory, Idaho Falls, ID
83401

^b Micron School of Materials Science and Engineering, Boise State University, Boise, ID 83725

^c Center for Advanced Energy Studies, Idaho Falls, ID 83401

^d Department of Chemical Engineering, University of Wyoming, Laramie, WY 82071

^e Department of Energy, Environment and Chemical Engineering, Washington University in
Saint Louis, Saint Louis, MO 63103

^f Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336

Abstract

Using the CO disproportionation (Boudouard) reaction as a probe reaction, an in-depth analysis of
temperature-programmed pulse response data shows that the addition of Pt to Mo₂C mitigates
deactivation of Mo active sites by acting as a carbon collector. CO₂ production on Mo₂C and
Pt/Mo₂C materials is dependent on both the activation energy and the CO surface concentration.

* Corresponding authors: rebecca.fushimi@inl.gov, dadixon@ua.edu

Detailed plane-wave density functional theory calculations of the CO adsorption and disproportion reactions on Mo₂C supported Pt nanoparticles (NPs) are reported. The Mo₂C was modeled by the β -Mo₂C (100) surface and the Pt/Mo₂C interface was modeled by the addition of 12 Pt atoms to the Mo₂C (100) surface (12Pt@Mo₂C). The potential energy surfaces of the Boudouard reaction were calculated on pure Mo₂C, 12Pt@Mo₂C as well as Pt (111) surfaces. CO dissociation readily occurs on the Mo₂C (100) surface, but not on the Pt (111) surface with the former being exothermic and the latter being endothermic. At the Pt/Mo₂C interface, CO dissociation is still exothermic, but with a larger energy barrier. The Boudouard reaction takes place on the Mo₂C region where CO₂ is formed from a surface O atom dissociated from one CO molecule in reaction with another CO molecule leaving one C atom on the surface. C adsorption is preferential on the Pt site in comparison to the Mo site. The supported Pt domains can collect remaining C atoms, facilitating further CO₂ formation on the active Mo sites. A Bader charge analysis shows that the surface metal-carbon bond is a mixture of covalent and ionic bonds whereas the surface metal-oxygen bond is ionic. Electron localization function (ELF) and partial charge density calculations agree well with the Bader charge analysis. These computational results are consistent with experimental observations of the interaction of CO with Mo₂C-nanotube supported Pt-domains in the transient regime under far-from equilibrium conditions. The Boudouard reaction is an important side reaction and the unexpected role found for Pt as a carbon collector, with Mo serving as a disproportionation site, provides a unique vantage point for understanding carbon and coke formation on catalytic materials.

Introduction

The adsorption and reaction processes of CO on transition-metal surfaces have been the subject of studies for decades, because they are key steps in many catalytic processes, such as CO oxidation, the water-gas shift (WGS) reaction,¹ CO methanation,² and Fischer-Tropsch synthesis.³ Despite extensive research efforts, there are still many open questions regarding the reaction mechanisms and active sites. It is known that the reactivity of CO depends critically on the electronic and geometric nature of the underlying metal surfaces. For instance, CO can readily decompose on Mo surfaces⁴ whereas dissociative adsorption of CO on Pt surfaces may only occur under high temperature and pressure conditions.⁵ Compared with the well-defined single crystal surfaces, the reaction mechanisms and active sites for CO activation are even more complex when transition metals are in the form of nanoparticles, which are usually dispersed on materials with high surface areas.

Transition metal carbides (TMCs), such as molybdenum carbide (Mo_2C), have been reported to exhibit excellent catalytic properties in many reactions including CO_2 reduction,⁶ CO_2 hydrogenation reactions,^{7,8} CO hydrogenation,⁹ and the WGS reaction^{10,11} etc. For the WGS reaction on Pt/ Mo_2C the reaction rate is significantly higher than the most active oxide-supported Pt catalysts, such as Pt/ CeO_2 and Pt/ TiO_2 .¹² In addition, it was shown that the reaction rate of the supported catalysts could be enhanced by a factor of 4-5 as compared to unsupported Mo_2C .^{12,13} Atomic layered Au clusters on α - MoC are active to convert CO through the WGS process at a low temperature of 150 °C.¹⁴ Highly dispersed copper over hexagonal β - Mo_2C has been reported to be an efficient and stable catalyst for the reverse water gas shift reaction.¹⁵ Other early transition metal carbides such as TM = Ti, Zr, Hf, V, Nb, Ta have been reported to be promising materials

for CO₂ activation as well as hydrogenation of CO₂.^{16,17,18,19,20} The reaction mechanisms and origin of the synergistic effect, however, are still not fully addressed.

The interaction of CO with various Mo₂C materials has been widely investigated with the density functional theory.^{21,22,23,24,25,26} Wang and Jiao studied the effect of coverage of CO adsorption and dissociation on the orthorhombic Mo₂C (100) surface and found that the dissociative chemisorption is favorable for up to ½ monolayer of CO on the Mo terminated surface.^{21,22} In addition, they found that the most stable surface of hexagonal β -Mo₂C changes as temperature increases and is also dependent on the surrounding gas compositions.²³ The doping of K has been reported to be favorable for CO molecular adsorption on a hexagonal β -Mo₂C (001) surface.²⁴ Li, et al found that the Ni doping can change the most favorable site for C adsorption from the hollow Mo site to the Ni-Mo interface on the hexagonal β -Mo₂C (001) surface.²⁵ However, the best site for O adsorption remains unchanged.

Among various approaches to study catalytic reactions, the Temporal Analysis of Products (TAP) probe molecule pulse response technique is particularly useful in extracting kinetic information for the development of detailed reaction mechanisms for catalytic reactions on complex materials.^{27,28} TAP provides a unique experimental regime, far-from equilibrium, in which industrial materials can be incrementally titrated with nanomole precision and millisecond time resolution. The evolution of kinetic properties from TAP data shows how processes, such as surface diffusion, number of active sites, reaction products, and effects of surface intermediates and products impact the reaction mechanism. By removing the material from the process setting, these detailed kinetic tests can be used to better understand at a fundamental level how/why one material functions differently than another.

In previous work by our group,¹⁰ Pt/Mo₂C materials were interrogated to understand electronic structure changes and CO bonds strengths using DRIFTS. Transient kinetic pulse response experiments in a TAP reactor were a smaller component of previous work to characterize CO adsorption, reaction pathways, and active sites in Mo₂C nanotube supported Pt nanoparticles prepared by atomic layer deposition (ALD). Temperature programmed experiments were conducted in a continuous CO pulsing mode to investigate CO adsorption capacity and reactivities on both Pt/Mo₂C and pure Mo₂C catalysts. Significant CO₂ was produced on both pure Mo₂C and Pt/Mo₂C surfaces with the maximum production at higher temperature for Pt/Mo₂C than that for pure Mo₂C. It was concluded that CO₂ formation occurs via the process of CO disproportionation (forward Boudouard reaction, $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) and that C atoms accumulate on the surface.

Herein, we provide greater focus on the mechanism for accumulation of carbon atoms and the role of platinum in assisting this process using density functional theory (DFT) to better understand the original TAP results. It is important to note that the TAP transient low-temperature CO₂ production is not likely to be observed under steady-state flow conditions since the time scale and sensitivity of typical detection systems (e.g. GC-MS) far exceed this rate of change and the total amounts of CO₂ produced are extremely low. The distinctive transient measurement setting is used as a precise method for comparing the fundamental kinetic features of these materials and hence a greater level of detail for comparison to DFT results. Nonetheless, it provides no direct structural information about the active center for the Boudouard reaction, the Pt domain and interface. To close the structure-kinetics gap we can rely on DFT electronic structure calculations to better understand the surfaces responsible for our experimental kinetic observations.

This work combines both experimental techniques including TAP and transmission electron microscopy (TEM) characterizations with periodic DFT to identify the active sites for CO

adsorption and disproportionation as well as the role of Pt nanoparticles in acting as a carbon collector. The catalysts were characterized by TEM after TAP experiments to investigate the structural change including carbon deposition. Previous work showed XRD patterns of Mo₂C nanotubes corresponding to the pure hexagonal phase of Mo₂C (β -Mo₂C).²⁹ There is no uniform definition of different phases of Mo₂C as well. We have noticed that the hexagonal and orthorhombic phases are called α -Mo₂C and β -Mo₂C respectively by some researchers.^{16,17,21} To be consistent with our previous work as well as some other experimental studies,^{10, 29,30} we use β -Mo₂C for the HCP phase in this work. The β -Mo₂C (100) surface was selected for the DFT calculations to model the CO adsorption and disproportionation reactions on a Mo₂C nanotube as the lattice fringes of the Mo₂C nanotube were in the direction of β -Mo₂C (100) plane from an HRTEM image.²⁹ We studied the potential energy surface of the Boudouard reaction on both a pure β -Mo₂C (100) surface and a Pt/Mo₂C interface. The Boudouard reaction on Pt (111) surface was also calculated for comparison. The C and O adsorption energies on different surfaces were calculated to further investigate the reaction mechanism as well as the nature of the active sites. A Bader charge analysis and the calculation of the electronic density of states were performed to understand the nature of adsorbates binding to the surface.

From these results we surmise the unique conclusion that the active center for the Boudouard reaction can be attributed to Mo while Pt serves in a role of preferentially collecting carbon. Such an observation has, to the best of our knowledge, hereto now not been described in the significant body of existing work on the Pt/Mo₂C system. While the service of this mechanism in a practical continuous flow reaction system may not be readily apparent, this result informs the fundamental mechanism of a common side reaction and provides an important vantage point for carbon and coke formation.

Methods

Experiment. Material synthesis and TAP experiments were performed as reported in our previous work.¹⁰ Briefly, the Pt/Mo₂C samples prepared with 50 and 100 ALD cycles are denoted as 50 Pt/Mo₂C and 100 Pt/Mo₂C respectively. The material was *ex situ* pretreated by flowing a gas mixture of 15% CH₄ in H₂ at a flow rate of 150 mL/min and a temperature of 590 °C for 4 h to reduce the Mo₂C surface that might be oxidized in air. Before starting the pulsing experiment, the catalyst was heated in the TAP reactor, under vacuum, from room temperature to 400 °C to desorb any surface species; the temperature programmed desorption (TPD) spectra is shown in the Supporting Information (SI). Minor CO₂ release was observed which can be attributed to the surface oxygen formed during the ambient transfer and the surface carbon either from uncoordinated C in Mo₂C or CH₄ decomposition in the reduction process. The catalysts were initially exposed to a sequence of CO pulses until the CO uptake reached a plateau followed by a TPD experiment to investigate the reaction of adsorbed CO at higher temperatures. Next, starting from the *in situ* TPD pretreated surface, the experimental temperature was linearly increased at a much slower rate (1 °C/min) from room temperature to 300 °C while pulsing CO. The exit flow pulse responses of unreacted CO and the CO₂ produced on the Mo₂C, 50 Pt/Mo₂C and 100 Pt/Mo₂C catalysts were recorded in the temperature-programmed pulsing experiments. The morphology of Pt/Mo₂C samples after TAP experiments were measured by TEM on a JEM-2100P electron microscope operating at 200 kV (JEOL Ltd., Tokyo, Japan).

It is important to note that the CO₂ produced in the pulsing experiment is mostly through the disproportionation process and the contribution of CO oxidation by the surface oxygen from the ambient is not significant. The reason is that the CO₂ fraction yield from converted CO was always less than 50% during the whole temperature programmed pulsing experiment. The

production of 1 mol CO₂ via CO oxidation by the surface oxygen only requires 1 mole CO. Additionally, only CO desorption was observed and no CO₂ desorption was detected below 300 °C in the temperature programmed desorption (TPD) experiment with CO preadsorption on pure Mo₂C and 50 Pt/Mo₂C (SI, Figure S5). In comparison, significant CO₂ was produced under the condition of continuous CO pulsing on pure Mo₂C and 50 Pt/Mo₂C below 300 °C. Thus, if the CO₂ produced in the temperature programmed pulsing experiment was mostly through CO oxidation, significant CO₂ production would have been observed in the TPD experiment with CO preadsorption.

More evidence of the Boudouard reaction was found in our DRIFTS experiment¹⁰ with CO purging on the studied materials (SI, Figures S1 and S2). The DRIFTS spectra collected right after purging CO indeed clearly showed the CO₂ peaks. Also, there was no air or oxygen detected in the down-stream mass spectra, indicating that the CO₂ was produced via the Boudouard reaction, not CO oxidation.

Electronic Structure Calculations. The periodic DFT calculations were performed with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional³¹ and the plane-wave basis sets first using the Vienna ab initio simulation package (VASP).^{32,33,34} The projector-augmented wave (PAW) method^{35,36} was employed to describe the interaction between the atomic cores and the electrons. The 5*p* semi-core electrons for Pt and the 4*s* and 4*p* semi-core electrons for Mo were treated as valence electrons. For the plane-wave basis sets, a kinetic energy cutoff of 520 eV was chosen for the reactions on Pt (111), β-Mo₂C (100) surfaces, and Pt/Mo₂C interface. Previous studies^{37,38,39} showed that GGA functionals such as PBE fail to properly describe the interaction between CO and Pt (111) surface due to the lack of dispersion corrections using the GGA functionals. We performed static calculations for the PBE relaxed structures using the Meta GGA

M06L functional⁴⁰ and the same basis sets employed for the relaxations. The M06L functional includes dispersion effects in its parameterization and correctly describes the CO adsorption on Pt (111) surface.³⁷

The bulk lattice constant for the face-center-cubic (FCC) bulk Pt was optimized with Monkhorst-Pack k-meshes of $15 \times 15 \times 15$. The lattice constant was calculated to be $a = 3.975 \text{ \AA}$ with PBE, agreeing well with literature.⁴¹ The lattice parameter is also consistent with the experimental value of 3.92 \AA .⁴² For the slab, a large surface model with low CO coverage was selected as the amount of the injected molecules was much smaller than the number of active sites on the surface under the TAP conditions. The Pt (111) surface was modeled by four layers using a 4×4 super cell with a 5×5 k-point grid. The top two layers were relaxed in the surface optimization as well as the adsorption reactions. The vacuum distance between two slabs was 12 \AA . The adsorbed molecules were added only on one side of the slab.

The hexagonal β -Mo₂C forms a disordered crystal lattice from X-ray diffraction experiment.^{43,44} Mo atoms form a hexagonal close packed array and C atoms statistically occupy one half of the octahedral interstitial sites. The most stable Mo-C-Mo-C stacking pattern has an eclipsed configuration.^{45, 46, 47,48} In the following sections, the Mo₂C (100) surface denotes the HCP β -Mo₂C (100) surface. We selected the model proposed by Wang et al.²³ and a unit cell of $2 \times 2 \times 1$ size of the primitive cell was optimized. The $5 \times 5 \times 6$ Γ -centered Monkhorst-Pack k-point grid was used. The lattice constants were optimized to be $2a = 6.062 \text{ \AA}$, $2b = 6.049 \text{ \AA}$, and $c = 4.706 \text{ \AA}$, which are consistent with the experiment values of $a = b = 3.011 \text{ \AA}$ and $c = 4.771 \text{ \AA}$.⁴⁹ Our calculated lattice parameters are in agreement with the model used by Shi⁴⁸ in which the carbons atoms are in a different orientation. The supercell for Mo₂C slab was 2×2 of the optimized unit cell. There are two different Mo terminated and one C terminated Mo₂C (100) surfaces. We select

the most stable Mo-terminated Mo₂C (100) surface to study the Boudouard reaction. The slab contains four Mo₂C layers and the top two Mo₂C layers are relaxed for the geometry optimization. The CO adsorption on the eight slab layers gives a physisorption energy with a difference of only 0.01 eV. Thus, accurate results can be obtained from the calculations on the slab with four Mo₂C layers. The vacuum distance was selected as 12 Å. Since the optimized Mo₂C surfaces are stoichiometric, we used the following equation (1) proposed by previous work^{23,47,48} to calculate the cleavage energies:

$$\sigma = (E_{\text{slab}} - n E_{\text{bulk}})/2A \quad (1)$$

where E_{slab} and E_{bulk} are the total energies of the slabs and the bulk; n is the number of Mo₂C units in the slab and A is the surface area.

Based on the most stable Mo-terminated Mo₂C (100) surface, we built a slightly tilted one layer 2 × 3 Pt slab by the adsorption of 12 Pt atoms on the surface. The building of this model started from the deposition of 6 Pt atoms and the most favorable additions are the C sites with the formation of Pt-C bonds. The addition of another 6 Pt atoms forms a tilted one layer (2 × 3) which is structurally close to the Pt (111) with slightly shorter Pt-Pt bond distances. We used this model to study CO reactions at the interface. For the Pt/Mo₂C interface surface calculations, the vacuum distance was also set to 12 Å. One should be aware that this interface model does not directly model either 50 Pt/Mo₂C or 100 Pt/Mo₂C material. The HRTEM images show the average Pt particle size on 50 Pt/Mo₂C and 100 Pt/Mo₂C ranges from 2.0 to 2.5 nm.¹⁰ Due to the high computational cost, it is nearly impossible to model 2 nm Pt nanoparticles on Mo₂C support with DFT. The Pt nanoparticles on 50 Pt/Mo₂C have more interface character and less domain of the Pt(111) surface compared to 100 Pt/Mo₂C.¹⁰

Geometries were relaxed until the residual force on each atom was 0.02 eV/Å. The calculations for the isolated gas phase molecules and atoms were carried out with a $8.0 \text{ Å} \times 8.0 \text{ Å} \times 8.0 \text{ Å}$ unit cell and one k-point for the Brillouin zone. The adsorption energy (E_{ads}) was calculated by equation (2):

$$E_{\text{ads}} = E_{\text{adsorbate/slab}} - E_{\text{adsorbate}} - E_{\text{slab}} \quad (2)$$

where, $E_{\text{adsorbate/slab}}$ and E_{slab} are the total electronic energies of the slab at 0 K with and without the adsorbate and $E_{\text{adsorbate}}$ is the total electronic energy of the adsorbate in the gas phase. The climbing image nudged elastic band (cNEB) method was used to locate the transition state.^{50,51} The transition state was characterized by the presence of one and only one imaginary frequency. A Bader charge analysis^{52,53} was performed to determine the local charges of atoms in the system. Adsorbate vibrational frequencies were calculated using finite differences with a step size of 0.015 Å. The corresponding vibrations were used to compute the zero-point energy (ZPE) corrections and vibrational partition functions for all adsorbed species and transition states. The detailed descriptions for the derivation of CO transient pressure, free energy and rate constant calculations are shown in Supporting Information. The local density of states (LDOS), electron localization function (ELF),^{54,55} and partial charge density (PCD) were calculated using $3 \times 4 \times 1$ Γ -centered k-points to investigate the nature of bonding. All calculations have been performed on Idaho National Laboratory Falcon clusters with an SGI ICE-X distributed memory system.

Experimental Results

TPD with CO Preadsorption The results for the TPD spectra with CO preadsorption at room temperature are shown in the Supporting Information (Figure S5). Surprisingly, the per pulse CO conversion on the 100 Pt/Mo₂C catalyst (Figure S5b) is about 60% even after dosing of 5000 nmols indicating that the plateau region represents an adsorption/desorption equilibrium. The total CO

uptake on 100 Pt/Mo₂C is approximately 600 nmol and about 1/3 monolayer of surface metal atoms (Pt and Mo, see Supporting Information for the calculation of surface metal atoms). The total CO uptake on Mo₂C and 50 Pt/Mo₂C are comparable and are only approximately one half of that on 100 Pt/Mo₂C. A broad CO desorption peak spanning from 50 °C to 250 °C was observed on all three materials. The total amount of CO desorbed up to 300 °C from the bare Mo₂C support is comparable to that from the 50 Pt/Mo₂C catalyst but is about one half of that from the 100 Pt/Mo₂C sample. From our previous DRIFTS results,¹⁰ the desorbed CO below 250 °C on 50 Pt/Mo₂C are from the Mo₂C sites. In addition, the CO added to the catalysts is observed to desorb as CO₂ below 300 °C only for the 4Pt/Mo₂C sample with a peak maximum near 250 °C. The production of CO₂ during the temperature ramp indicated the role of Boudouard chemistry but was limited by the capacity for CO retention.

Temperature Programmed Pulsing The temperature programmed experiments with the continuous pulsing of CO on the clean surfaces of Mo₂C, 50 Pt/Mo₂C and 100 Pt/Mo₂C are shown in Figure 1. While this data was presented previously,¹⁰ the Pt-assisted carbon mediation mechanism had not been considered. Here we provide a more detailed kinetic analysis. Throughout the experiment, significant CO₂ production was observed on the bare Mo₂C support at low temperature (<100 °C) in a process that quickly dissipated. The Pt-modified catalysts also showed low-temperature CO₂ production, but the intensity was much lower.

The CO conversion and fractional CO₂ yield during CO pulsing over the three samples are calculated and plotted as a function of temperature (Figure 1a and 1b). The fractional CO₂ yield is defined as the fraction of the adsorbed CO molecules being transformed into CO₂. A basic evaluation of this data indicates that while the conversion of CO is generally the same for these materials, the presence of Pt results in remarkably distinct production trends for CO₂. For all

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2
3 catalysts the per pulse CO conversion is very high (>40%) throughout the experiment, especially
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5 for the pure Mo₂C support and the 50 Pt/Mo₂C catalyst at low temperatures (<50 °C).
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8 On a pure Mo₂C surface, a simultaneous decrease in CO conversion and CO₂ production
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10 is observed at low temperatures (below 50 °C). CO conversion drops as sites are occupied. Surface
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12 oxygen is then consumed, slowing the production of CO₂. However, as the temperature increases,
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14 the declining conversion of CO passes through a turning point near 50 °C. The temperature
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16 dependence of both CO and CO₂ exhibit an apparent plateau and near 225 °C, CO conversion
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18 begins to drop.
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22 For 50 Pt/Mo₂C, the CO conversion trend is the same as that on Mo₂C below 200 °C. This
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24 suggests that the same Mo active sites are used for CO conversion and the small Pt domains do
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26 not directly contribute to low-temperature CO conversion. The production of CO₂, however, is
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28 not observed below 200 °C, as it is for Mo₂C, indicating that Pt participates in the accumulation
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30 and storage of CO. At 250 °C, the CO conversion of Mo₂C begins dropping, but the Pt samples
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32 continue increasing with temperature. This indicates that the Pt catalyst may assist in maintaining
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34 CO conversion sites on Mo₂C through collecting carbon.
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38 Compared to the reactions on the pure Mo₂C and 50 Pt/Mo₂C surfaces, the total conversion
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40 of CO is lower and the rate of deactivation is slower on the 100 Pt/Mo₂C surface at the low
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42 temperatures (< 100 °C). CO might adsorb reversibly on the Pt (111) sites (not present on 50
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44 Pt/Mo₂C)^{10,29} in addition to the Mo sites. The reversible adsorption decreases the low-temperature
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46 CO conversion. In the low-temperature region, however, CO₂ production is observed with the
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48 exception of the 50 Pt sample, suggesting that the 100 Pt sample must have sites that
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50 disproportionate CO at the lower temperatures. This process declines with temperature, similar to
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52 the case of Mo₂C. The transition point where CO conversion begins increasing occurs at the higher
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temperature (100 °C). Above 100 °C, CO conversion is essentially the same for all three materials. However, CO₂ production for the 100 Pt sample demonstrates a dramatic acceleration. Its acceleration is shifted to the lower temperatures, compared to that of 50 Pt/Mo₂C.

Figures 1c through 1f show the mass balance of converted CO by three different materials. The total converted CO molecules can undergo two different pathways. One pathway is to produce CO₂ via the Boudouard process with the residue of one C atom per CO₂ molecule formed. The other pathway is to remain on the surface in the form of either physisorbed or chemisorbed CO. The mass balance equation of converted CO can be written as: $N_{\text{converted}} = N_{\text{C}} + N_{\text{CO}_2} + N_{\text{CO}}$, where $N_{\text{converted}}$ is the total conversion (adsorption + reaction), N_{C} is cumulative surface C atoms from the Boudouard reaction, N_{CO_2} is the total CO₂ molecules produced, and N_{CO} is cumulative surface CO. Here N_{C} is the same as N_{CO_2} . $N_{\text{converted}}$ equals the difference of the CO pulsed into the reactor and the CO out of the reactor detected by the mass spectrometer. One should be aware that N_{C} does not include the C from the CO which undergo chemisorption only and do not proceed to form CO₂. The cumulative surface carbonaceous species (N_{carb} , figure 1d) is the summation of N_{C} and N_{CO} .

Figure 1c gives the total conversion of CO on three different materials during the temperature programmed pulsing experiment. The total conversion is comparable on Mo₂C and 50 Pt/Mo₂C materials, which is ~ 200 nmol less than that on 100 Pt/Mo₂C. The cumulative surface carbonaceous species (Figure 1d) shows that more carbonaceous species were observed on 50 Pt/Mo₂C than on Mo₂C. This also indicates 50 Pt/Mo₂C is less reactive to produce CO₂ than Mo₂C under the reaction temperature less than 300 °C. Figure 1e and 1f show the surface CO and C accumulation with respect to temperature. The cumulative surface CO follows the order of 100 Pt/Mo₂C > 50 Pt/Mo₂C > Mo₂C. The cumulative surface C is similar for 100 Pt/Mo₂C and Mo₂C

at the temperature lower than 150 °C. At temperatures above 150 °C, significantly more surface C atoms are accumulated on 100 Pt/Mo₂C than on Mo₂C. The cumulative surface C is not sufficient for 50 Pt/Mo₂C until 200 °C. If all CO underwent the Boudouard reaction, then one would expect a constant CO₂ fractional yield of 0.5 according to the Boudouard reaction stoichiometry. In all cases, however, the fractional yield is lower, indicating an additional pathway for CO storage.

Structural Characterization The catalysts were retrieved after the TAP experiments and subjected to TEM characterization in order to investigate potential structural changes and deposition of carbon species during the TAP experiments. The representative TEM results on the 100 Pt/Mo₂C catalysts (Figure 2) show considerable carbon formation on the surface of the catalysts with multi-wall nanosheets or onion-like structures. It is important to note that the Pt nanoparticles are encapsulated by multi-layers of carbon species, most likely graphene sheets in view of its comparable layer distance to that of carbon nanotubes.^{56,57} EDX analysis (shown in SI) of the catalyst in the same region clearly shows that some of the Pt nanoparticles migrate onto the surface of carbon structures.

Theoretical Results

To understand the nature of active sites as well as the role of the deposited Pt nanoparticles, DFT was used to calculate the potential energy surfaces of the Boudouard reaction on the pure Mo₂C surface and the Pt/Mo₂C interface. The CO, C, and O adsorption energies as well as the bond distances on three different surfaces are summarized in Table 1 and Figure 6. The calculated rate constants for key steps are shown in Table 2. The optimized β -Mo₂C (100) surface structures and the surface energies are shown in Figure 3. The optimized structures for Pt/Mo₂C interface are shown in Figure 4. The potential energy surfaces (PESs) for Boudouard reaction on Pt (111), Mo₂C (100), and Pt/Mo₂C surfaces are shown in Figures 5 and the SI. The calculated free energy surfaces

on Mo₂C (100), and Pt/Mo₂C surfaces are also shown in the SI. The results with the PBE functional as well as the less stable structures for CO reactions on three different surfaces are shown in SI. Unless otherwise specified, we use the M06L results for the following discussion. The calculated partial charge densities are shown in Figure 7 and the LDOS and ELF figures are shown in the SI.

Mo₂C Surfaces and Pt/Mo₂C Interfaces Figure 3 shows the two different relaxed Mo-terminated and a C-terminated Mo₂C (100) surfaces and their surface energies. The Mo-terminated surfaces are more stable than the C-terminated surface with a difference in surface energies of 0.33 J/m². The most stable Mo₂C (100) surface has a stepped configuration. There are two different types of surface Mo atoms, upper-layer and lower-layer Mo's. The lower-layer Mo atoms are bonded to three C atoms with two C atoms in the first layer and one C atom in the second carbon layer. In contrast, the upper-layer Mo atoms are bonded with two C atoms in the first carbon layer. There are, in total, four different adsorption sites on this stepped surface: upper top (UT), upper bridge (UB), lower top (LT), and lower bridge (LB). The second lowest energy Mo-terminated Mo₂C (100) surface is also a stepped surface. Both the upper-layer and lower-layer Mo atoms are bonded with two C atoms in the first carbon layer. The C-terminated surface has the highest cleavage energy, 0.96 J/m² higher than the most stable surface. The surface energies with the PBE functional are predicted to be ~ 0.8 J/m² less than the M06L results. Our calculated cleavage energies with PBE are slightly larger than previous work by ~ 0.4 J/m², where a 400 eV cutoff energy was used.

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Figure 4 shows the Pt/Mo₂C interface structures. The deposition of 6 Pt atom on the most stable Mo-terminated Mo₂C (100) surface (6Pt@Mo₂C) gives the structure shown in Figure 4a. The 6 Pt atoms are separated into two rows in a linear array with each Pt bonded to one C and four adjacent Mo atoms. The Pt-C bond distances range from 2.10 Å to 2.12 Å. The Pt-Mo bond distances are predicted to be 2.65 to 2.68 Å for the upper Mo's and 2.83 to 2.88 Å for the lower

Mo's. The higher energy structures with 3 out of the 6 Pt atoms adsorbed on the upper bridge (UB) sites are shown in Supporting Information (SI). We calculated Pt adsorption energies with equation (2) using the adsorbate of 6 Pt atoms. For the structures with three of 6 Pt atoms bonded to three upper-layer Mo atoms and three Pt atoms, the Pt adsorptions energies are 1.89 and 3.01 eV less negative than the most stable one (Figure 4a) with the M06L functional. Starting from the most stable 6Pt@Mo₂C, the structure of a tilted one-layer Pt (2 × 3) on Mo₂C (100) (12Pt@ Mo₂C) generated by the addition of an additional 6 Pt atoms is shown in Figure 4b. The Pt-Pt bond distances range from 2.53 Å to 3.04 Å, which are comparable to the Pt-Pt bond distance of 2.82 Å for the FCC Pt bulk in the current study and an experimental value of 2.76 Å⁵⁸ for the solid. For the Pt (2 × 3) region on the interface, each of the Pt top, bridge, and hollow sites may be slightly different as the one layer Pt (2 × 3) is not a perfect Pt (111) slab. Another 12Pt @ Mo₂C structure with the 9 Pt atoms more like one-layer Pt (3 × 3) (Figure 4c) is higher in energy by 1.39 eV.

CO Adsorption and Disproportionation We first studied the Boudouard reaction on Pt (111) (4×4) surface for the addition of two CO molecules and the coverage of 1/8 ML using the M06L functional. The potential energy surfaces from both PBE and M06L functionals are shown in Supporting Information. Consistent with the literature,^{37,39} our M06L results show the top site is preferred over the other sites, which is in agreement with experiment.^{59,60} In contrast, PBE gives the FCC site as the most stable adsorption site (Figure S13). The CO adsorption energy with PBE on a 4×4 surface with a coverage of 1/16 ML (Table 1 and Figure S13) is slightly more exothermic by up to 0.1 eV than previous reports with the CO coverage of 1/12 to 1/4.^{37,38,39,61,62} The dissociation of CO on Pt (111) (4×4) surface is endothermic by 1.26 eV with M06L, which is in reasonable agreement with the value of 0.9 eV,⁵ which was calculated with the PW91 functional.^{63,64} The barrier energy for the dissociation of CO is calculated to be 4.25 eV from the CO

adsorbed structure. The addition of a second CO on the C and O preadsorbed surface still prefers a top site with the adsorption energy slightly lower by 0.6 eV compared to that on a clean surface. The formation of CO₂ occurs by surface O diffusion to the second CO with an energy barrier of 0.73 eV at the M06L level. Although the overall Boudouard reaction process on Pt (111) is exothermic by -1.43 eV, the dissociation step to produce the 'reactive' surface O is a 1.26 eV endothermic step with a substantially high barrier energy of 4.25 eV. Thus, the Boudouard reaction will not occur readily on Pt (111) surface.

CO on β -Mo₂C (100) Figure 5 shows the potential energy surface for the Boudouard reaction on the most stable Mo-terminated Mo₂C surface with M06L. The PBE results as well as the potential energy surfaces with higher energy intermediates are shown in the SI. CO adsorption on the stepped Mo₂C (100) surface prefers a tilted configuration on an upper top (UT) Mo site. The adsorption energy is predicted to -2.19 eV and -2.15 eV with the M06L and PBE functionals respectively, and both functionals give the same site preference. Although, PBE fails to predict the correct adsorption site for the adsorption of CO on Pt (111) surface, it does describe the interaction between CO and Mo₂C successfully. The CO adsorption energies on the upper bridge (UB) and the lower top (LT) sites are 0.36 and 1.37 less negative than the UT site. The tilted configuration for CO adsorption on Mo₂C (100) surface is consistent with that on the HCP β -Mo₂C (001) surface,⁶⁵ where the adsorption energy is predicted to be -2.61 eV with the PBE functional. Our calculated CO adsorption energy on β -Mo₂C (100) surface is slightly more negative than that on orthorhombic Mo₂C (001) surface which is predicted to be -1.85 eV with RPBE.^{66,67}

Different from CO dissociation on Pt (111), CO dissociation on Mo₂C (100) is an exothermic process by -4.36 eV calculated using independent Mo₂C (100)-C and Mo₂C (100)-O calculations. The exothermicity for C and O co-adsorption on Mo₂C (100) surface is -4.05 eV. The

independent C and O adsorption calculations are performed to eliminate the role of the coverage effect of the adsorbate. Thus, the low coverage of adsorbed CO is favorable for the dissociation. The most favorable site for C is the Mo LB site with C bonded to two lower Mo atoms and one C atom. The C adsorption energy is predicted to be -10.23 eV with M06L, which is more exothermic than C on the FCC site of Pt (111). Interestingly, the most favorable site for O adsorption is the Mo UB site and an O atom is bonded to two upper Mo atoms. The O adsorption energy is only 0.3 eV less negative than that for C. Again, O adsorption on Mo₂C (100) is also more exothermic than Pt (111). PBE gives a comparable CO dissociation energy with a difference of less than 0.2 eV from the M06L result. The dissociation energy on the Mo₂C (100) surface is slightly more exothermic than that on the flat β -Mo₂C (001) surface, which is predicted to -3.40 eV⁶⁸ with PBE. The energy barrier for CO dissociation is predicted to be only 0.81 eV and the energy of the transition state structure is still below the reactant asymptotic energy of gas phase CO and pure Mo₂C (100) slab. Thus, under low coverage conditions, CO should readily dissociate on clean β -Mo₂C (100) surface to produce surface O atoms for further oxidation reactions.

The second CO addition also prefers an adjacent Mo UT site with a physisorption energy of -2.18 eV on the C and O preadsorbed Mo₂C (100) surface, which is essentially the same as CO physisorption on the clean surface. CO₂ is produced from the surface O generated from the first CO and an adjacent CO with an energy barrier of 1.79 eV. CO₂ binding on Mo₂C (100) surface forms a bidentate carbonate-type configuration with two O atoms bonded to two adjacent UT Mo atoms respectively. The CO₂ is now bent with \angle O-C-O = 134.3°. The respective Mo-O bond lengths are 1.955 Å and 2.194 Å. The energy required for CO₂ desorption is predicted to be 2.22 eV. Similar CO₂ bending is also predicted on Mo-terminated β -Mo₂C (001) surface and \angle O-C-O = 133°. ⁷ The corresponding CO₂ binding energy is predicted to be -1.38 eV with PBE, less

exothermic than our result of -2.22 eV on Mo₂C (100) surface. We also examined linear O=C=O physisorption on the surface. The adsorption site is still the upper top with a tilted configuration (SI). This tilted binding interaction is calculated to be only -0.46 eV, consistent with a physisorption process.

CO on Pt/Mo₂C Interface Figure 5 shows the potential energy surface for Boudouard reaction at the Pt/Mo₂C interface. CO dissociation starts from the adsorption on the Pt of the interface followed by the diffusion of CO from the Pt to the Mo sites at the interface. The most favorable CO adsorption takes place at the top site of the Pt atoms. This physisorption energy is predicted to be -2.44 eV, which is more exothermic than those on the pure Pt (111) and Mo₂C (100) surfaces, which shows a significant synergistic effect between the deposited Pt and the Mo on a pure β -Mo₂C (100) surface. The bimetallic synergistic effect significantly changing the CO binding energy on Pt nanoparticles is also reported on Pt shell on TiWC and TiWN core nanoparticles, where the TiWC and TiWN cores weaken the strength of CO binding.⁶⁹ The dissociation of CO leading to the formation of a surface O atom and a surface C atom on the deposited Pt atoms, however, is endothermic by 1.06 eV.

Thus, CO dissociation on the interface, if it occurs, is likely to take place at different sites, potentially on the Mo sites via a preliminary step of CO diffusion from Pt to Mo sites. The CO diffusion barrier from the Pt site to the Mo site is predicted to be 0.88 eV and most of this is due to the endothermicity of the process. CO physisorption on the Mo top site is predicted to be exothermic by -1.69 eV, which is less exothermic than that on the pure β -Mo₂C (100) surface. It is also less exothermic than the CO adsorption on the top site of Pt on the Pt/Mo₂C interface by 0.75 eV. The molecular axis of CO is perpendicular to the Mo₂C (100) surface, which is different from the tilted configuration on the pure Mo₂C (100) surface. The vertical configuration is mostly

due to the conformation change of Mo₂C (100) surface after the deposition of Pt atoms. In comparison to the endothermic process on the Pt of the Pt/Mo₂C interface, the CO dissociation step on the Mo sites of the interface is still exothermic by -1.24 eV. The coadsorption of C and O on the interface has a three-coordinate configuration with two upper Mo atoms and one adjacent Pt atom for both C and O leading to a dissociation energy of -0.67 eV. Consistent with CO dissociation on the pure Mo₂C (100) surface, a lower coverage of CO leads to a more negative dissociation energy. Again, on the Mo site of the interface, the CO dissociation is less exothermic than the pure Mo₂C (100) surface, with a dissociation energy of -4.05 eV. The dissociation barrier from the adsorbed species is calculated to be 2.27 eV, which is larger than that on pure β -Mo₂C (100) surface. This suggests that the CO dissociation at Pt/Mo₂C interface takes place at a higher temperature than pure Mo₂C (100) surface.

The addition of a second CO on an adjacent Mo top site is slightly different from the first CO addition. CO prefers a Mo-Pt bridge site with the C-Pt and C-Mo bond distances of 2.093 Å and 2.156 Å respectively. The \angle Mo-C-O bond angle distorts to 151.1°. The energy for CO physisorption is predicted to be -1.75 eV. The C-Mo bond distance is longer than that on the pure Mo₂C (100) surface, consistent with a smaller adsorption energy on the interface than the pure (100) surface. Similar to the Pt (111) and pure Mo₂C (100) surface, CO₂ is also produced from the surface O from the first CO dissociation and the second CO. The energy barrier is predicted to be 0.63 eV. CO₂ is chemisorbed at the interface with a tridentate configuration, which is similar to that on the pure β -Mo₂C (100) surface with a difference of the C in CO₂ binding to an adjacent Pt with the bond distance of 1.986 Å. The Mo-O bond distances are comparable to that on the Mo₂C (100) surface. The C-O bond lengths in CO₂ are elongated by 0.18 Å in comparison to those on the pure Mo₂C (100) surface. The \angle O-C-O in adsorbed CO₂ is further bent to 122.8° as

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3 compared to that of 134.3° on pure Mo_2C (100) surface. The release of CO_2 from the interface
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5 requires 0.88 eV, which is much less than the CO_2 binding energy on Mo_2C (100) surface (2.22
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7 eV). The overall process to produce CO_2 from two CO molecules is still an exothermic reaction
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9 on the interface. Again, it is less exothermic than that on the pure Mo_2C (100) surface.
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12 After the release of CO_2 , the surface C atom bonded to the bridge site of upper Mo atoms
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14 is likely to diffuse to the Pt region on the interface as the structure with C adsorption on a Pt hollow
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16 site is more stable than that with C adsorption on a bridge Mo site. The migration barrier is
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18 calculated to be 0.90 eV.
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21 **C and O Adsorption** The adsorption energies of C and O on Mo_2C (100) surface and Pt/ Mo_2C
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23 interface are helpful in understanding the active sites for the formation of CO_2 and the collection
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25 of surface C atoms. The results with the M06L functional are shown in Figure 6. The adsorption
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27 energies with PBE as well as the results on Pt (111) are shown in Supporting Information. On the
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29 most stable Mo-terminated Mo_2C (100) surface, the most exothermic site for C adsorption is the
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31 lower bridge site with the formation of a strong C-C bond. C adsorption on a lower top Mo site is
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33 2.47 eV less exothermic and forms an additional C-Mo bond with an upper top Mo atom
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35 simultaneously. On Pt/ Mo_2C , we calculated C adsorption on both the Pt sites and the Mo sites at
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37 the interface. C adsorption on a Pt hollow site has a stronger binding than that on a Mo bridge site
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39 at the interface. The C adsorption energies on different sites follow the order of $\text{C}^*-\text{Mo}_2\text{C} > \text{Pt}^*-\text{Pt}/\text{Mo}_2\text{C} > \text{Mo}^*-\text{Pt}/\text{Mo}_2\text{C} > \text{Mo}^*-\text{Mo}_2\text{C}$. C adsorption on Pt (111) is slightly less exothermic than
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41 on the Pt region at the interface (see SI). This is probably due to the contribution of a synergistic
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43 effect between Pt and Mo as noted above. Although, the formation of a C-C bond is most favorable
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45 for C adsorption, the most favorable sites at the interface are most likely occupied by the deposited
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47 Pt atoms as Pt atoms prefer the formation of Pt-C bonds instead of Pt-Mo bonds. Thus, at the
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Pt/Mo₂C interface, the accumulated C atoms from the Boudouard reaction produced on the Mo sites most likely diffuse to the Pt region or surface C area if the active sites are not occupied by Pt atoms. The preference of Pt sites over Mo sites for C adsorption on the interface is partly attributed to the bond dissociation energy (BDE) of Pt-C that is larger than the Mo-C bond in the diatomic molecules.⁷⁰ The BDEs of diatomic Pt-C and Mo-C bonds are 5.99 ± 0.07 and 5.00 ± 0.17 eV respectively; both are weaker than the C-C bond energy in diatomic C₂ (6.41 ± 0.16 eV).⁷⁰

O adsorption on the Mo₂C (100) surface and the Pt/Mo₂C interface (Figure 6) is different from C adsorption. The Mo bridge site is preferred for O adsorption on both the Mo₂C (100) surface and the Pt-Mo₂C interface. The most exothermic adsorption site is the Mo upper bridge site with an adsorption energy of -7.89 eV. The adsorption energy of the same site at the interface is predicted to be 1.63 eV less exothermic. We also tried adsorption on a lower bridge site with the formation of a C-O bond, but the adsorption energy is less exothermic than on the Mo sites. For the structure with O adsorption on a lower bridge Mo site, the C-O bond distance is predicted to be 1.550 Å, which is longer than that of CO with the distance of 1.16 Å. Similarly, the Mo-O bond distance of 2.324 Å is also longer than the Mo-O bond distance of 1.955 Å with O bonded to an upper bridge site. The least exothermic adsorption site in Figure 6 is the Pt hollow site with an adsorption energy of only -6.87 eV. Thus, the O adsorption energies on different sites follow the order of Mo*-Mo₂C > Mo*-Pt/Mo₂C > C*-Mo₂C > Pt*-Pt/Mo₂C. The O adsorption energy on the FCC site of Pt (111) (see SI) is 3.50 eV less exothermic than that on the most favorable site on Mo₂C (100). Again, the preference of Mo sites over Pt sites for O adsorption at the interface is partly due to the fact that the BDE of Mo-O bond is larger than Pt-O bond. The BDEs of diatomic Pt-O and Mo-O are 4.34 ± 0.12 and 6.29 eV respectively.⁷⁰ Thus, the structure with the formation of a Mo-O bond at the interface is more stable than that with the formation of a Pt-O bond.

Bader Charge Analysis A Bader charge analysis provides insights into the nature of the binding of CO, CO₂, C and O to the surfaces. The calculated local atomic charges via Bader charge analysis on various CO, CO₂, C and O adsorption structures as well as their adsorption energies are shown in the Supporting Information. The net charge is calculated from the difference of the electrons of a neutral atom and the calculated electrons of that atom in the system. For the adsorption of an atom, the net charge is also the adsorbate-surface charge transfer. For CO adsorption on Pt (111), Mo₂C (100) and Pt/Mo₂C surfaces, the adsorbate-surface charge transfer ranges from 0.02 e to 0.59 e with PBE. The charge transfer with M06L is similar to that with PBE. The charge transfer from Mo* to CO is generally larger than that from Pt* to CO and there is a reciprocal electron donation between CO and the active metal on the surface. The charge transfer does not correlate with the CO adsorptions energies. The CO binding is a combination of π -backbonding (M to C) and σ donation (C to M). For CO adsorption on the Mo-Pt bridge site of Pt/Mo₂C, the Mo donates electrons to CO and the Pt gains electrons from the C of CO. For CO₂ chemisorption on Mo₂C (100), there is 0.96 e charge transfer from two upper Mo atoms to CO₂. Similar charge transfer is predicted for a tridentate configuration for CO₂ chemisorption on Pt/Mo₂C. Thus, the adsorbed CO₂ on Mo₂C (100) and Pt/Mo₂C surfaces behaves as CO₂⁻. The predicted O-C-O bond angles of 134° on Mo₂C (100) surface is consistent with that in the gas phase anionic CO₂⁻⁷¹ and anionic CO₂ clusters with explicit H₂O molecules,⁷² which are predicted to be 135° and 137° respectively at the CCSD(T)^{73,74} and MP2^{75,76} levels. The interaction between CO₂ and Pt (111) is dominated by the van der Waals force as the charge transfer is insignificant.

The charge transfer for C and O adsorptions on various surfaces are also shown in the SI. Similar to the charge transfer from the surface to CO, more charge transfer to a C atom is predicted on Mo* sites than that on Pt* sites. Again, there is no significant correlation between C adsorption

energies and the corresponding charge transfers. The transition metal carbide M-C bond on a surface is characterized as a mixture of metallic, covalent and ionic bonds.⁷⁷ Thus, the adsorption energy is not only dependent on the charge transfer, but also the bonding nature itself mostly determined by different valence *d* electrons in the metal. For O adsorption, there is more electron transfer than for C adsorption, consistent with the higher electronegativity of O. There is a good correlation between the O adsorption energy on the active metal site and the charge transfer (Figure 6). Thus, the M-O bond can be characterized as an ionic bond and the more charge transfer, the greater the adsorption energy is predicted. The larger adsorption energy on a Mo* site than a Pt* site is also consistent with the stronger BDE of a Mo-O than a Pt-O bond.

Electronic Density of States The LDOS is shown in the SI and mapped onto the structures as PCD in Figure 7. A different method of mapping the electrons to the structure, the ELF, is shown also shown in SI. While the PCD can be used to view a specific energy region of the LDOS, the ELF depicts all calculated electrons. In general, the LDOS shows the C adsorbate bond to the surface as a combination of ionic and covalent bonding and the chemical bond of O adsorbate to the surface is mostly ionic, consistent with the Bader charge analysis. Several regions exhibit covalent bonding as shown by the overlap in states, especially for C.

The ELF diagrams in Figure S23 (a-d) shows that the adsorbed C prefers to bond covalently, recalling that moving from left to right in Figure 7 showed less stable structures. In Figure S23 (a), the adsorbed C is able to form a strong covalent bond with the surface C, indicated by a blue region showing a large concentration of charge surrounding two C atoms. In Figure S23 (b), the C adsorbate also bonds covalently to Pt, although the ionic nature of the bonding is still observed as the most charge (shown in blue) is localized on C whereas less charge (shown in green) is localized on Pt. In Figure S23 (c), the adsorbate C is largely ionically bonded to the surface Mo

atoms which have almost no charge (shown in red). This structure (Figure S23 (c)) is only close in adsorption energy to the previous structure (Figure S23 (b)) because the adsorbed C is still able to bond covalently with Pt (in the (010) plane, perpendicular to the (100) plane shown in Figure S23 (b)). The last C adsorption ELF (Figure S23 (d)) shows ionic bonding between the adsorbed C and surface Mo.

Narrowing the energy window to -2 eV relative to the Fermi energy in Figure 7 (a-d) shows that the electron densities most likely to be involved in continuing the reacting are localized on the C-adsorption structures. There is a general trend of structures with less charge on the adsorbed C in this energy region being more stable. While the C in Figure 7 (a) is shown to still be active, it is likely the most stable structure as shown by the strong covalent bonding in the ELF. The most stable C adsorption on the Pt-Mo₂C (Figure 7 (b)) shows that the C has very little charge (shown in yellow). The adsorbed C in Figure 7 (c) shows the covalent nature of the M-C bond as the C orbitals deform slightly towards the surface Mo. This C contains more active electrons than in Figure 7 (b), exhibited by a green region. In the last C adsorption PCD (Figure 7 (d)), the C remains highly active, shown by regions of blue.

Figure 7 (e-h) shows that the O prefers to have the most charge, without sharing electrons with the surrounding atoms. Thus, the M-O bond has more ionic character than the M-C bond. An energy window of -8 to -5 eV was selected to investigate the O adsorbate structures as this region shows the most variation in the LDOS (Figure S22 e-h). Figure 7 (e) shows ionic bonding with charge localized on O and some covalent character as the charge density deforms towards the surface Mo atoms. Moving from Figure 7 (f) through Figure 7 (h) shows the deformation towards the metal reduced until the charge is localized completely on the O adsorbate.

Calculated Rate Constants On the basis of the above results, the essential reaction steps can be summarized in the following reaction sequence, where * represents an active site on the Mo₂C catalyst:

1. $2(\text{CO (g)} + * \rightarrow \text{CO}^*)$ Adsorption (Physisorption)
2. $\text{CO}^* + * \rightarrow \text{C}^* + \text{O}^*$ Disproportionation (and deactivation of 1 metal site)
3. $\text{CO}^* + \text{O}^* \rightarrow 2* + \text{CO}_2(\text{g})$ CO₂ formation
4. $\text{C}^* + *_{\text{Pt}} \rightarrow * + \text{C}^*_{\text{Pt}}$ Carbon collection on Pt and regeneration of metal site

Steps (1, 2 and 3) can proceed solely on the Mo₂C material. This pathway leads to the deactivation of 1 metal site with the deposition of a carbon atom. The addition of Pt in step 4 enables a complete catalytic cycle with the regeneration of the active disproportionation site by collection of the C species.

Transition state theory⁷⁸ was employed to estimate the rate constants based on the calculated electronic energies. The various terms used the harmonic vibrational frequencies and the rigid rotor approximation. The calculated rate constants for the key steps on β -Mo₂C (100), Pt/Mo₂C, and Pt (111) surfaces with both PBE and M06L functionals are shown in Table 2. One should be aware that the rate constant for the reaction with gas phase CO involved varies along the curve of the transient pressure with respect to the time in each pulse. In addition, our experimental conditions are far from equilibrium (backward reactions can be neglected). The transient behavior of the gas pressure on the catalyst surface at selected temperature of 25, 100, 200, 300 °C is shown in the Supporting Information (Figure S3). We chose one half of the maximum pressure for each temperature as a representative pressure to investigate the different reaction rate on different materials. We used the effective activation energy for the reactions

involving the gas phase CO. The calculated rate constants with PBE and M06L are comparable for the studied reactions.

On the β -Mo₂C (100) surface, the rate constants for the dissociation of CO are sufficiently high at the experimental temperatures to generate surface O species for the further CO₂ formation. With large rate constants, the dissociation of CO is mostly a diffusion-controlled step rather than an activation-controlled step on the β -Mo₂C (100) surface. The formation of CO₂ is predicted to be a slower step compared to the dissociation of CO. On Pt/Mo₂C, the rate limiting step is the dissociation of CO and the formation of CO₂ is a much faster step than the dissociation. CO dissociation on Pt/Mo₂C is much slower than that on Mo₂C based on the calculated rate constants. The diffusion rate constants for both CO diffusion from *_{Pt} to *_{Mo} and C diffusion from *_{Mo} to *_{Pt} are large at temperatures above 200 °C. The results for Pt (111) are very different. The rate constants for the CO dissociation on Pt (111) are so small that this process is unlikely to occur under experimental temperatures lower than 300 °C. In comparison, the CO₂ formation step is a much faster step on Pt (111), and is also faster than that on both β -Mo₂C (100) and Pt/Mo₂C. The calculated rate constants indicate that the Boudouard reaction is unlikely to occur on the Pt domain under the current experimental conditions. The Boudouard reaction on β -Mo₂C (100) is fast but is limited by the deactivation of residual C atoms.

Discussion On pure Mo₂C, significant CO₂ is produced at temperatures below 50 °C, which is consistent with our calculations with a substantial exothermicity for the Boudouard reaction. The energy barrier for the chemisorption of CO is also below the reactant asymptote, which indicates that CO readily dissociates on a pure Mo₂C surface. The fact that CO conversion as well as CO₂ production drop quickly can be attributed to the active lower-level Mo sites on the pure Mo₂C surface that are occupied quickly by the residual C atoms from the Boudouard reaction. This

surface deactivation process is expected to take place rapidly with the low energy barrier of the disproportionation process.

The amount of CO conversion observed on 50 Pt/Mo₂C is nearly identical to that on pure Mo₂C at temperatures below 200 °C; this indicates that a small amount of Pt does not change the storage capacity of CO on Mo₂C. However, the deposition of a small amount of Pt on Mo₂C significantly decreases the production of CO₂ (Figure 1b) at temperatures below 200 °C. To some extent, the deposited Pt nanoclusters block the active lower-layer Mo sites for the dissociation of CO as the deposited Pt atoms prefer the more stable lower bridge sites with the formation of Pt-C bonds (Figure S22). Significant production of CO₂ on 50 Pt/Mo₂C is not observed until the experimental temperatures exceed 250 °C, which is due to a larger barrier for CO dissociation for the Boudouard reaction predicted on Pt/Mo₂C.

On 100 Pt/Mo₂C, CO conversion shows a minor decline as temperature increases to 100 °C, which is consistent with our calculations that CO adsorption preferentially takes place on Pt sites at the Pt/Mo₂C interface in our 12Pt@Mo₂C model and that the production of a small amount of CO₂ does not deactivate the active sites significantly. It is important to note that the active sites on Pt nanoparticles per unit area are larger than pure Mo₂C as all surface Pt atoms are active for CO adsorption. The production of CO₂ on 100 Pt/Mo₂C is greater than that on 50 Pt/Mo₂C at temperatures below 300 °C because the 50 Pt/Mo₂C has more limited CO storage capacity; this limits the production of CO₂ as the formation of one mole of CO₂ requires two moles of CO. CO₂ production is dependent on both the activation energy and the CO surface concentration. At temperatures lower than 150 °C, the factor of activation outweighs the CO concentration and the CO₂ yield on three materials follows the order of Mo₂C > 100 Pt/Mo₂C > 50 Pt/Mo₂C. At

temperatures between 150 °C and 300 °C, both factors contribute the CO₂ production, which follows a different order: 100 Pt/Mo₂C > Mo₂C > 50 Pt/Mo₂C.

The total conversion of CO (Figure 1c) on different materials follows the order of Mo₂C < 50 Pt/Mo₂C < 100 Pt/Mo₂C. The more Pt deposited, the greater the storage capacity for CO adsorption as surface C atoms of Mo₂C are not active for CO adsorption and the surface Pt atoms as well as the Pt-Mo interface are active for CO storage. The estimate of the total number of surface metal atoms (SI) also shows more active sites for CO adsorption on 100 Pt/Mo₂C than on 50 Pt/Mo₂C. CO readily dissociates on a β -Mo₂C (100) surface at a low coverage from our DFT calculation, which suggests one dissociated CO occupies two active Mo sites. In addition, CO does not dissociate on Pt (111) surface under experimental conditions. Thus, the 100 Pt/Mo₂C with greater Pt (111) domain has a larger capacity to store CO.

With respect to the accumulation of surface C atoms, a slightly smaller amount of C atoms are produced on 100 Pt/Mo₂C compared to pure Mo₂C below 150 °C as the larger energy barrier of CO disproportionation on Pt/Mo₂C leading to the slower reaction rate for the production of CO₂. At temperatures greater than 175 °C, more CO₂ production results in greater accumulation of surface C on 100 Pt/Mo₂C. Following the experiment, TEM observed C accumulation around Pt nanoparticles on 100 Pt/Mo₂C is also consistent with the C adsorption energies on Pt sites being more exothermic than that of Mo. A similar phenomenon was reported in carbon nanotube synthesis by the decomposition of CH₄ on Mo/Co/MgO catalysts at temperatures higher than 650 °C.⁷⁹ The active Co sites on Co/MgO catalysts could be poisoned by carbon deposition due to the rate of CH₄ decomposition reaction larger than the rate of graphene formation. The addition of Mo component is able to slow down CH₄ decomposition step and avoids the deactivation of Co.

In our previous work, TPD DRIFT experiments¹⁰ with CO preadsorption under flow conditions showed that higher temperatures are needed to desorb CO on 50 Pt/Mo₂C than on 100 Pt/Mo₂C. This is consistent with the calculated CO adsorption energies on the Pt (111) surface and the Pt/Mo₂C surface with the former having weaker binding than the latter. The CO binding energy is predicted to be -1.53 eV on the Pt (111) surface (SI) as compared to CO adsorption energies of -2.44 and -1.75 eV on the Pt and Pt-Mo sites at the Pt/Mo₂C interface (Figure 5 and Table 1, the first and second CO adsorption respectively). From the characterization in our previous study¹⁰, the Pt nanoparticles on 100 Pt/Mo₂C are expected to have greater Pt(111) domains which are weaker for binding CO. In comparison with thinner Pt nanoparticles that were more dispersed,¹⁰ the 50 Pt/Mo₂C sample may generate more bimetallic Mo-Pt interface for stronger CO adsorption and the desorption of CO thus requires higher temperature.

The DFT results describing C, O, CO and CO₂ species can also be helpful to understand the WGS performance on pure Mo₂C nanotubes, 50 Pt/Mo₂C and 100 Pt/Mo₂C observed in our previous experiments under flow conditions.¹⁰ Nagai and Tominaga⁸⁰ predicted that the WGS reaction on the β -Mo₂C(001) slab begins with the dissociation of H₂O into surface H and O atoms followed by CO oxidation by oxygen and surface recombination of H atoms leading to the formation of CO₂ and H₂ using DFT. The formation of CO₂ was calculated to be the rate determining step. In this work, CO readily dissociates on the Mo₂C nanotube modeled with the β -Mo₂C(100) surface and high temperatures are needed for the recombination of dissociated C and O atoms. However, the WGS is an exothermic reaction at 298 K with a free reaction energy of -0.29 eV;⁸¹ also high temperature is favorable for the reverse water gas shift (RWGS) reaction. This helps to explain why experimentally we observed that pure Mo₂C nanotubes were not as efficient as Pt/Mo₂C materials in regards to the WGS performance.¹⁰ The flow experiment¹⁰ also shows

that a higher WGS reaction rate takes place on 50 Pt/Mo₂C than on 100 Pt/Mo₂C at temperatures above 300 °C. Our calculations predict that the CO binding is stronger on 50 Pt/Mo₂C than on 100 Pt/Mo₂C, which suggests that the CO binding energies correlate with the WGS reaction rate on 50 Pt/Mo₂C and 100 Pt/Mo₂C materials. A stronger CO binding correlates with a higher reactivity of WGS reaction on 50 Pt/Mo₂C as compared to a weaker CO binding and a lower reactivity on 100 Pt/Mo₂C. The correlation between the binding energy and the reactivity has been reported for the hydrogenation of CO₂ on Pt, Pt/SiO₂ and Pt/TiO₂,⁸² where the material with stronger binding of CO₂ shows more reactive for the reaction.

Orthorhombic Mo₂C and Mo₂C-supported copper clusters are reported to be active for the CO₂ hydrogenation reactions.^{7,8} It is interesting to note that CO₂ dissociation readily occurs with the breaking of a C-O bond and formation of CO on an orthorhombic Mo₂C (001) surface.⁷ In current work, CO₂ formation from the reaction of CO with surface O was observed. The process of CO₂* → CO* + O* on an orthorhombic Mo₂C (001) surface was reported to be exothermic by ~ 3.0 eV with PBE. In comparison, the reaction energy of CO₂* + C* + * → CO* + O* + C* on the pure β-Mo₂C (100) and Pt/Mo₂C surfaces in this work is predicted to be only -0.86 eV and 0.07 eV respectively with PBE (SI). The different reaction energies are most likely due to different CO₂ binding energies; CO₂ binding energies on pure β-Mo₂C (100) and Pt/Mo₂C surfaces are predicted to be 2.43 eV and 0.84 eV, which are smaller than the binding energy of 3.27 eV on an orthorhombic Mo₂C (001) surface predicted with the PBE functional. Thus, the reactivity of CO₂ on the Mo₂C material is significantly affected by the CO₂ binding strength and varies significantly on different surfaces.

Similarly, CO and C adsorption on various Mo₂C surfaces also behave differently. Wang and Jiao studied CO adsorption and dissociation on a variety of orthorhombic Mo₂C surfaces.²²

Generally, they found that CO dissociation reaction on the surface with a stronger CO binding energy has a smaller reaction energy barrier. The dissociation is not always thermodynamically more favorable than adsorption. The different reactivities of different hexagonal β -Mo₂C surfaces have been predicted for the activation of H₂, O₂, H₂O, CO₂, CO, and small hydrocarbon molecules and a β -Mo₂C (001) surface is reported to be more reactive than a β -Mo₂C (101) surface.²⁶ Also, C adsorption is more exothermic on a more reactive β -Mo₂C (001) surface than on a β -Mo₂C (101) surface which is predicted with PBE.

The surface dependent reactivity is helpful to explain the phenomenon of Pt as carbon collector from our experimental results. Our CO dissociation on a β -Mo₂C (100) surface with an exothermicity of -4.05 eV is more exothermic than that on a β -Mo₂C (001) surfaces with a dissociation energy of -3.40 eV²⁴ as predicted with PBE. CO adsorption on β -Mo₂C (001) is predicted to be more stable than that on β -Mo₂C (101) with PBE.⁶⁵ Also, the cleavage energy predicted by PBE follows the order of β -Mo₂C (100) > β -Mo₂C (001) > β -Mo₂C (101).²³ Thus, the stable β -Mo₂C (100) surface selected in this work is most likely one of the very reactive surfaces on the Mo₂C nanotube. The deposited Pt nanoparticles prefer the formation of Pt-C bonds and occupy the most reactive sites, C*-Mo₂C for C adsorptions on the pure Mo₂C (100) surface. The residual carbon atoms from the Boudouard reaction on Pt/Mo₂C most likely adsorb other different active sites. In current work, C adsorption on the C*-Mo₂C sites of other less active surfaces is most likely less exothermic than that on a β -Mo₂C (100) surface and is also probably less exothermic than on the Pt sites of Pt/Mo₂C material. Thus, the deposited Pt particles on Pt/Mo₂C were able to absorb residual carbon atoms in the Boudouard process although the C adsorption energy on Pt*-Pt/Mo₂C is less exothermic than on C*-Mo₂C (100).

The role of Pt nanoparticles as a carbon collector may be helpful for the design of new catalytical materials. Carbon and coke formation resulting in deactivation of catalysts is generally unavoidable in various industrial processes such as CO methanation⁸³ and steam reforming.⁸⁴ The Boudouard reaction is also an important side reaction in many catalytic processes.⁸⁵ For such processes, the doping of a small amount of Pt on the catalytic active species could be potentially useful to mitigate the deactivation if C atoms prefer to adsorb on the Pt domain rather than the catalytic active sites. Admittedly, practical implementation in a continuous process is not immediately apparent and the surprising feature of carbon collection mechanism may be more useful for fundamental understanding of the role of different active sites in multicomponent catalysts.

Conclusions

DFT studies on the potential energy surfaces of the Boudouard reaction on β -Mo₂C (100), Pt(111) and Pt/Mo₂C surfaces have been used to support the hypothesis of Pt-assisted carbon remediation of Mo₂C active sites originally derived from transient kinetic experimental observations.¹⁰ The model of 12Pt@Mo₂C was used to simulate the reactions on the Pt nanoparticle-supported Mo₂C nanotubes and the results are consistent with experiments. From temperature-programmed CO pulsing experiments using the TAP technique, the production of CO₂ on both pure Mo₂C and Pt/Mo₂C was observed to proceed via the Boudouard reaction. The Boudouard reaction begins with the dissociation of adsorbed CO on Mo sites to generate surface C and O species. The active O species then oxidize another adsorbed CO to form CO₂. After the release of CO₂, residual surface C atoms deactivate the Mo sites on pure Mo₂C. In contrast, the addition of Pt nanoparticles to Mo₂C enables collection of surface C atoms and help reactivate the Mo sites. C atom migration to the Pt region is favorable according to our DFT calculations. The

deposited Pt nanoparticles also increase the storage capacity of CO, making 100 Pt/Mo₂C, with greater Pt(111) domains, more productive to form CO₂ than 50 Pt/Mo₂C. The maximum CO₂ production rate on 50 Pt/Mo₂C takes place at a higher temperature than 100 Pt/Mo₂C due to a stronger CO binding strength at the interface.

Our calculated CO adsorption energies on Pt(111), pure Mo₂C and the Pt/Mo₂C interface help explain the different WGS performance among bare Mo₂C nanotubes and those with uniquely sized Pt-domains.¹⁰ The reactivities of 50 Pt/Mo₂C and 100 Pt/Mo₂C correlate with the CO adsorption energies; the catalyst with a strong CO binding is more reactive for the WGS reaction. These CO adsorption energies may be useful references for understanding the selectivity of CO₂ hydrogenation and other reactions on Pt/Mo₂C and related materials where CO is an intermediate. The role of Pt acting as a carbon collector presents an alternative viewpoint of the mechanistic role of cooperative active centers that hereto now has not been expressed for the Pt/Mo₂C system.

ORCID

Zongtang Fang: 0000-0001-6034-1083

Lucun Wang: 0000-0002-4930-8618

Shuai Tan: 0000-0003-3200-7875

Dongmei Li: 0000-0002-0529-9203

David A. Dixon: 0000-0002-9492-0056

Rebecca Fushimi: 0000-0002-7570-0234

Notes

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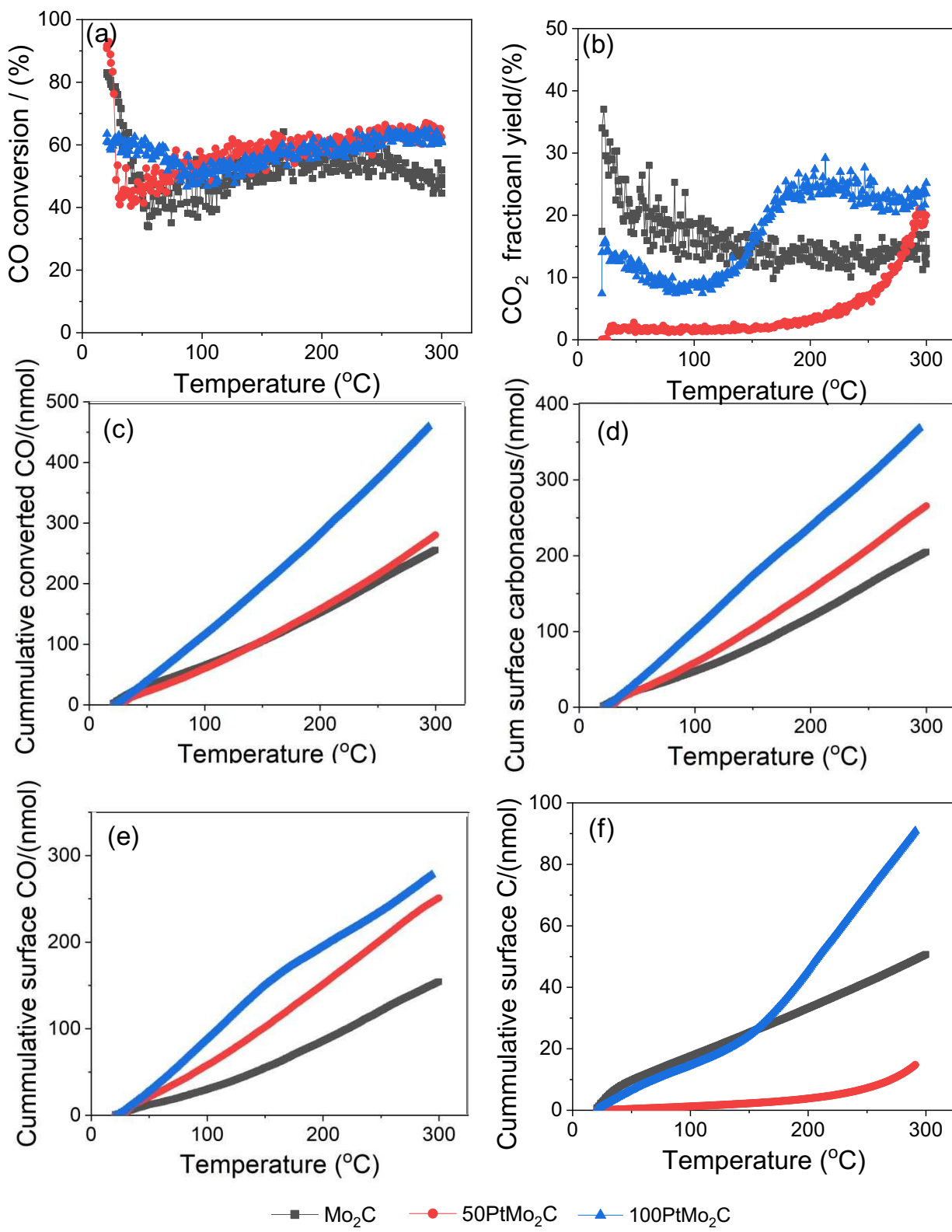
Table 1. Adsorption Energies in eV with the M06L and PBE Functionals ($E_{\text{ads, M06L}}$ and $E_{\text{ads, PBE}}$) and Optimized Bond Distances in Å for CO, C, O, and CO₂ Adsorption on Pt (111), Mo₂C (100), and Pt/Mo₂C Interface on the Most Stable Adsorption Sites with PBE.

Adsorbates	Site	$E_{\text{ads, M06L}}$	$E_{\text{ads, PBE}}$	$d_{\text{C-Pt}}$	$d_{\text{O-Pt}}$	$d_{\text{C-Mo}}$	$d_{\text{O-Mo}}$	$d_{\text{C-O}}$
Pt (111)								
1 st , CO	Top	-1.53	-1.69 ^h	1.841	-	-	-	1.152
2 nd , CO ^a	Top	-0.93	-1.04	1.858	-	-	-	1.150
C	FCC	-8.49	-7.34	1.899	-	-	-	-
O	FCC	-6.45	-4.53	-	2.049	-	-	-
CO ₂ ^b	Top	-0.18	-0.24	3.973	-	-	-	1.174
β -Mo ₂ C (100)								
1 st , CO	UT	-2.19	-2.15	-	-	2.015	-	1.186
2 nd , CO ^a	UT	-2.18	-2.13	-	-	2.020	-	1.183
C ^c	LB	-10.23	-8.29	-	-	2.266 2.282	-	-
O	UB	-9.96	-7.89	-	-	-	1.955	-
CO ₂ ^{b,d}	UT	-2.22	-2.43	-	-	2.226	2.194	1.127
Pt/Mo ₂ C								
1 st , CO ^e	Pt, Top	-2.44	-2.27	1.848	-	-	-	1.161
2 nd , CO ^{a,f}	Mo, Top	-1.75	-1.82	2.093	-	2.156	-	1.181
				1.870				
C	Pt, Hollow	-8.92	-7.46	1.907	-	-	-	-
				1.926				
O	Mo, Bridge	-8.33	-5.81	2.100	-	-	2.041 2.076	-
CO ₂ ^{b,g}	Mo, Top	-0.88	-0.84	1.986	-	2.472 2.554	2.163 2.176	1.297 1.305

^a CO adsorption energy on C and O preadsorbed surface; ^b CO₂ adsorption on C pre-adsorbed surface; ^c Bonded to a surface carbon with the C-C bond distance of 1.392 Å; ^d ∠ O-C-O is 134.3°; ^e ∠ Pt-C-O is 174.7°; ^f ∠ Mo-C-Pt is 81.2° and ∠ Mo-C-O is 151.1°. ^g ∠ O-C-O is 122.8°; ^hThe CO adsorption energy on a FCC site is predicted to be -1.79 eV with PBE.

Table 2 Calculated Reaction Energies at 25°C (ΔH_{298} , in eV) and Rate Constants (k , in s⁻¹) from the Transition State Theory at 25, 100, 200, and 300 °C with both M06L and PBE Functionals. (g) Means the Reaction from the Gas Phases.

Reaction	M06L	k				PBE	k			
	ΔH_{298}	25 °C	100 °C	200 °C	300 °C	ΔH_{298}	25 °C	100 °C	200 °C	300 °C
β -Mo ₂ C (100)										
CO(g) + 2* → TS → C* + O*	-4.05	2.4x10 ²⁴	6.1x10 ¹⁹	9.5x10 ¹⁵	3.4x10 ¹³	-3.91	5.1x10 ²³	1.8x10 ¹⁹	3.6x10 ¹⁶	1.7x10 ¹⁴
CO(g) + C* + O* → TS → CO ₂ * + C*	-1.27	3.6x10 ⁷	3.0x10 ⁶	4.0x10 ⁵	1.2x10 ⁵	-1.20	3.6x10 ¹⁰	1.4x10 ⁹	8.6x10 ⁷	1.6x10 ⁷
CO* + * → TS → C* + O*	-1.90	1.4x10 ⁻¹	5.8x10 ¹	9.1x10 ³	2.5x10 ⁵	-1.80	1.4x10 ⁻¹	5.6x10 ¹	8.9x10 ³	2.4x10 ⁵
CO* + C* + O* → TS → CO ₂ * + C* + *	0.88	2.7x10 ⁻¹⁸	3.5x10 ⁻¹²	4.6x10 ⁻⁷	9.9x10 ⁻⁴	0.89	2.9x10 ⁻¹⁵	9.2x10 ⁻¹⁰	3.7x10 ⁻⁵	3.7x10 ⁻²
Pt/Mo ₂ C										
CO(g) + 2* _{Mo} → TS → C* _{Mo} + O* _{Mo}	-0.69	3.3x10 ¹	3.5x10 ¹	4.2x10 ¹	5.2x10 ¹	-0.40	8.2x10 ⁻³	4.7x10 ⁻²	2.3x10 ⁻¹	7.0x10 ⁻¹
CO(g) + C* _{Mo} + O* _{Mo} → TS → CO ₂ * _{Mo} + C* _{Mo}	-1.82	1.1x10 ¹⁵	3.1x10 ¹²	2.5x10 ¹⁰	1.2x10 ⁹	-1.69	8.7x10 ¹⁵	1.6x10 ¹³	9.3x10 ¹⁰	3.5x10 ⁹
CO* _{Mo} + * → TS → C* _{Mo} + O* _{Mo}	0.96	9.3x10 ⁻¹⁶	2.6x10 ⁻¹⁰	1.0x10 ⁻⁵	1.0x10 ⁻²	0.96	6.3x10 ⁻¹⁵	1.2x10 ⁻⁹	3.4x10 ⁻⁵	2.7x10 ⁻²
CO* _{Mo} + C* _{Mo} + O* _{Mo} → TS → CO ₂ * _{Mo} + C* _{Mo} + * _{Mo}	-0.08	2.5x10 ⁻³	4.8x10 ⁰	2.8x10 ³	1.8x10 ⁵	0.12	1.4x10 ⁻³	3.0x10 ⁰	2.0x10 ³	1.4x10 ⁵
CO* _{Pt} → TS → CO* _{Mo}	0.74	9.9x10 ⁻³	8.1x10 ⁰	2.3x10 ³	9.2x10 ⁴	0.85	2.8x10 ⁻⁴	4.8x10 ⁻¹	2.5x10 ²	1.5x10 ⁴
C* _{Mo} → TS → C* _{Pt}	-0.18	5.3x10 ⁻³	6.1x10 ⁰	2.3x10 ³	1.8x10 ⁵	-0.62	5.3x10 ⁻¹	1.5x10 ³	1.8x10 ⁵	3.9x10 ⁶
Pt (111)										
CO(g) + 2* → TS → C* + O*	1.26	1.3x10 ⁻⁴⁵	2.7x10 ⁻³⁶	1.9x10 ⁻²⁸	2.8x10 ⁻²³	0.43	2.3x10 ⁻³¹	6.4x10 ⁻²⁵	1.8x10 ⁻¹⁹	7.1x10 ⁻¹⁶
CO(g) + C* + O* → TS → CO ₂ * + C*	-2.77	2.8x10 ¹⁴	9.5x10 ¹¹	8.8x10 ⁹	4.5x10 ⁸	-2.39	1.1x10 ¹⁵	2.8x10 ¹²	2.0x10 ¹⁰	9.1x10 ⁸
CO* + * → TS → C* + O*	2.73	9.3x10 ⁻⁶⁰	1.5x10 ⁻⁴⁵	1.3x10 ⁻³³	7.8x10 ⁻²⁶	2.06	2.7x10 ⁻⁴⁸	2.1x10 ⁻³⁶	2.1x10 ⁻²⁶	7.1x10 ⁻²⁰
CO* + C* + O* → TS → CO ₂ * + C* + *	-1.31	2.1x10 ⁰	5.8x10 ²	6.4x10 ⁴	1.4x10 ⁶	-0.83	3.7x10 ⁻¹	1.4x10 ²	2.2x10 ⁴	5.6x10 ⁵



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Figure 1. (a) CO Conversion, (b) CO₂ Fractional Yield, (c) Cumulative Converted CO ($N_{\text{converted}}$, Adsorption + Reaction), (d) Cumulative Surface Carbonaceous Species ($N_{\text{carb}} = N_{\text{CO}} + N_{\text{C}}$), (e) Cumulative Surface CO (N_{CO}) and (f) Cumulative Surface C (N_{C} , the C atoms from the Boudouard process only) During CO Pulsing over the Mo₂C and Pt/Mo₂C Catalysts While Heating up to 300 °C at 1 °C/min. (a) and (b) are reprinted with permission from Tan, S.; Wang, L.; Saha, S.; Fushimi, R. R.; Li, D. Active Site and Electronic Structure Elucidation of Pt Nanoparticles Supported on Phase-Pure Molybdenum Carbide Nanotubes. *ACS Appl. Mater. Interfaces* **2017**, *9*, 9815–9822. Copyright 2017 American Chemical Society.

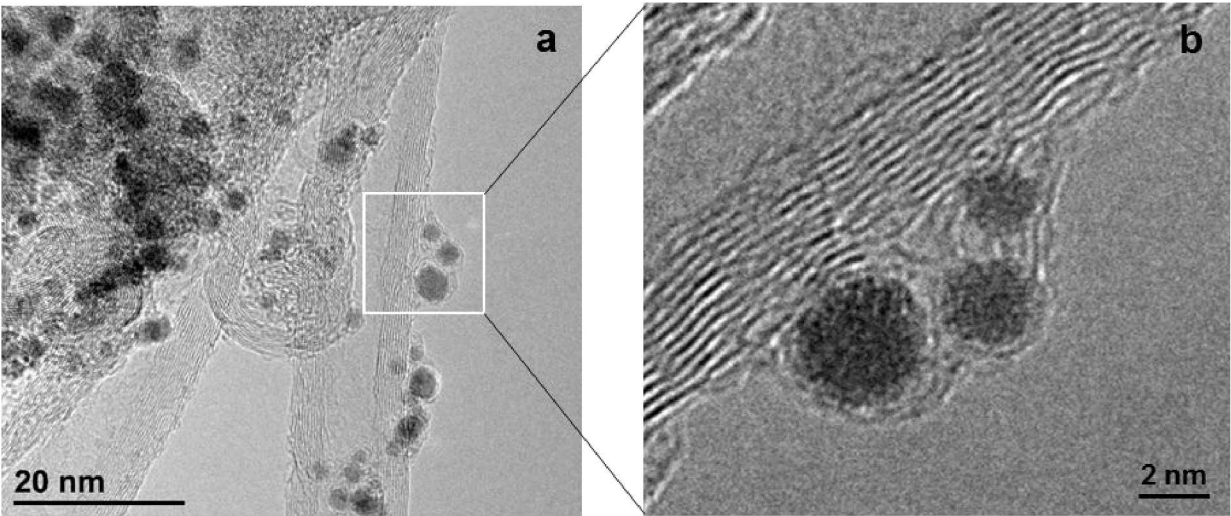


Figure 2. (a) TEM and (b) High-resolution TEM images of 100 Pt/Mo₂C Catalyst After Temperature Programmed Reaction with CO Pulses.

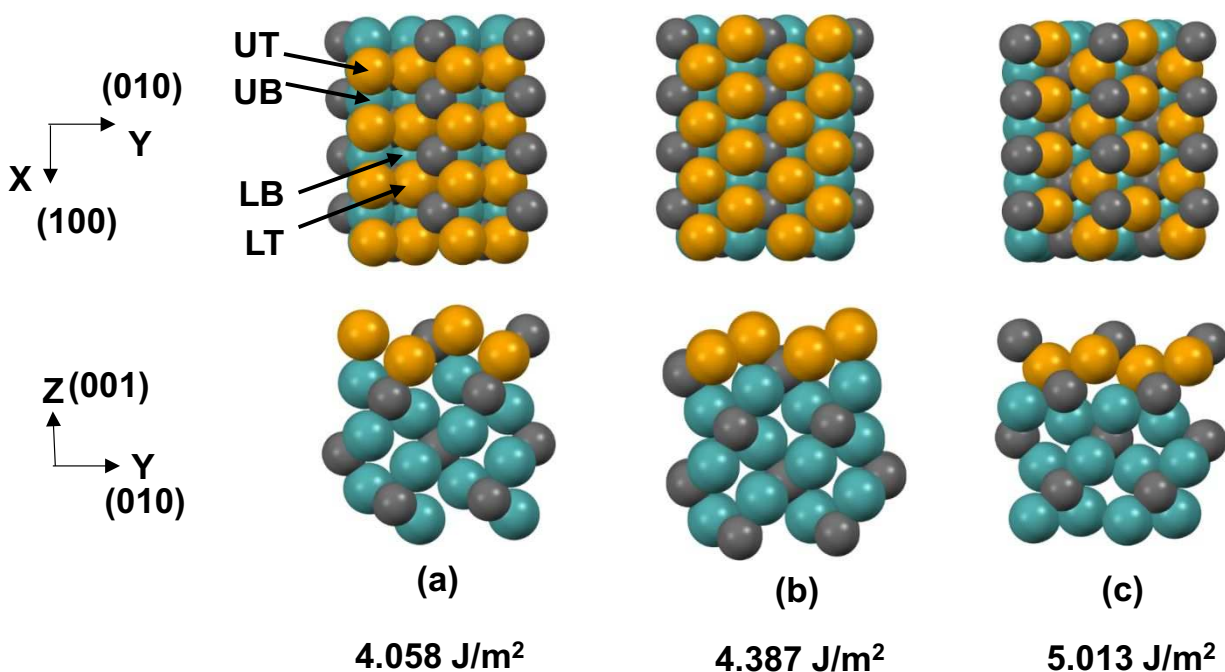


Figure 3. Top and Side View of (a) Most Stable Mo-Terminated Surface, (b) A Second Mo-Terminated Surface, and (c) C-Terminated Surface for β -Mo₂C (100). The Cleavage Energies Are Shown Below with the M06L Functional. Five Different Adsorption Sites: Upper Top (UT), Upper Bridge (UB), Lower Top (LT), and Lower Bridge (LB) on the Most Stable Mo-Terminated Surface (a). C Atoms Shown in Grey and Mo Atoms Shown in Steel Blue. For Clarity, the First Layer Mo Atoms are shown in Orange.

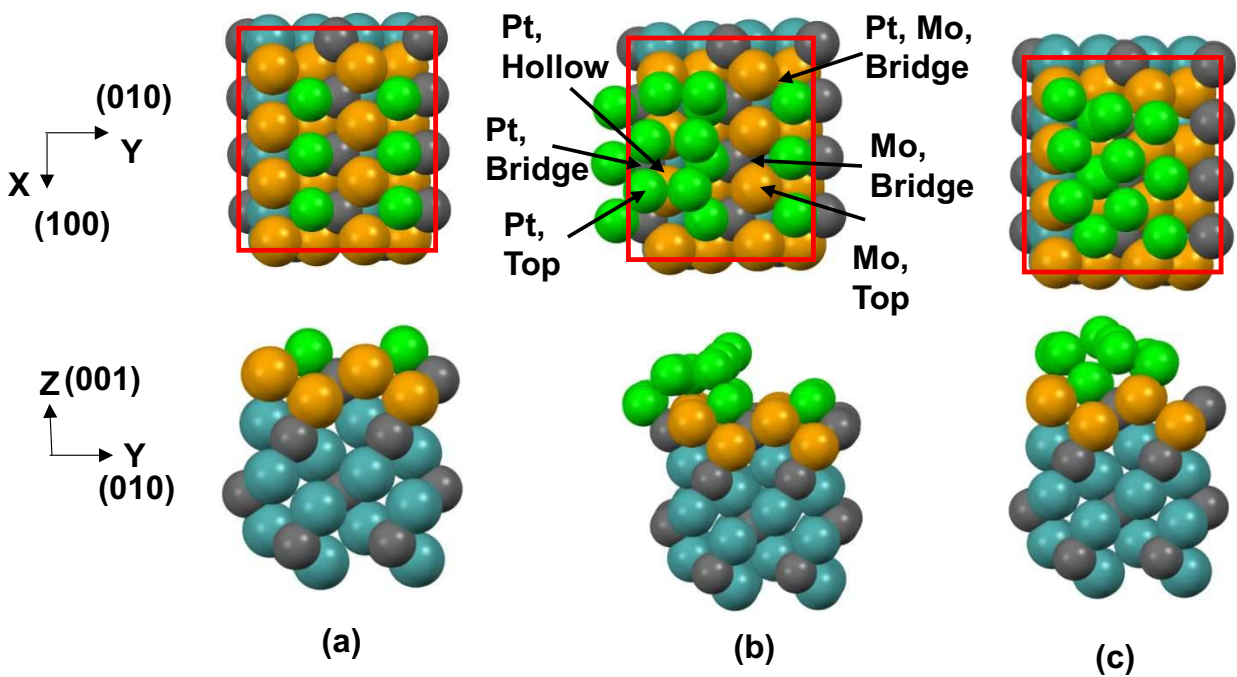
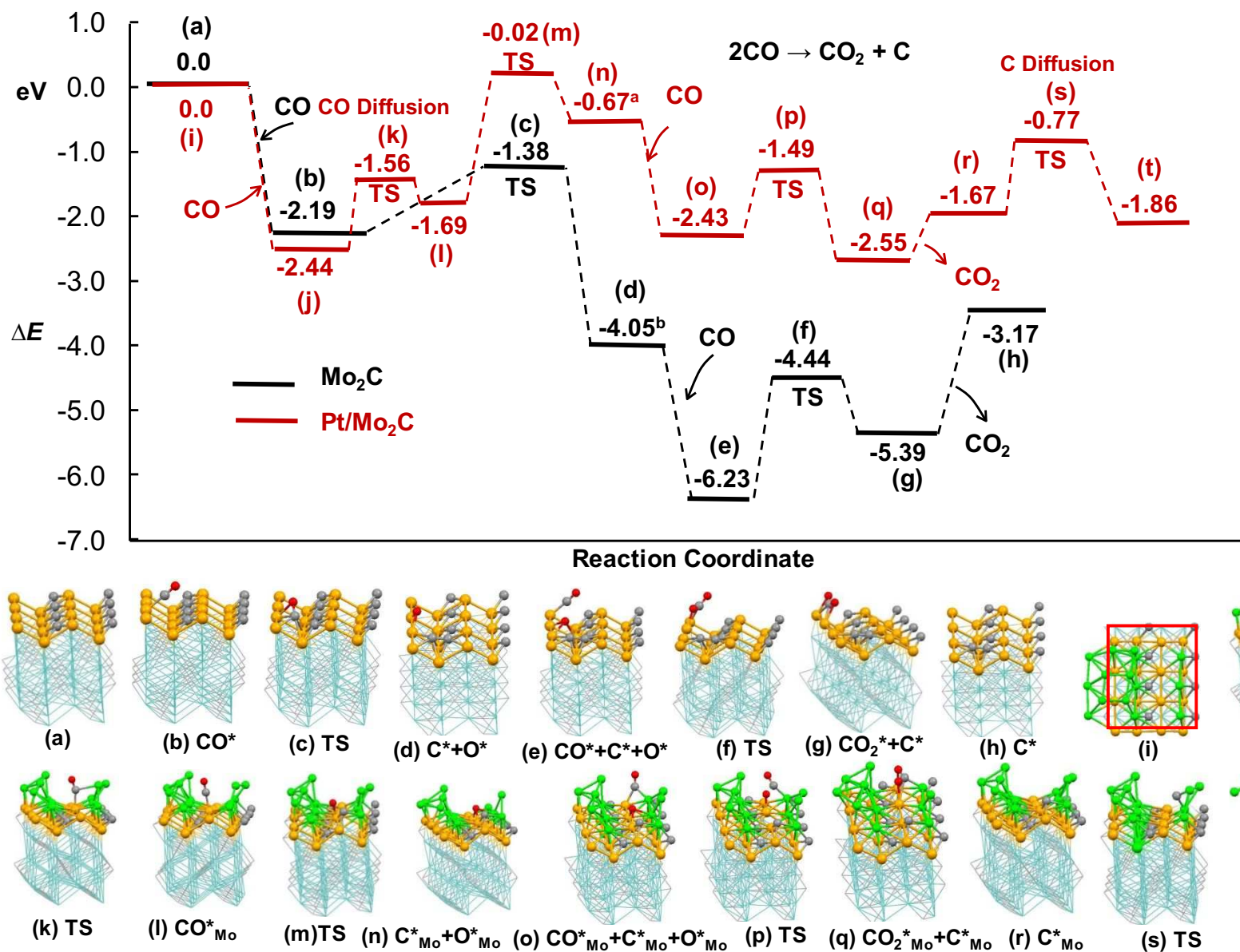


Figure 4. Top and Side View of (a) Most Stable 6Pt@Mo₂C Surface, (b) Most Stable 12Pt@Mo₂C Interface, and (c) a Second 12Pt@Mo₂C Interface. C Atoms Shown in Grey, Mo Atoms Shown in Blue and Pt Atoms Shown in Green. For Clarity, the First Layer Mo Atoms are shown in Orange.



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Figure 5. Potential Energy Surface for Boudouard Reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ on Pure $\beta\text{-Mo}_2\text{C}$ (100) Surface and Pt/ Mo_2C (100) Interface at 0 K with M06L. ^a Dissociation Energy Calculated from Independent Pt/ Mo_2C (100)-C and Pt/ Mo_2C (100)-O Calculations is -1.24 eV. ^b Dissociation Energy Calculated from Independent Mo_2C (100)-C and Mo_2C (100)-O Calculations is -4.36 eV. Oxygen Atoms Shown in Red and See Figure 3 and 4 Captions for the Colors of the Other Atoms.

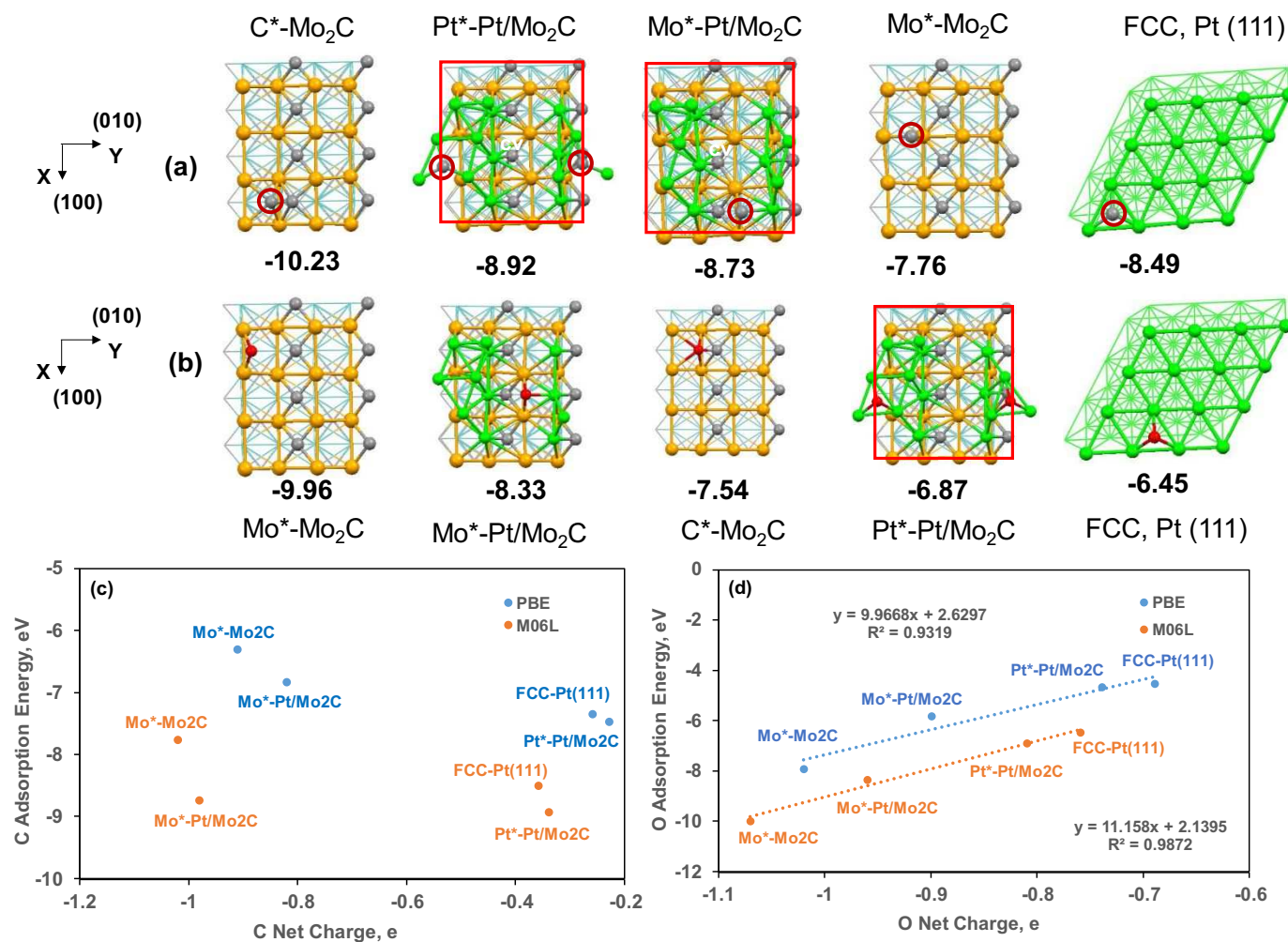


Figure 6. Adsorption Energies of C (a) and O (b) on Different Sites of the Most Stable Mo-Terminated β - Mo_2C (100) and Pt/Mo $_2$ C Interface in eV with M06L; The Correlation Between the Adsorption Energies and the Net Charges of the Adsorbates for C (c) and O (d).

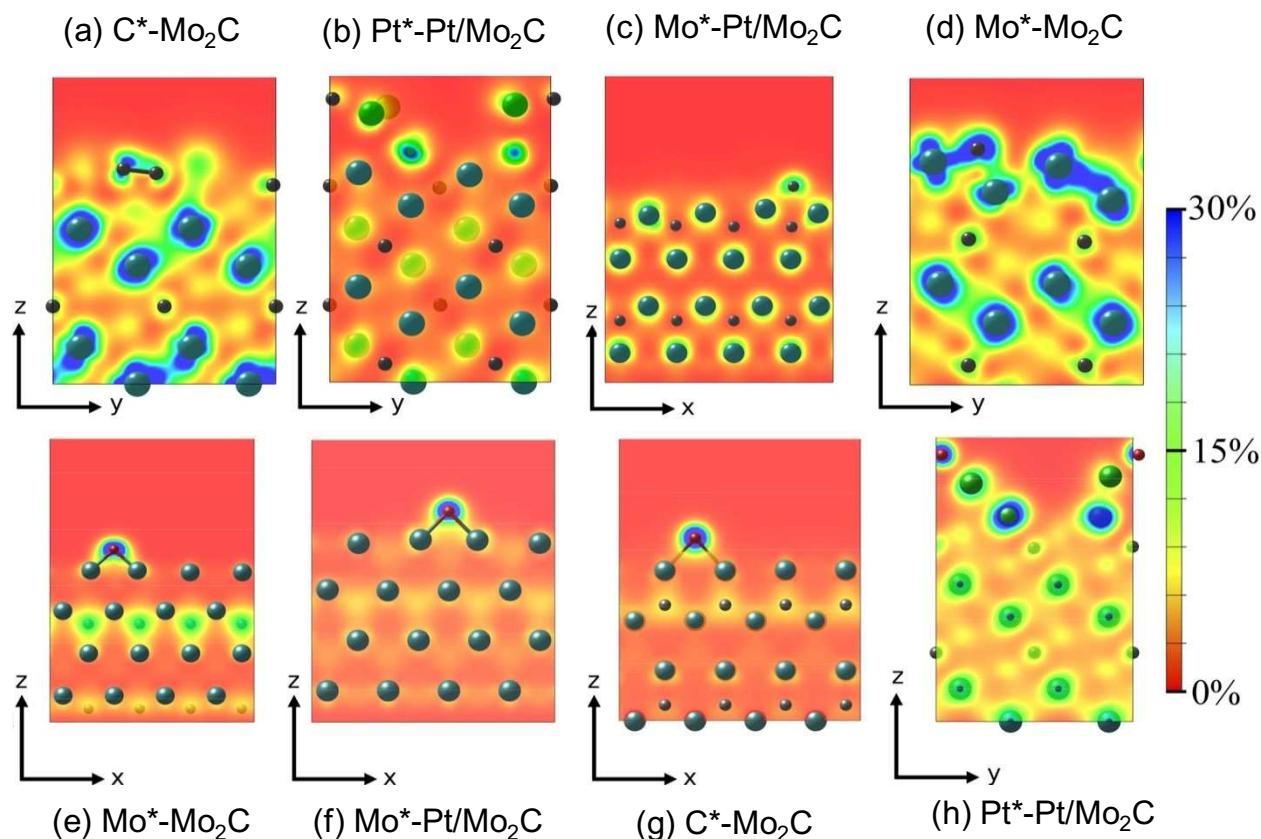


Figure 7. Cross Sections of the Partial Charge Density of C from -2 eV to the Fermi energy (a-d) and O from -8 eV to -5 eV (e-h) on Different Sites of the Most Stable Mo-Terminated β - Mo_2C (100) and Pt/ Mo_2C Interface. The Energy Range Has Been Narrowed to 30% of the Total Electronic States to Improve Bond Visibility. Red Represents No Density of States While Blue Represents the Most Density of States. C, Mo, O, and Pt Atoms are Shown in Dark Grey, Steel Blue, Red, and Green Respectively. In Figures c and f, the Bonding of the Adsorbate with Both Mo and Pt Cannot be Seen in One Plane.

Supporting Information. DRIFTS experiment shows CO₂ peaks on Pt/Mo₂C; Derivation of transient pressure; Number of surface atoms estimation; Free energy and rate constant calculations; Detailed description of CO on Pt (111); Figures: DRIFT spectra; Transient pressure at different temperatures; TPD spectra before pulsing experiment; TPD spectra with CO preadsorption; EDX analysis after pulsing experiment; Calculated potential energy surfaces and free energy surfaces; CO₂, C and O adsorptions on Pt(111), β -Mo₂C(100), and Pt/Mo₂C surfaces; DOS and ELF for C and O adsorption structures; Tables: Bader charge analysis for CO, CO₂, C, and O adsorption structures. This material is available free of charge via the internet at <http://pubs.acs.org>.

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