FIRST-PRINCIPLES STUDY OF CO$_2$ REDUCTION ON MO$_2$C

by

Xi Peng

B.S. Chemical Engineering, University of Mississippi, 2015

Submitted to the Graduate Faculty of
Swanson of Engineering in partial fulfillment
of the requirements for the degree of

Master of Science

University of Pittsburgh

2017
This thesis was presented

by

Xi Peng

It was defended on

June 14, 2017

and approved by

J Karl Johnson, Ph.D., W. K. Whiteford Professor
Department of Chemical and Petroleum Engineering

Goetz Veser, Ph.D., Nickolas A. DeCecco Professor
Department of Chemical and Petroleum Engineering

Thesis Advisor: Giannis Mpourmpakis, Assistant Professor
Department of Chemical and Petroleum Engineering
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Periodic Density Functional Theory (DFT) calculations are widely used to study the interactions between reagents and catalysts, as well as to understand the reaction mechanisms occurring on the catalyst surface. In this work, we investigated the CO\textsubscript{2} adsorption, activation and reduction to CO on (1) pristine, (2) K-promoted, and (3) oxygen-covered (001) orthorhombic Molybdenum carbide (β-Mo\textsubscript{2}C) surfaces. We calculated the CO\textsubscript{2} interaction with both surface terminations of β-Mo\textsubscript{2}C, Mo-terminated and C-terminated, and we found a thermodynamically feasible chemisorption and dissociation of CO\textsubscript{2} on the Mo-terminated surface. The activation energy for CO\textsubscript{2} dissociation on β-Mo\textsubscript{2}C (001) surface was found to be 16.8 kcal/mol. The presence of surface promoter atom, potassium (K), enhanced the binding of CO\textsubscript{2}, and lowered the activation barrier for CO\textsubscript{2} dissociation from 16.8 kcal/mol to 14.0 kcal/mol. Due to the high oxophilicity of the (001) Mo\textsubscript{2}C surface, we further investigated the CO\textsubscript{2} adsorption and dissociation profile on O-covered (001) Mo\textsubscript{2}C (simulating experimental conditions), and we found that CO\textsubscript{2} can still adsorb and dissociate on β-Mo\textsubscript{2}C (001) surface, even in the presence of surface oxygen up to 0.5ML. As O-coverage increases, the activation barrier for CO\textsubscript{2} dissociation increases. Our results rationalize a series of experimental observations.
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PREFACE

First, I want to say thank you to my thesis advisor, Dr. Giannis Mpourmpakis, for all the patience and guidance he gives me. Without his support and mentoring, I would not be able to overcome the obstacles. I would also like to thank Dr. Mudit Dixit, who gives me tons of guidance and training with my calculations, and helps me understanding theory into a deeper level. Also, I want to say great thank you to all the students in our research group: Ms. Natalie Austin, Mr. Pavlo Kostetskyy, Mr. Michael Taylor, Mr. James Dean. Their selfless support helps me go through my days in graduate school, and their great enthusiasm in science will always be a motivation to me to keep up pace with them.

Last, but not least, I would like to express my love to my friends and family; without your support and encouragement, I would never become who I am today.
1.0 INTRODUCTION

The atmospheric concentration of carbon dioxide (CO\textsubscript{2}) is increasing steadily since the past century. CO\textsubscript{2} is one of the major contributors to the greenhouse effect, therefore, several environmental concerns are associated with its excess presence in the atmosphere.\textsuperscript{1-4} Countries around the globe have been announcing and amending regulations to control CO\textsubscript{2} emission.\textsuperscript{5} In 2013, environmental organizations around the world reported that a critical level of CO\textsubscript{2} concentration of 400 ppm had been reached.\textsuperscript{6} The fact that the amount of CO\textsubscript{2} being produced is greater than CO\textsubscript{2} being removed impairs the effectiveness of the measurements taken by human society. As increasing amount of CO\textsubscript{2} is inevitable as our society develops, more problems associated with CO\textsubscript{2} are yet to come. Therefore, solutions that are effective and efficient in removing CO\textsubscript{2} from the atmosphere are in urgent need more than ever.\textsuperscript{7} In spite of several problems associated with CO\textsubscript{2}, due to its low cost, abundance, nontoxicity, and nonflammable nature, it is still a very attractive renewable C\textsubscript{1} feedstock for manufacturing several valuable chemicals, fuels, and materials.\textsuperscript{8-11} Researchers have made several attempts to achieve the goal of removing CO\textsubscript{2} from the atmosphere: in general, these methodologies can be grouped into two categories—CO\textsubscript{2} capture, and CO\textsubscript{2} transformation.\textsuperscript{7}
1.1 CO₂ CAPTURE

CO₂ capture, is based on the idea that CO₂ can be selectively captured and “trapped” in systems in a safe, stable, and efficient manner. The concept of CO₂ capture is closely related to other concepts such as CO₂ storage, and CO₂ capture can be achieved by either absorption (gas molecules permeate/diffuse into absorbents), or adsorption (adhesion of gas molecule onto the surface of adsorbents), as described in Figure 1. Some of the vastly applied/investigated methods for CO₂ capture by both absorption and adsorption are introduced in the following section.

![Flow diagram for CO₂ capture by absorption and adsorption](Figure was obtained from ref: 13)
1.1.1 CO₂ capture by absorption

Traditionally, chemical absorption is carried out by using liquid amine-based absorbent, which can undergo chemical reactions and therefore stabilize CO₂ and eventually reach the goal of “CO₂ capture”. A typical chemical absorption process contains an absorber and a stripping column, and by flowing a gas mixture containing CO₂ and liquid absorbent co-currently or counter-currently, CO₂ removal from the gas mixture is achieved. Followed by the CO₂ adsorption, the CO₂-rich absorbent enters the stripping column for thermal regeneration. Subsequently, pure CO₂ releases from the column, and undergoes compression for storage and transportation. The absorption/stripping process is considered as one of the most matured technologies for CO₂ capture, and has been commercialized for many decades, yet exhibiting several disadvantages. One significant limitation of CO₂ capture by this process is that no more than 10 wt% of CO₂ can be absorbed in such systems. Other limitations include high equipment corrosion rate, high amine degradation rate, and high energy consumption. These drawbacks associated with absorption process drive researchers and engineers to search for alternative approaches to achieve the goal of CO₂ capture.

Among the others, Ionic liquids (IL) are promising absorbents that have been extensively used in catalysis and synthesis because of their unique properties including low vapor pressure, high thermal stability, and non-toxicity. ILs containing amino-functional groups are particularly important due to the large CO₂ absorbing capabilities. The fact that ILs can be synthesized with the desired properties gives researchers much flexibility in developing ILs for wide range of industrial applications including CO₂ capture. However, their high viscosity (slow diffusion) leads to very slow absorption (low rate of absorption) of CO₂ which leads to slow kinetics of the adsorption process. Dealing with this major drawback of ILs used in CO₂
capture, researchers proposed that by mixing of ILs with organic compounds (i.e., alkanolamine), the viscosity of mixture can be controlled without compromising the capability of capturing CO\textsubscript{2}. However, this approach still has all the other problems associated with organic compounds including the volatility issues.\textsuperscript{22}

High Gravity (HiGee) technology is an innovative method which employs the high centrifugal field using a rotating packed bed (RPB). This method involves to the enhancement in momentum, heat, and mass transfer.\textsuperscript{23} RPB has been used in various unit operation processes including desorption\textsuperscript{24}, dehydrogenation\textsuperscript{13}, and synthesis of nanoparticles\textsuperscript{25}, and has been proposed as capable of capturing CO\textsubscript{2}.\textsuperscript{26, 27} By using aqueous solutions (such as NaOH) in the RPB, it was found that the CO\textsubscript{2} adsorption rate was significantly enhanced compared to the adsorption rates of traditional packed bed columns.\textsuperscript{13} However, some of the limitations of the most matured adsorption/stripping process, such as high maintenance and operating costs, also exist here, and thus limit the application of HiGee technology in large industrial scale.

1.1.2 CO\textsubscript{2} capture by adsorption

Due to the fact that traditional absorption processes using the liquids have several disadvantages including low CO\textsubscript{2} loading, low CO\textsubscript{2} absorption rate, and high energy consumption, researchers have been searching for alternatives to achieve the goal of CO\textsubscript{2} capture. Adsorption by solid materials, has been regarded as a promising alternative because of their higher stability under wide temperature ranges and decrease in waste production.\textsuperscript{28} Materials such as carbon based, and zeolite based adsorbents have high surface area and large pore volume for interaction with CO\textsubscript{2} gas molecules, but the adsorbents-adsorbates interaction is usually very weak (physisorption), and CO\textsubscript{2} molecules are easily detached from the adsorbates
under optimal conditions. Zeolites are considered to be good candidates for CO$_2$ adsorption. These are porous crystalline materials, usually containing periodic array of TO$_4$ tetrahedra (T = Si or Al). Several research reports show a great and increasing promise of these materials. The molecular-sized cavities and large pores inherently existing in zeolitic structures enable the zeolites to selectively adsorb molecules (such as CO$_2$ molecules) by size and polarity. However, experimental studies revealed a substantial decrease in CO$_2$ uptake at elevated temperatures (higher than 373 K) or under humid conditions, and thus zeolites are considered to be efficient in CO$_2$ capture only under mild conditions. Another type of materials, alkali metal carbonated based adsorbents, are capable of capturing CO$_2$ by undergoing reversible chemical reactions with CO$_2$, but their durability under industrial operating conditions are yet to be discovered. Other materials such as Metal Organic Frameworks (MOFs), Zeolitic Imidazole Frameworks (ZIFs) (a subclass of MOFs) have been under spotlights in recent years as good candidate for separation and storage of CO$_2$. These represent a class of materials which have high thermal stability, adjustable chemical functionality, and highly ordered structures. The high surface area presented in MOFs, which can reach up to an extraordinary value of 3000 m$^2$g$^{-1}$, exceeded the previously reported materials with high surface areas, such as zeolites (904 m$^2$g$^{-1}$). The highly-complicated frameworks in the structures of MOFs give them intrinsic capabilities of selectively adsorbing and storing small gas molecules, and their adjustable chemical functionality gives MOFs endless potential in applications. ZIFs have been experimentally tested in applications such as separation of similar size molecules such as CO$_2$ and CO, and have been reported to be able to selectively capture CO$_2$ from the mixture with a much higher selectivity compared to other state-of-the-art materials such as BPL carbon.
1.2 CO₂ TRANSFORMATION

Instead of storage of CO₂ through the approaches that were discussed in the last section, another approach is to transform CO₂ into useful chemicals, such as long chain hydrocarbons by hydrogenation.⁴⁰ The molecular CO₂ molecule is linear in its ground state. Due to the inherent polarity of C-O bonds in CO₂, the carbon atom acts as an electrophile whereas the oxygen atoms act as nucleophiles. However, CO₂ is a very stable molecule with a strong C=O bond strength of 192 kcal/mol, and therefore any reaction relating to CO₂ conversion will have to overcome the C=O bond cleavage⁴¹. The conversion of CO₂ is often limited by its strong bond strength. However, high energy materials such as hydrogen or organometallics are often capable to convert CO₂ to useful chemicals.¹⁰ One of the promising routes for CO₂ utilization is to convert CO₂ to carbon monoxide(CO), which can be used to obtain valuable hydrocarbons via Fischer-Tropsch process.¹¹

In industry, CO₂ reforming of methane⁴² (described in Equation (1-1)), one approach to convert CO₂ to CO, has been used to adjust the feed for Fischer-Tropsch process (FT), a process that utilizes CO and H₂ gas mixture to produce liquid hydrocarbons.⁴³

\[
\text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{CO} + 2 \text{H}_2
\]  

(1-1)

The overall process for CO₂ reforming of methane is an endothermic reaction (ΔHr = +59.1 kcal/mol), and many studies had investigated different metal catalysts including Rh, Ru, Pd, Ir, for this process. It was reported that Rh and Ru exhibit the highest conversion of CO₂, but these catalysts are too expensive to be applied in industrial scale productions.³⁶ Direct polymerization of CO₂ (Equation (1-2)) is another approach to convert CO₂ into higher hydrocarbons, and even
though the overall reaction is exothermic, the fully dissociation of CO₂ requires large energy input, and thus have been considered not to be practical in industry. However, CO₂ can be converted into CO via reverse water-gas-shift reaction (RWGS) (Equation (1-3)), and CO can then be hydrogenated using the FT process to produce long chain hydrocarbons (Equation (1-4)). The most commonly used catalysts in industry for FT processes are slight variations of Fe and Co-based catalysts, these catalysts however, have several limitations. One of the major problems include the poisoning of the Fe-based catalysts by the produced water during the FT process, and therefore the reactivity of the catalysts are impaired after a certain period. Co-based catalysts are comparatively water tolerant and show a relatively high activity for the RWGS reaction. The products from FT process when co-feeding CO₂ almost always has a high methane (CH₄) selectivity instead of higher hydrocarbon selectivity. Other traditional metal catalysts such as Pt, Ru, Pd exist, but due to their high cost, they have rarely been used in industrial scale productions. CO₂ is a promising renewable C₁ feed for manufacturing numerous high-value chemicals fuels and materials, due to its high abundance, searching for new catalysts that can convert CO₂ in a more efficient manner is in urgent need.

\[
\begin{align*}
\text{CO}_2 + 3 \text{H}_2 & \rightarrow (\text{CH}_2) + 2 \text{H}_2\text{O} & \Delta H_r &= -30.6 \text{ kcal/mol} & (1-2) \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} & \Delta H_r &= + 9.1 \text{ kcal/mol} & (1-3) \\
\text{nCO} + (2n+1)\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} & \Delta H_r &= -39.7 \text{ kcal/mol} & (1-4)
\end{align*}
\]

In the previous studies relating to Fe-based FT catalysts, researchers had identified that iron carbides are important active phases in Fe-based catalysts during FT synthesis. Other studies also showed that on Co-based catalysts, the chain growth in FT synthesis occurs at the carbide
In recent years, plenty of studies have shown that metal carbides have high catalytic activity. Experimental and theoretical studies have shown that transition metal carbides (TMCs) can act as catalysts as well as supports for metal nanoparticles in various reactions, and in many cases they show even better activity than traditional metal catalysts.\textsuperscript{48,49,50,51,52} Considering the high activity and relatively lower cost of TMCs compared to traditional metal catalysts, the interaction of CO\textsubscript{2} with TMC surfaces is of marked interest.\textsuperscript{53,54} The work done by Rodriguez \textit{et al.} has shown that CO\textsubscript{2} can be activated on hexagonal $\alpha$-Mo\textsubscript{2}C (001) and orthorhombic $\beta$-Mo\textsubscript{2}C (001) (C-terminated) surfaces, and undergoes C-O bond dissociation on $\beta$-Mo\textsubscript{2}C (001) (Mo-terminated) surface.\textsuperscript{49} Porosoff \textit{et al.} have demonstrated that Mo\textsubscript{2}C is an active catalyst for CO\textsubscript{2} conversion, and the active phase of Mo\textsubscript{2}C was found to be the carbide phase.\textsuperscript{11}

\textit{Pistonesi et al.} investigated the effects of surface additives on the binding of molecules on the Mo\textsubscript{2}C surfaces. By investigating K-doped Mo\textsubscript{2}C surfaces, they showed that the addition of potassium (K) atoms promotes CO adsorption.\textsuperscript{55} These findings suggest that TMCs can find application in CO\textsubscript{2} hydrogenation, however, a fundamental understanding of catalytic properties of TMCs is still lacking, especially towards elucidating the detailed reaction mechanisms, and catalysts structure under reaction conditions activation and dissociation.

In this thesis, the adsorption behavior of CO\textsubscript{2} on $\beta$-Mo\textsubscript{2}C (001) as well as the effects of K promoter in the reaction mechanism was investigated using Density Functional Theory (DFT) calculations.
1.3 THEORETICAL BACKGROUND

In DFT, according to the Hohenberg-Kohn (H-K) theorem, the ground state properties of a many-electron system can be uniquely determined by an electron density that depends on three spatial coordinates. However, the H-K theorems has limitations due to the fact that a universal functional form of the density functional that provides this minimum energy is not known exactly, especially the energies of interacting electrons. Most DFT calculations are carried out using the Kohn-Sham (KS) DFT, where the challenges of presenting energies of interacting electrons within the density is treated as a static external potential that is mapped onto a non-interacting system of electrons moving in a common effective potential using fictitious orbitals. The overall ground-state density of the system is identical to the real system and then simply becomes the sum of densities of the occupied orbitals

$$\rho(r) = \sum |\psi_n(r)|^2$$  \hspace{1cm} (1-5)

The energy functional in KS-DFT is

$$E[\rho] = T_s[\rho] + \int V_{\text{ext}}(r)\rho(r)dr + J[\rho] + E_{\text{xc}}[\rho]$$  \hspace{1cm} (1-6)

where $T_s$ represents the kinetic energy of the non-interacting elections, which is the sum of the kinetic energies of individual electrons. The integral represents the electrostatic interaction of the electron density with an external potential $V_{\text{ext}}$. $J$ represents the Hartree repulsion energy, and $E_{\text{xc}}$ is the exchange-correlation energy for all electron-electron interactions.

In general, solving Schrodinger’s equation is the approach of the wavefunction-based \textit{ab initio} methods to study the atomistic interactions of the many-body problems of electronic structures at the fundamental level. The approach is very complicated because the wavefunction of the many-particle system depends on the position, i.e., coordinates of all the individual particles, and thus, for the systems containing large number of electrons, solving Schrodinger’s
equation becomes not feasible. DFT provides a compromise between the system size and computational cost, and can be applied to systems containing many electrons. The most important point for the actual applications of KS-DFT is the functional $E_{xc}$, which is not known exactly, and approximations are needed. Local-Density Approximation (LDA), which assumes that the exchange correlation energy at each point in the system is the same as that of a uniform electron gas of the same density, provides approximation to the exchange-correlation energy. Yet LDA is considered to be a crude approximation, although it gives reliable results for many cases. LDA played an important role in the construction of the more sophisticated approximation: generalized gradient approximation (GGA), which counteracts the overestimation of binding of LDA. Instead of LDA which assumes that the density can be treated as a uniform electron gas, GGA considers the gradient of electron density, which is more accurate in approximation because density undergoes rapid changes in molecules. In many applications, GGA provides a substantially improved description of the ground state properties, in particular for 3d transition metals. In the present thesis, the Vienna Ab Initio Simulation Package (VASP) is used, which is a powerful and popular *ab initio* program. VASP has been employed to a wide range of problems and materials including bulk systems, surfaces, and interfaces.
Density Functional Theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was employed with generalized gradient approximation (GGA). The crystal structure of β-Mo$_2$C has an orthorhombic ground state structure with the space group (Pbcn) and lattice parameters of $a = 6.022$ Å, $b = 5.195$ Å, and $c = 4.725$ Å. By applying geometry optimizations based on minimization of the total energy of the unit cell, the DFT lattice parameters are obtained: $a = 6.071$ Å, $b = 5.250$ Å, and $c = 4.749$ Å, which are in good agreement with experimental obtained lattice parameters. The (001) facet of β-Mo$_2$C is the closest-packed surface, and due to the symmetry of the β-Mo$_2$C bulk unit cell, the (001) facet can be either Mo-terminated, or C-terminated surface. For all the studies relating to β-Mo$_2$C (001) surface, a (2x2) supercell was employed. For both terminated surfaces, the supercells of the slab model have 32 atoms of molybdenum (Mo), and 16 atoms of carbon (C), with a cell dimension of $12.15 \times 10.50 \times 14.55$ Å. The vacuum space was set to 10 Å in all calculations. For K-promoted β-Mo$_2$C(001), one K atom was placed on the top layer at different sites, and after geometry optimization, the site that exhibited the strongest binding to K atom was selected for further calculations (K-promoted β-Mo$_2$C(001) surface). To study the effect(s) of oxygen coverage, several possible oxygen binding sites were considered to find the most energetically preferential sites for oxygen atoms to bind to the surface. Including the clean surface (0ML
coverage), 5 different oxygen coverage was investigated: 0.25ML, 0.50ML, 0.75ML, 1.00ML, and 1.25ML, and CO₂ adsorption behavior on these systems were studied. The kinetic energy cutoff was set to 415 eV, and the convergence criteria to 10E-6 eV for the total electronic energy and 0.01 eV Å⁻¹ for the forces acting on atoms and the k-point mesh was 5x5x1 k-point grid generated by Monkhorst-Pack scheme. The Climbing Image-Nudged Elastic Band (CI-NEB) method has been applied to locate transition states in the CO₂ dissociation pathway. During geometry optimization, the bottom two layers were fixed in their bulk positions and all the other atoms were fully relaxed. Vibrational frequencies on the adsorbates were performed to verify local minima and transition states (presence of one imaginary mode).

Two different CO₂ adsorption configurations on the surfaces were considered: horizontal and perpendicular to the surface. In addition, different sites (top and hollow) were taken into consideration for CO₂ adsorption. The binding energy (BE) is calculated as:

\[
BE_{\text{adsorbate}} = E_{\text{surface + adsorbate}} - E_{\text{surface}} - E_{\text{adsorbate}}
\]  

Where \( E_{\text{surface + adsorbate}} \) is the total electronic energy of the surface with the adsorbed CO₂, \( E_{\text{surface}} \) is the corresponding energy of the clean surface (without any adsorbate), and \( E_{\text{adsorbate}} \) is that of the CO₂ molecule.

In this work, we applied DFT calculations to investigate the CO₂ adsorption and dissociation on β-Mo₂C, and to understand the effect of K-doping on CO₂ adsorption and dissociation on the same systems. Under experimental conditions, the metal carbide surface exposed can turn into oxy-carbide, and therefore CO₂ adsorption on varying O-coverage surfaces was investigated as well. The findings in this work are in excellent agreement with the findings provided by the experimental collaborators at Naval Research Laboratory (NRL).
3.0 CO₂ ADSORPTION ON MOLYBDENUM CARBIDE

Our experimental collaborator from NRL conducted a series of experiments and demonstrated that potassium-promoted Mo₂C is a low-cost, stable, and highly-selective catalyst for RWGS. Their EDS mapping of the catalyst were showed that in Mo₂C/γ-Al₂O₃, Mo atoms are evenly distributed, while on K-Mo₂C/γ-Al₂O₃, a large segregation between Mo and Al was noted, and K is preferentially found in Mo-rich domains. These findings suggested that K might affect the electronic properties of the on Mo₂C phase. In conversion of CO₂ on catalysts, their experiments showed that with the addition of 2 wt% K to Mo₂C/γ-Al₂O₃, the selectivity towards CO was improved significantly, and also showed that a significant improvement in catalytic stability with the addition of K. Futhermore, they showed that as K doping increases, selectivity of CO increases. With lower or no K doping, CH₄ is produced in significant amounts. The apparent activation barrier for CO formation under RWGS conditions at 5 different temperatures between 270 and 330 °C was also studied for both Mo₂C/γ-Al₂O₃ and K-Mo₂C/γ-Al₂O₃, and from their calculations, the activation barriers for CO formation are 14.0 and 11.4 kcal mol⁻¹ for Mo₂C/γ-Al₂O₃ and K-Mo₂C/γ-Al₂O₃, respectively. ⁶¹
3.1 CO$_2$ ADSORPTION ON PRISTINE MO$_2$C (001) SURFACE

To understand the adsorption of CO$_2$ on the Mo$_2$C surface, two different adsorption orientations were considered: the horizontal configuration, with the CO$_2$ molecule being parallel to the surface, and the perpendicular configuration, where one oxygen atom interacts with the surface atoms. Table 1 summarizes the binding energies (kcal/mol) of the CO$_2$ molecule on both the Mo- and C- terminated β-Mo$_2$C (001) surfaces. From our results, the horizontally oriented CO$_2$ molecule exhibits higher binding energy with the surface compared to that with the perpendicularly orientation. On both C-terminated and Mo-terminated surfaces, the CO$_2$ adsorption on hollow sites and top C/Mo sites (based on surface termination) were investigated, and the hollow site was found to have stronger binding with CO$_2$ molecule on both the surfaces. Moreover, CO$_2$ chemisorption and activation are thermodynamically feasible on the Mo-terminated β-Mo$_2$C (001) surface, whereas, the CO$_2$ does not chemisorb on the C-terminated surface as shown in Table 1.
Table 1. Adsorption energy (kcal/mol) of CO$_2$ on both Mo- and C-terminated $\beta$-Mo$_2$C(001) surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$BE(CO_2,\text{phys})$ kcal/mol</th>
<th>$BE(CO_2,\text{chem})$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$C-C terminated</td>
<td>-1.91 (perpendicular) hollow site</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>-2.37 (horizontal) hollow site</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.33 (horizontal) top Mo site</td>
<td></td>
</tr>
<tr>
<td>Mo$_2$C-Mo terminated</td>
<td>-0.27 (perpendicular) hollow site</td>
<td>-31.40 hollow site</td>
</tr>
<tr>
<td></td>
<td>-0.52 (horizontal) hollow site</td>
<td>-24.31 top Mo site</td>
</tr>
<tr>
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<td>-0.33 (horizontal) top Mo site</td>
<td>-74.81 (CO* + O*)</td>
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</tbody>
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The activation of CO$_2$ on Mo-terminated surface was identified by the bending of the CO$_2$ molecule, and bond elongation of the C=O bond. Showing in Figure 2: at hollow site (the site that exhibits stronger binding of CO$_2$), the activated CO$_2$ had a O-C-O bond angle of 114.5 degrees, and the C-O bond was elongated from 1.16 A (C=O bond length in a gas-phase CO$_2$ molecule) to 1.34 A.

![Figure 2: activated CO$_2$ (left), and dissociated CO$_2$ (right) on Mo-terminated Mo$_2$C (001) surface. Color code: cyan-Mo, black-C, red-O.](image)

15
Since activation of CO$_2$ is thermodynamically feasible on the Mo-terminated $\beta$-Mo$_2$C (001) surface, we considered whether CO$_2$ can undergo further dissociation, which involves C=O bond cleavage. Several dissociated CO$_2$ configurations (CO* and O*) on the Mo-terminated $\beta$-Mo$_2$C (001) surface were studied, and after minimizing the total energy of the systems, the most stable structure which has one oxygen atom bonded to hollow position was obtained as shown in Figure 2. In this dissociated configuration, CO* was attached to the surface with C atom at a hollow position interacting with three surface Mo atoms with an average bond length of 2.1 Å, and C-O length in CO* is 1.28 Å. The BE (CO*+O*) = -74.8 kcal/mol (reference: total energy of the clean surface and CO$_2$ gas molecule at infinite separation). While the whole process of CO$_2$ dissociation on the Mo-terminated surface appeared to be thermodynamically feasible, we applied a climbing image-NEB (CI-NEB) calculations to study the kinetics of the reaction, to study the dissociation pathway, and to obtain transition state (T.S.) and associated activation energy. From our result, first, CO$_2$ barrierlessly activates (-31.4 kcal/mol), and then dissociates to CO* and O*, with an activation barrier of 16.8 kcal/mol. The C-O bond length for the T.S. was 1.92 Å (figure 3). In Figure 4, the dissociation profile of CO$_2$ on Mo-terminated surface is presented. All of these steps are exothermic with respect to the initial, CO$_2$ physisorption state.

Figure 3: Transition state (T.S.) for CO$_2$ dissociation on Mo-terminated Mo$_2$C (001) surface. Color code: grey-C, cyan-Mo, red-O
Figure 4: CO$_2$ dissociation profile on Mo-terminated, β-Mo$_2$C (001) surface (energy in kcal/mol). Color code: grey-C, cyan-Mo, red-O

3.2 CO$_2$ ADSORPTION ON K-PROMOTED MO$_2$C (001) SURFACE

DFT calculations were performed on K-modified β-Mo$_2$C(001) surfaces because we also wanted to know how surface adatoms effect adsorption capability of the surface. Similar to that on the pristine surface, CO$_2$ does not chemisorb on the K-promoted C-terminated surface, but can be activated and dissociated on the K-promoted Mo-terminated surface. Table 2 summarized the calculated CO$_2$ binding energy on the K-promoted surfaces. The activated CO$_2$ on the K-doped surface was identified by tracking the change in the CO$_2$ bond angle and C-O bond length. At the hollow site, the activated CO$_2$ has a bond angle of 123.5 degrees, and the bond length was
1.35 Å (Figure 5). By directly comparing the BE of CO₂ on pristine and K-promoted surfaces, it becomes clear that the presence of K significantly enhances the CO₂ physisorption on Mo₂C (001) (from -0.5 to -6.5 kcal mol⁻¹ at hollow site, from -0.3 to -2.2 kcal/mol at top Mo site), and moderately increases the BE of the chemisorbed states (from -74.8 to -80.9 kcal mol⁻¹ for dissociated CO₂, and from -31.4 to -46.6 kcal mol⁻¹ for activated CO₂, respectively). The activated CO₂ and dissociated CO₂ are presented in Figure 5.

**Table 2:** Adsorption energy (kcal/mol) of CO₂ on both K doped Mo- and K doped C-terminated β-Mo₂C(001) surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>BE(CO₂,phys) kcal/mol</th>
<th>BE(CO₂, chem) kcal/mol</th>
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<td>K-Mo₂C-C terminated</td>
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<td>-46.57 hollow site</td>
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<tr>
<td></td>
<td>-2.19 (horizontal) top Mo site</td>
<td>-42.17 top Mo site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-80.90 (CO*+O*)</td>
</tr>
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</table>
These energy changes in the presence of K are due to electronic effects. As the DFT calculations suggest (Bader charge analysis), K loses almost one electron, which is delocalized on the surface of the Mo$_2$C. As a result, the presence of a point charge (K-cation) increases the dipole-dipole interaction character in the CO$_2$ physisorption (thus, the physisorption energy). On the other hand, the partially negatively charged surface of the Mo$_2$C, facilitates the activation of CO$_2$, and the adsorption of electrophilic species, such as atomic oxygen.$^{62}$
Since the dissociation of CO$_2$ on K-doped Mo-terminated Mo$_2$C (001) is thermodynamically favorable, we conducted a CI-NEB calculation to study the actual dissociation pathway and locate T.S. In Figure 6, CO$_2$ dissociation profiles on both pristine and K-promoted Mo$_2$C (001) surfaces are presented and compared. On the K-promoted, Mo-
terminated surface (purple), CO₂ is first barrierlessly activated to a chemisorbed state (≈46.6 kcal/mol), and then dissociates to CO and O with a barrier of 14.0 kcal/mol. The bond length of C-O of the T.S. was 2.04 Å (Figure 7). All of these steps are again exothermic with respect to the initial, CO₂ physisorbed state. It is worth noting that the barrier for CO₂ to dissociate from the activated state to CO* + O* in the presence of K is 2.8 kcal mol⁻¹ lower than that of the pristine β-Mo₂C(001) surface. Taking into consideration the decrease in activation energy for CO₂ dissociation and the increase of the CO₂ physisorption on the Mo-terminated, β-Mo₂C(001) surface in the presence of K, it is apparent that K doping facilitates the formation of CO. These DFT calculated reaction barriers are in excellent agreement with those obtained experimentally, as shown in Table 3.

Table 3. Comparison of theoretical activation barrier (Ea) calculated by DFT and experimentally determined apparent activation barrier (Ea_app) for CO formation from CO₂ over pristine and K-promoted Mo₂C-based catalysts. (kcal/mol)

<table>
<thead>
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<th>Theoretical Ea</th>
<th>Experimental Ea_app</th>
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</thead>
<tbody>
<tr>
<td>Pristine (No K) Mo₂C</td>
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<td>14.0</td>
</tr>
<tr>
<td>K-Promoted Mo₂C</td>
<td>14.0</td>
<td>11.4</td>
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</table>
3.3 CO$_2$ ADSORPTION BEHAVIOR ON O-COVERED MO$_2$C (001) SURFACE

Under experimental conditions, and based on the affinity of MO$_2$C to dissociate CO$_2$, the metal carbide surface may be converted to an oxygenated carbide surface. Also, the surface oxygen is likely to be produced by dissociative adsorption of H$_2$O molecule under RWGS conditions. As a result, we calculated the binding energy of oxygen on five different oxygen surface coverages ranging from 0.25 ML (monolayer) to 1.25 ML, as shown in Figure 8. The binding energy of oxygen was calculated by equation (3-1):

$$E(O) = E(nO_{-surf}) - nE(H_2) - nE(H_2O)$$

(3-1)

where $n$ is the number of oxygen atoms adsorbed in one super cell. The optimized O-covered MO$_2$C (001) surface are shown in Figure 8. The most preferred adsorption site for oxygen atom was found to be the hollow site, where the oxygen atom is stabilized by three surface Mo atoms. At one ML O-coverage, all of the hollow sites have been occupied by oxygen, and therefore further addition of more oxygen atoms to the surface are expected to be of higher energy. From Figure 9, one can observe that the binding energy of oxygen increases (more exothermic) as the O-coverage increases, and this trend was found to be changed when the surface O-coverage is greater than 1 ML (decrease in binding energy).
Figure 8. (from left to right) Optimized O-Mo\textsubscript{2}C (001) surfaces at 0.00ML (clean surface), 0.25ML, 0.50ML, 0.75ML, 1ML, and 1.25ML oxygen coverage. (up: top view; bottom: side view)

Figure 9. Binding energy of oxygen at a given coverage from 0.25 ML to 1.25 ML (Mo-terminated Mo\textsubscript{2}C).

It is interesting to see that how the CO\textsubscript{2} adsorption behavior changes with surface O-coverage. As noted earlier, on clean $\beta$-Mo\textsubscript{2}C (001) surface, the most preferential site for CO\textsubscript{2} chemisorption is found to be the hollow site. However, on O-covered surfaces, some of these sites may be occupied by oxygen, and therefore, different sites must be investigated in order to obtain the most stable chemisorption configuration of CO\textsubscript{2}. On 0.25 ML O-coverage, three different sites (shown in Figure 10) were observed to be capable of activating CO\textsubscript{2}, with the strongest binding energy at the hollow site (-18.8 kcal/mol). The O-C-O bond angle of activated
CO$_2$ was 134.2 degrees, and the C-O bond length was 1.27 Å. The average Mo-O distance is 2.37 Å.

Figure 10. (left) Top view of 0.25ML O-Mo$_2$C(001), with 3 adsorption sites pointed in blue. (right) CO$_2$ adsorption on 0.25ML O-Mo$_2$C (001) surface at hollow site (up: top view, bottom: side view). The O-C-O bond angle of activated CO$_2$ was 134.2 degrees, and the bond length was 1.27 Å.

Figure 11: CO$_2$ adsorption on (a) 0.50ML and (b) 0.75ML O-Mo$_2$C(001) (left: top view, right: side view).

On 0.5 ML O-covered surface, the hollow site was found to activate CO$_2$ with BE of -5.37 kcal/mol, which shows weaker binding compared to that on 0.25 ML (-18.8 kcal/mol) and
clean surface (-29.8 kcal/mol). The O-C-O bond angle of activated CO$_2$ was 137.5 degrees, and the C-O bond length was 1.25 Å. The average Mo-O length was 2.31 Å.

On 0.75 ML O-covered surface, no chemisorption of CO$_2$ was obtained, and a positive BE of +12.0 kcal/mol was noted, indicating that the interaction of CO$_2$ becomes endothermic at high O-coverage surfaces. The activation/adsorption of CO$_2$ on 0.5 ML and 0.75 ML O-covered surfaces are shown in Figure 11.

Figure 12 summaries the binding energy of CO$_2$ vs. O-coverage. One can observe that the binding energy of CO$_2$ follows a linear trend: the lower the O-coverage, the stronger the CO$_2$ adsorption (larger negative BE (CO$_2$) values). However, at O-coverage larger than 0.75 ML, the interaction of CO$_2$ with the surface becomes endothermic, the adsorption of CO$_2$ is no longer favorable.

![Figure 12](image_url)

**Figure 12.** Binding energy of CO$_2$ (BE$_{CO_2}$) vs. O-coverage on Mo$_2$C (001) surface (the most preferred binding sites on each O-coverage surface).
To find the activation energy for CO$_2$ dissociation, CI-NEB calculations were carried out. Several CO$_2$ dissociated (CO*+O*) configurations were constructed as described below: holding the CO* at a particular site, and varying the location of O* at neighboring sites, and minimize the total energies of these different configurations. After obtaining the most stable dissociated configuration, this structure was considered as the final state (dissociated CO$_2$) for CI-NEB calculations, and the corresponding reaction path was then constructed. Figure 13 and 14 showed the CO$_2$ dissociation profiles on 0.25ML and 0.5ML O-Mo$_2$C surfaces (surfaces that still chemisorb CO$_2$). The activation barriers on 0.25ML and 0.50ML O-Mo$_2$C surfaces are 23.57 kcal/mol and 26.89 kcal/mol, respectively. The distances of O-CO bond of the T.S. are 1.750 Å (0.25ML) and 1.753 Å (0.50ML).

Figure 13: CO$_2$ dissociation profile at hollow site on 0.25 ML O-Mo$_2$C surface
In Figure 15 we summarize the activation energy of CO$_2$ dissociation (kcal/mol) on (1) pristine surface, (2) K-doped surface, (3) 0.25 ML O-covered, and (4) 0.50 ML O-covered Mo$_2$C (001) surface. We found by our NEB calculations that, while the presence of surface K atom decrease the activation energy of CO$_2$ dissociation, surface O atoms have a different effect on CO$_2$ adsorption behavior on Mo$_2$C(001) surface. The activation energy of CO$_2$ dissociation increases as O-coverage increases, which is in line with the binding energy calculations of CO$_2$ and oxygen on surfaces with different O-coverage (the weaker the CO$_2$ binding, the higher the CO$_2$ dissociation barrier). Surface K atom acts as an electron donor, loses almost one electron, and thus creates the partially negatively charged Mo$_2$C surface and enhances adsorption of CO$_2$. O atoms, however, stay at active sites for CO$_2$ adsorption, and form Mo oxide, which can
introduce repulsion to the adsorbents containing oxygen, and consequently decrease the adsorption of CO$_2$ on the surface.

![Figure 15. CO$_2$ dissociation profiles on pristine surface (green), K-doped surface (red), 0.25 ML O-covered (black), and 0.50 ML O-covered surface (blue). Ea represents activation energy in kcal/mol.](image-url)
4.0 CONCLUSIONS

The adsorption behavior of CO$_2$ on β-Mo$_2$C (001) was studied, and the effects of K promotion and oxygen coverage on adsorption and dissociation of CO$_2$ have been investigated. On clean β-Mo$_2$C (001) surface, CO$_2$ undergoes a barrierless activation, with a binding energy of -31.4 kcal/mol, and dissociated to CO* and O* with an activation barrier of 16.8 kcal/mol. When the surface is promoted by K atom, the changes in the charges surface atoms results in a stronger binding of CO$_2$ (-46.4 kcal/mol) and CO$_2$ dissociates through a lower activation barrier (14.0 kcal/mol). Under experimental conditions, the surface is likely to be covered with oxygen atoms, and therefore the effect(s) of O-coverage on Mo$_2$C (001) were also studied. According to our results, the binding of oxygen on the surface increases as the surface coverage increases, until it reaches a maximum at 1ML coverage. Then, further oxygen adsorption becomes unfavorable (decrease in oxygen adsorption energy). CO$_2$ binding energy decreases with the increase in surface oxygen atoms, therefore, CO$_2$ can no longer strongly chemisorb at high oxygen coverage (O-coverage > 0.5ML). We show that the activation barriers for CO$_2$ dissociation also increase as O-coverage increases. Finally, it should be noted that even though the Mo$_2$C surface can become an oxy-Mo$_2$C surface, under reaction conditions, our study shows that CO$_2$ can still adsorb and dissociate at low O-coverage (<0.50ML).
APPENDIX A

EXAMPLE OF VASP INPUT FILES
1. INCAR (CI-NEB) (8 intermediate images for example)

SYSTEM = NEB_for_test2_1
ENCUT = 415
PREC = ACC
ISTART = 0
ICHARG = 2
#ISPIN = 2 !spin polarized calculation, collinear
#MAGMOM = 32*0.6 48*0.6 3*2 8*2
NELM = 100
NELMIN = 8
NELMDL = -15
EDIFF = 1.0E-6
ISMEAR = 1
SIGMA = 0.2
EDIFFG = -0.01
ISIF = 2

IBRION = 3
POTIM = 0
# IVDW = 12
NPAR = 8

NSW = 1000
LREAL = A
ALGO = Fast
ADDGRID = .TRUE.
ALGO = Fast
# IALGO = 48
# IALGO = 38
# NSIM = 4
# NPAR = 2
# NCORE = 12
# NCORE = 4
LPLANE = .TRUE.
LSCALU = .FALSE.
ISYM = 0
#SYMPREC = 1.0E-5
LWAVE = .FALSE.
LCHARG = .FALSE.
ICHAIN = 0
IMAGES = 8
LCLIMB = .TRUE.
INVCURV = 0.01
MAXMOVE = 0.1
SPRING = -5
IOPT = 1

### MIXING
AMIX = 0.2
BMIX = 0.0001
AMIX_MAG = 0.8
BMIX_MAG = 0.0001
2. INCAR (GEOMETRY OPTIMIZATION)

SYSTEM = Co2C_unit_cell

ISTART = 0
ICHARG = 2
ENCUT = 415
EDIFF = 10E-5
EDIFFG = -0.01
NSW = 600
IBRION = 2
POTIM = 0.5
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SIGMA = 0.2
LORBIT = 11
ISIF = 2
ISPIN = 2

# MAGMOM = 12*2.73 6*0.6
# KSPACING = 0.3
# KGAMMA = .TRUE.

NPAR = 8
3. KPOINTS FILE

k-points
0
Monkhorst Pack
5 5 1
0 0 0
4. POSCAR FILE (COORDINATES)

Example: system: CO2 adsorption on 0.25ML O-covered surface. The supercell contains 32 Mo, 17 C, and 6 O atoms. Bottom two atom layers are frozen.

```
025_CO2
1.000000000000000000
10.5006999689999999 0.0000000000000000 0.000000000000000000
0.000000000000000000 12.1464004516999999 0.000000000000000000
0.000000000000000000 0.000000000000000000 14.5508003235000007
Mo   C    O
32    17     6
Selective dynamics
Direct
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