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Potassium-promoted molybdenum carbide as a highly active and selective catalyst for CO₂ conversion to CO

Marc D. Porosoff^[a], Jeffrey W. Baldwin^[b], Xi Peng^[d], Giannis Mpourmpakis^[d] and Heather D. Willauer^{[c]*}

Abstract: The high concentration of CO₂ bound in seawater represents a significant opportunity to extract and use this CO₂ as a C₁ feedstock for synthetic fuels. Through an existing process patented by the U.S. Navy, CO₂ and H₂ can be concurrently extracted from seawater, then catalytically reacted to produce synthetic fuel. Hydrogenating CO₂ directly into liquid hydrocarbons is exceptionally difficult, but by first identifying a catalyst for selective CO production via reverse water-gas shift (RWGS), CO can then be hydrogenated to fuel through Fischer-Tropsch (FT) synthesis. Results of this study demonstrate that potassium-promoted molybdenum carbide supported on γ -Al₂O₃ (K-Mo₂C/ γ -Al₂O₃) is a low-cost, stable and highly selective catalyst for RWGS over a wide range of conversion. These findings are supported by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations.

Introduction

The high concentration of CO₂ in seawater, ca. 100 mg L⁻¹, represents a significant opportunity to extract and use this CO₂ as a C₁ feedstock for synthetic fuels. Through an existing process patented by the U.S. Navy,^[1] CO₂ and H₂ can be concurrently extracted from seawater and used as reactants for direct Fischer-Tropsch from CO₂ (CO₂-FT) to produce valuable oxygenates, specialty chemicals and intermediate hydrocarbons (C₂-C₆) for synthetic fuel.^[2-3] If the energy input is nuclear or renewable, the entire process can be considered CO₂-neutral.^[4]

The most commonly used catalysts for CO₂-FT are slight variations of Fe and Co-based Fischer-Tropsch (FT) catalysts, which show promise, but are not specifically designed for the CO₂ reactant.^[5-7] The current optimal catalyst, K-Mn-Fe/ γ -Al₂O₃, achieves a CO₂ conversion of 41.4% and a selectivity towards C₂-C₅+ hydrocarbons of 62.4% at a gas hourly space velocity (GHSV) of 0.0015 L g⁻¹ s⁻¹, but the mechanism is poorly understood, making catalyst improvements challenging.^[8] There is some consensus that an Fe carbide formed during the reaction is the catalytically active phase,^[9] however, reports also state that Fe catalysts are poisoned by water, an unavoidable

byproduct, negatively influencing catalytic activity and product selectivity.^[10-11] Conversely, Co-based catalysts are water tolerant^[12] and modifying an Fe catalyst with Co improves catalytic performance and selectivity towards C₂+ hydrocarbon products.^[13-14] Improvements have also been made to Fe-based catalysts by adding Cu, which enhances CO₂-FT activity and selectivity.^[14]

Although there are promising catalysts for CO₂-FT, the structure-property relationships that control activity and selectivity to intermediate hydrocarbons are not well studied.^[15] Furthermore, because of the complexity of CO₂-FT, the alternative route of feeding CO produced via reverse water-gas shift (RWGS) into a FT reactor must also be considered. For industrial RWGS, operating temperatures are very high, typically at or above 600 °C at 2.8 MPa, over ZnO/ γ -Al₂O₃ and ZnO/Cr₂O₃ catalysts. Because methane (CH₄) is thermodynamically favored below 600 °C, these catalysts require high temperatures to selectively produce CO, which results in substantial deactivation.^[16-17] To make fuel synthesis from CO₂ viable, a low-cost and stable RWGS catalyst is first required, which can achieve high selectivity to CO over a wide range of conversion and operating temperatures.

Recently, Pt-based catalysts have been investigated for RWGS,^[18-19] but they are expensive, and thus, unviable for an industrial scale CO₂ conversion process. As an alternative, transition metal carbides (TMCs) are low-cost, with similar electronic properties to precious metals.^[20-21] Density functional theory (DFT) calculations over the TMC, molybdenum carbide (Mo₂C) demonstrate that Mo-terminated Mo₂C has many properties similar to transition metals including Ru, Fe, Co and Ni, all of which are active for CO₂ conversion.^[22] DFT calculations by Shi et al. further illustrate that CO₂ dissociation (CO₂ → CO + O) is more favorable than CO₂ hydrogenation (CO₂ + H → HCOO or COOH) over Mo₂C, suggesting high CO selectivity.^[23] Reactor experiments over unsupported-Mo₂C powder catalysts for RWGS at 300 °C and 0.1 MPa show 8.7% conversion and 93.9% selectivity towards CO,^[24] confirming the DFT calculations. Another study over Mo₂C nanowires also reports high activity and CO selectivity at 600 °C.^[25] The high intrinsic activity of Mo₂C originates from CO₂ binding in a bent configuration, leading to spontaneous breakage of a C=O bond, leaving CO and O bound to the surface.^[26] The CO can desorb from the surface, while the oxy-carbide (O-Mo₂C) is restored to the active carbide through hydrogenation.^[24]

Mo₂C can also be modified with metal nanoparticles (Cu, Co, Ni), which influence the product selectivity, leading to MeOH with Cu,^[27] C₂+ hydrocarbons with Co and CH₄ with Ni.^[28-29] Because modifying Mo₂C with a metal promoter can further tune the selectivity between MeOH, C₂+ hydrocarbons or CH₄, it may be possible to modify Mo₂C to selectively produce even more CO across a wide range of conversions and temperatures. Experimental and theoretical studies suggest that potassium (K) promoters increase the binding energy, and therefore, reactivity

[a] Dr. Marc D. Porosoff
NRC Postdoctoral Research Associate

[b] Dr. Jeffrey W. Baldwin
Acoustics Division

[c] Dr. Heather D. Willauer*
Materials Science and Technology Division
Naval Research Laboratory
4555 Overlook Avenue, Washington DC, 20375
E-mail: heather.willauer@nrl.navy.mil

[d] Prof. Giannis Mpourmpakis, Xi Peng
Department of Chemical and Petroleum Engineering
University of Pittsburgh

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of CO₂, thereby promoting C=O bond scission and formation of CO.^[30-31]

In this paper, kinetic experiments and characterization tools have been combined with DFT calculations to probe the catalytic properties of K-promoted Mo₂C and understand the reaction mechanisms of CO₂ dissociation. Flow reactor results indicate that K-Mo₂C/γ-Al₂O₃ is a highly active and stable RWGS catalyst exhibiting high selectivity towards CO over a range of operating conditions, with the presence of K promoting CO₂ dissociation to CO. These findings are supported by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) measurements and DFT calculations.

Results and Discussion

To experimentally determine the effect of K addition on Mo₂C-based supported catalysts, K-Mo₂C and the corresponding Mo₂C, Mo and K-Mo control catalysts, all supported on γ-Al₂O₃, were synthesized through an evaporation-deposition procedure, as outlined in the experimental section. XRD measurements over the reduced catalysts, shown in Fig. 1, indicate that each of the synthesized catalysts contain a combination of MoO₂ [JCPDS 32-671], β-Mo₂C [JCPDS 35-787] and metallic Mo [JCPDS 42-1120]. Each of these phases is assigned to the synthesized catalysts by comparing the XRD spectra with the standard database for specific bulk Mo phases.

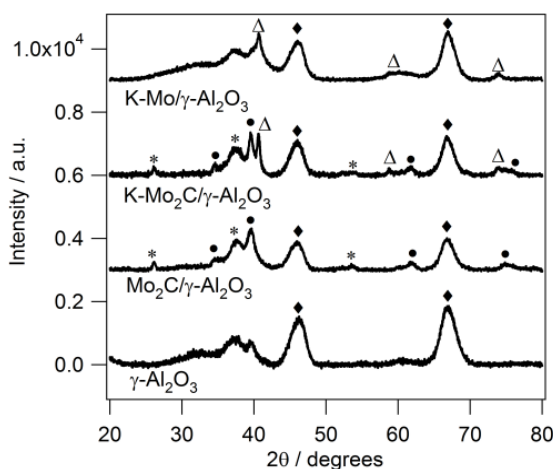


Figure 1. XRD spectra of the reduced Mo₂C/γ-Al₂O₃, 2 wt% K-Mo₂C/γ-Al₂O₃ and 2 wt% K-Mo/γ-Al₂O₃ with the γ-Al₂O₃ support as a reference. Symbols correspond to: γ-Al₂O₃ (♦), MoO₂ (*), β-Mo₂C (•) and metallic Mo (Δ).

XRD measurements of the Mo-based catalysts indicate that Mo₂C/γ-Al₂O₃ and 2 wt% K-Mo₂C/γ-Al₂O₃ contain a mixture of β-Mo₂C and MoO₂ supported on γ-Al₂O₃. All supported Mo-based catalysts exhibit large peaks at 45.8° and 66.6°, from the γ-Al₂O₃ support, and no identifiable peaks for MoO₃ [JCPDS 35-609] are present in any of the samples. Closer inspection of the XRD spectra reveals the presence of a phase assigned to metallic Mo at 40.5°, 58.7° and 73.7° on the K-Mo₂C/γ-Al₂O₃ and K-Mo/γ-

Al₂O₃ catalysts. These peaks are not present in Mo₂C/γ-Al₂O₃, suggesting that the addition of K promotes the formation of a metallic Mo phase.

To better identify the structure of K-Mo₂C/γ-Al₂O₃, SEM images with EDS mapping of the reduced catalyst is shown in Fig. 2. Overall, the morphology and particle size of K-Mo₂C/γ-Al₂O₃ (Fig. 2a) and Mo₂C/γ-Al₂O₃ (Fig. S2) appear to be similar. The EDS maps, however, show that the distribution of Mo over each catalyst is notably different. The EDS map of the Mo₂C/γ-Al₂O₃ catalyst, found in the SI, indicates that molybdenum is evenly distributed over the γ-Al₂O₃ support. On K-Mo₂C/γ-Al₂O₃ in Fig. 2b-d, there is both (1) a large degree of segregation between Mo (blue) and Al-rich (red) areas and (2) K (green) is preferentially found in the Mo-rich areas, which suggests K directly affects the electronic properties of the active Mo₂C phase.

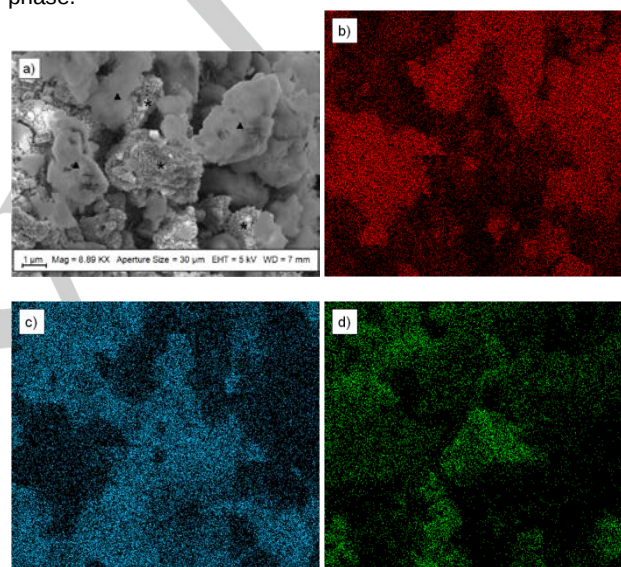


Figure 2. (a) SEM micrograph for the reduced 2 wt% K-Mo₂C/γ-Al₂O₃, with (*) and (Δ) representing Mo rich and Al rich phases, respectively. EDS maps are included of (b) Al in red, (c) Mo in blue and (d) K in green.

The difference in distribution of molybdenum between the two catalysts can be explained by polymerization of a layer of molybdenum oxide over the γ-Al₂O₃ support in the Mo₂C/γ-Al₂O₃ catalyst, as seen in the SEM image in the SI, which may occur during the calcination step of synthesis.^[32] Alternatively, the Mo particles are simply too small to be resolved by SEM and must be imaged through other techniques. On the K-Mo₂C/γ-Al₂O₃ catalyst, there are clearly large K-Mo aggregates seen in Fig. 2, which could be a result of the K promoter lowering the affinity of Mo for the γ-Al₂O₃ support.

Regardless of the differences in catalyst particle size and morphology, there is no significant difference in catalytic activity between the two samples. As seen in Fig. 3a, the conversion of Mo₂C/γ-Al₂O₃ and K-Mo₂C/γ-Al₂O₃ is similar. Although the activity of the two catalysts is comparable, the addition of 2 wt% K to Mo₂C/γ-Al₂O₃ significantly improves the selectivity towards CO. The effect of K addition becomes more apparent in Fig. 3b, where CO selectivity of Mo₂C/γ-Al₂O₃ and 2 wt% K-Mo₂C/γ-Al₂O₃ is reported across a range of conversions, by adjusting the gas

hourly space velocity (GHSV). Clearly, there is a strong promotional effect from the addition of K, which leads to high CO selectivity (~95%) from 6 to 23% conversion. The equilibrium conversion for RWGS is 22.8% at 300 °C with a 3:1 H₂:CO₂ ratio. Furthermore, as seen in Fig. 3a, the addition of the K promoter decreases the deactivation percentage from 11.7% to 7.3% after 68 h on stream, an improvement in catalytic stability. A summary of the catalytic performance for both catalysts under typical RWGS conditions can be found in Table 1.

Table 1 also includes K-Mo₂C/γ-Al₂O₃ with 1 – 3 wt% K loading to demonstrate the effect of K on catalytic performance. The 1 wt% K-Mo₂C/γ-Al₂O₃ has a slightly higher CO yield than 2 wt% K-Mo₂C/γ-Al₂O₃, but with increased methane production, which wastes valuable H₂ and requires a separation step before FT. Furthermore, as K loading increases, there is a drop in catalytic activity, likely from the blocking of active sites. This relationship between K loading and CO yield is not linearly dependant on temperature, as clearly shown by Fig. S4 and Table S1 for RWGS at 450 °C. At the higher temperature, the 3 wt% K-Mo₂C/γ-Al₂O₃ achieves 40.5% conversion and 98.2% CO selectivity, which outperforms the 2 wt% K-Mo₂C/γ-Al₂O₃ and industrial ZnO/γ-Al₂O₃ and ZnO/Cr₂O₃ catalysts.^[16] A comparison of the current catalyst with other relevant catalysts is also included in Table 1 and the SI to demonstrate the high selectivity of K-Mo₂C/γ-Al₂O₃. Further reactor and spectroscopic studies are required to fully understand the effect of K loading on K-Mo₂C/γ-Al₂O₃ for RWGS at different temperatures.

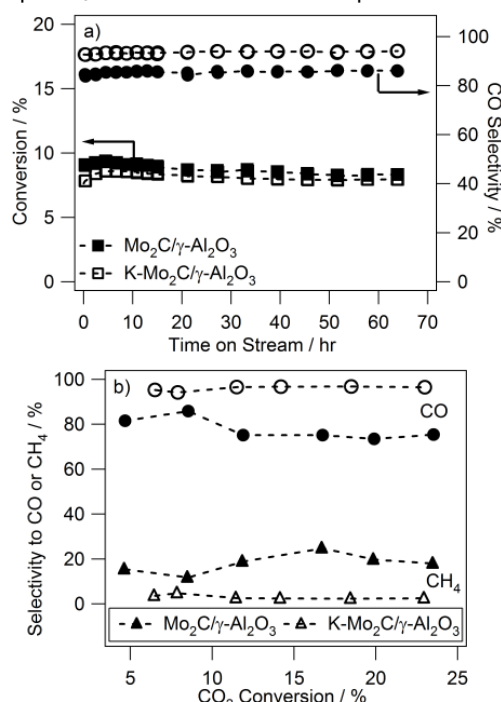


Figure 3. Performance of Mo₂C/γ-Al₂O₃ (solid symbols) and 2 wt% K-Mo₂C/γ-Al₂O₃ (hollow symbols) during RWGS. (a) Conversion (■/□) and selectivity to CO (●/○) versus time on stream, and (b) CO (●/○) and CH₄ (▲/△) selectivity versus conversion. Experiments in (a) conducted at a GHSV of 0.0021 L g⁻¹ s⁻¹ and range from 0.00084 to 0.0042 L g⁻¹ s⁻¹ in (b). All reactor studies are under a 3:1 H₂:CO₂ reactant ratio at 300 °C and 2.1 MPa.

Uncarburized Mo/γ-Al₂O₃ and 2 wt% K-Mo/γ-Al₂O₃ catalysts are also included in Table 1 to clarify the role of the metallic Mo identified in K-Mo₂C/γ-Al₂O₃ in the XRD measurements in Fig. 1. The Mo/γ-Al₂O₃ and K-Mo/γ-Al₂O₃ control catalysts are reduced *ex situ* in pure H₂ at 600 °C prior to reaction to form metallic Mo. The pre-reduction step ensures the high activity and CO selectivity of the Mo₂C-based catalysts originate from the Mo carbide phase, and not metallic Mo. Clearly, as seen in Table 1, the Mo carbides, synthesized with CH₄, are more active than the corresponding uncarburized catalysts, indicating that the carburization step is necessary for high catalytic activity and that the metallic Mo phase in K-Mo₂C/γ-Al₂O₃ is not solely responsible for the high performance.

Table 1. Summary of catalyst performance data for RWGS experiments at 300 °C, 2.1 MPa and 3:1 H₂:CO₂ ratio at GHSV of 0.00084 L g⁻¹ s⁻¹. Deactivation percentage calculated for experiments at higher GHSV of 0.0021 L g⁻¹ s⁻¹, shown in Fig. 3a. RWGS catalysts from literature are also included as a basis of comparison with the current K-Mo₂C/γ-Al₂O₃ catalyst.

Catalyst	Conversion / %	Carbon Based Selectivity / %			CO Yield / %	Deactivation / %
		CO	CH ₄	C ₂ -C ₄		
Mo ₂ C / γ-Al ₂ O ₃	19.9	73.5	19.7	6.8	14.6	11.7
1%K-Mo ₂ C / γ-Al ₂ O ₃	24.3	81.0	12.4	6.6	19.7	N/A
2%K-Mo ₂ C / γ-Al ₂ O ₃	18.1	95.9	2.7	1.4	17.3	7.3
3%K-Mo ₂ C / γ-Al ₂ O ₃	7.5	98.5	1.5	0	7.4	N/A
Mo / γ-Al ₂ O ₃	7.1	82.5	15.3	2.2	5.9	N/A
2%K-Mo / γ-Al ₂ O ₃	6.5	96.9	3.1	0	6.3	N/A
Mo ₂ C / 250 °C ^[29]	17	34	N/A	N/A	5.8	N/A
Cu-Mo ₂ C / 250 °C ^[29]	13	40	N/A	N/A	5.2	N/A
Pd/Al ₂ O ₃ / 260 °C ^[33]	N/A	78	N/A	N/A	N/A	N/A
Mo/γ-Al ₂ O ₃ / 600 °C ^[34]	34.2	97	N/A	N/A	32.1	N/A

The difference in CO yield between Mo₂C/γ-Al₂O₃ and K-Mo₂C/γ-Al₂O₃ is further explained by measuring the apparent activation barrier for CO formation under RWGS conditions at 5 different temperatures between 270 and 330 °C. For activation barrier measurements, the GHSV is adjusted to operate at lower conversions to ensure measurements are within the reaction limited region. As seen calculated in Fig. 4, 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. The lower activation barrier for K-Mo₂C/γ-Al₂O₃ confirms the addition of 2 wt% K facilitates CO formation through a decrease of the apparent activation barrier.

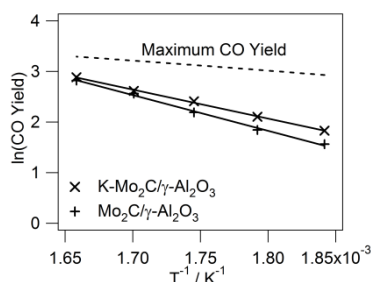


Figure 4. Activation barrier plots represented as $\ln(\text{CO yield})$ versus $1/T$ for (+) $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ and (x) 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$. The values of CO yield are calculated by averaging data points between 15 – 17 h on stream. The dashed line, representing maximum thermodynamic CO yield, is included as a reference.

To further elucidate the effect of K on catalyst activity and selectivity, XPS measurements of the Mo_2C -based catalysts are found in Fig. 5. Fig. 5a contains the spectra of both the as-prepared (fresh) and after reaction (spent) Mo_2C -based catalysts. As evidenced by the figure, there is a shift towards lower binding energies for both catalysts after reaction. On 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$, there is an additional large peak at 227.6 eV after reaction. From the deconvoluted XPS fits in Fig. 5b, the peak is from the appearance of Mo^0 , likely metallic Mo, which is supported by the additional peaks seen on 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ in the XRD measurements in Fig. 1.

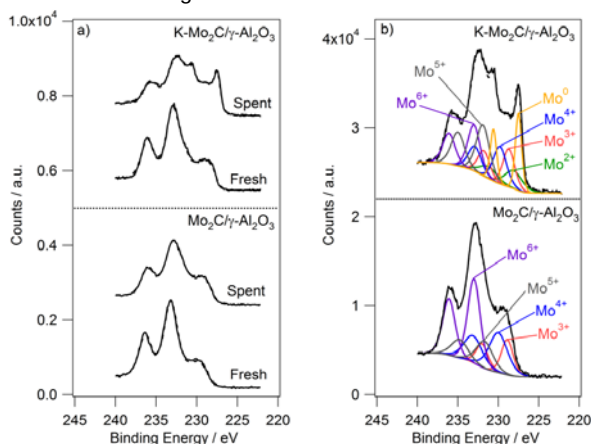


Figure 5. Mo3d spectra (solid line) of (a) $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ and 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ before and after RWGS reaction with fits (dashed line) and (b) deconvoluted Mo3d spectra of spent $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ and $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$. Contributions include Mo^{6+} , Mo^5 , Mo^{4+} and Mo^{3+} for both samples, while spent $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ also includes Mo^{2+} and Mo^0 .

The quantitative composition of each catalyst from the deconvoluted XPS spectra before and after reaction can be found in Table 2. Each deconvoluted spectra is fit with the following values obtained from a report by Oshikawa et al, Mo^0 : 227.6 eV, Mo^{2+} : 228.2 eV, Mo^{3+} : 228.8 eV, Mo^{4+} : 229.9 eV, Mo^{5+} : 231.8 eV and Mo^{6+} : 233.1 eV.^[35] Clearly, as seen in Table 2, the $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ sample is further reduced than $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ after reaction. The facile reduction of $\text{K-Mo}_2\text{C}$ leads to the decrease of MoO_3 (Mo^{6+}) and MoO_2 (Mo^{4+}) phases and formation of larger amounts of Mo_2C (Mo^{2+}) and O- Mo_2C (oxy-

carbides), represented by Mo^{3+} and Mo^{5+} on the catalyst surface. It is also clear from the XPS measurements that metallic Mo is present in $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$, but it alone is not the catalytically active phase. From XRD measurements in Fig. 1, 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ exclusively contains metallic Mo and $\gamma\text{-Al}_2\text{O}_3$ features, but as seen in Table 1, the catalyst is one-third as active as 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ under the same reaction conditions.

Table 2. Composition of deconvoluted spectra for $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ and 2 wt% $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ before and after RWGS reaction indicated in Table 1 with 3:1 H_2/CO_2 ratio at 300 °C and 2.1 MPa.

Catalyst	Condition	Mo Composition					
		Mo^0	Mo^{2+}	Mo^{3+}	Mo^{4+}	Mo^{5+}	Mo^{6+}
$\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$	Fresh	0	0	2.4	32.3	2.3	63.1
	Spent	0	0.2	15.7	27.6	16.8	39.8
$\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$	Fresh	0	12.7	6.5	20.6	11.3	48.8
	Spent	16.3	10.7	15.0	16.4	22.5	19.1

Although the XPS results in Fig. 5 show both Mo_2C and Mo-oxides, the exact nature of the active phase is difficult to confirm because the XPS measurements in this study are *ex situ*. During transfer of the catalyst samples from the reactor into the XPS, there is likely some degree of catalyst oxidation. As shown in Table 2, there is a much larger amount of Mo^{2+} and other reduced phases in $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ relative to $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$, which suggest reduced Mo phases and oxy-carbides may be critical for high catalyst stability and selectivity towards CO. To fully reveal the nature of the active phase, further *in situ* studies are required over $\text{K-Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$.

To better understand the reaction mechanism of CO_2 dissociation and the electronic effects of K addition on Mo_2C -based catalysts, DFT calculations were performed on pristine and K-promoted $\beta\text{-Mo}_2\text{C}(001)$ surfaces. The DFT results indicate that CO_2 chemisorption and activation are thermodynamically feasible on the Mo-terminated $\beta\text{-Mo}_2\text{C}(001)$ surface (CO_2 activates on hollow position, and can further dissociate), as shown in Fig. 6, whereas, it does not chemisorb on the C-terminated surface (not shown). 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. By directly comparing the BE of CO_2 on pristine and K-promoted surfaces, it becomes clear that the presence of K enhances the binding energies of both the physisorbed (from -0.5 to -6.5 kcal mol⁻¹) and chemisorbed states (from -31.4 to -46.4 kcal mol⁻¹ for activated CO_2 and from -74.8 to -80.9 kcal mol⁻¹ for dissociated CO_2 , respectively, as shown in the intermediate states of Fig. 6 and Fig. S6 in the SI).

These adsorption energy changes in the presence of K are due to electronic effects. Bader charge analysis^[36-37] suggests that K (Bader charge = 0.82 e) loses almost one electron, which is transferred to the surface of Mo_2C . As a result, the presence of a positive point charge (K-cation) increases the dipole-dipole interaction during CO_2 physisorption, thus increasing the physisorption energy. Concurrently, the partially negatively charged Mo_2C surface facilitates the activation of CO_2 (by transforming the molecule from a linear to bent configuration),

and the adsorption of electrophilic species, such as atomic oxygen.^[38] The presence of K also affects the CO₂ dissociation kinetics through reduction of the barrier for CO₂ dissociation, as shown in Fig. 6 (CI-NEB calculations appear in the SI).

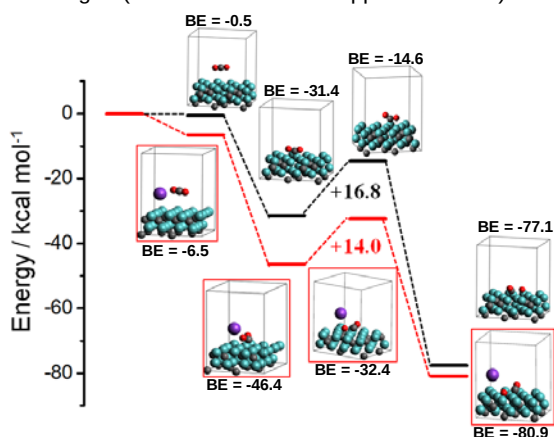


Figure 6. CO₂ dissociation profile on Mo-terminated, pristine (black) and K-promoted (red), β -Mo₂C(001) surfaces (energy in kcal mol⁻¹). Color code: grey-C, cyan-Mo, red-O, purple-K.

For the surface without K (black profile), CO₂ is first activated without a barrier (BE = -31.4 kcal mol⁻¹), and then dissociates to CO and O, with a barrier of 16.8 kcal mol⁻¹. On the K-promoted, Mo-terminated surface (red profile), CO₂ is first barrierlessly activated to a chemisorbed state (BE = -46.4 kcal mol⁻¹), and then dissociates to CO and O with a barrier of 14.0 kcal mol⁻¹, 2.8 kcal mol⁻¹ lower than that of the pristine β -Mo₂C(001) surface. In both cases, all of the steps are exothermic with respect to the initial, CO₂ physisorbed state. By considering the decrease in activation energy for CO₂ dissociation with the increase in CO₂ physisorption energy on the K-promoted, Mo-terminated β -Mo₂C(001) surface in Fig. 6, it is apparent that K promotion 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 (E_a) calculated by DFT and experimentally determined apparent activation barrier (E_{a,app}) for CO formation from CO₂ over pristine and K-promoted Mo₂C-based catalysts.

	Theoretical E _a / kcal mol ⁻¹	Experimental E _{a,app} / kcal mol ⁻¹
Pristine (No K) Mo₂C	16.8	14.0
K-Promoted Mo₂C	14.0	11.4

In addition to the lower activation barrier for CO₂ dissociation over K-promoted β -Mo₂C(001), the higher CO selectivity and lower CO uptake of K-Mo₂C/ γ -Al₂O₃ (1.7 μ mol g⁻¹) relative to Mo₂C/ γ -Al₂O₃ (21.4 μ mol g⁻¹) might indicate that addition of K decreases the CO binding energy, allowing CO to desorb before it is further hydrogenated into CH₄ or other hydrocarbons. However, DFT studies in the literature report that the addition of K to Mo₂C increases the binding energy and dissociation of CO.^[31, 39] Previous surface science experiments using high resolution electron energy loss spectroscopy (HREELS) and

temperature programmed desorption (TPD) also confirmed that the presence of K on Mo₂C surface increases the CO binding energy thereby promoting its dissociation.^[40]

Interestingly, our DFT calculations reveal that the desorption energy of CO from the surface with coadsorbed O* from CO₂ dissociation (see final state in Fig. 6), seems to be less sensitive to the presence of K. The desorption energy of CO is almost isoenergetic for the K-promoted and pure Mo₂C(100) surfaces (51.2 and 51.0 kcal mol⁻¹, respectively). As a result, the higher selectivity towards CO formation in the presence of K can be attributed to electronic effects (surface charging) causing enhancement in CO₂ adsorption (both physisorption and chemisorption) and reduction of the CO₂ dissociation barriers. Furthermore, it should be noted that the CO₂ dissociation step forms an oxy-carbide, as indicated by the high exothermicity of the last reaction step in Fig. 6. These findings agree with the XPS data in Fig. 5 and a previous study of Mo₂C for RWGS, which uses *in situ* X-ray absorption near edge spectroscopy (XANES) and ambient pressure-XPS to show that the active phase of Mo₂C is an oxy-carbide under reaction conditions.^[24, 41] Furthermore, the lack of CH₄ and other hydrogenated products over K-Mo₂C/ γ -Al₂O₃ is likely a result of less molecular hydrogen available on the K-promoted surface.

Conclusions

By modifying Mo₂C/ γ -Al₂O₃ with a K promoter, the CO selectivity and yield increase significantly, and can approach the maximum thermodynamic yield for RWGS under the appropriate reaction conditions. Addition of K also improves the catalyst stability, with only 7.3% deactivation after 68 h on stream. Catalyst characterization by SEM with EDS clearly shows that K is preferably found in Mo-rich regions, while Mo is more evenly distributed in Mo₂C/ γ -Al₂O₃. Furthermore, K-Mo₂C/ γ -Al₂O₃ maintains the Mo in a reduced and active state as evidenced by XPS measurements. These experimental results are supported by DFT calculations, which show enhanced CO₂ adsorption and reduced CO₂ dissociation barriers on the K-promoted, compared to the pristine, Mo-terminated β -Mo₂C(001) surfaces. Notably, the DFT calculations predict a 2.8 kcal mol⁻¹ lower activation barrier for CO formation upon K addition, which is in excellent agreement with the experimentally measured difference of 2.6 kcal mol⁻¹. The findings of this paper show that K-Mo₂C/ γ -Al₂O₃ is a highly selective catalyst for producing CO from CO₂ and has the potential to be used as a commercial RWGS catalyst for the first step of synthesizing jet fuel from seawater for the U.S. Navy. Future studies will focus on large-scale reactions and *in situ* measurements to better understand and characterize the catalytically active phase of K-Mo₂C/ γ -Al₂O₃.

Experimental Section

Catalyst Preparation. Potassium-promoted molybdenum carbide, supported on gamma alumina (K-Mo₂C/ γ -Al₂O₃) was synthesized by co-impregnation of KNO₃ and (NH₄)₆Mo₇O₂₄·4H₂O precursors onto a γ -

Al₂O₃ support by the evaporation-deposition method. All chemicals were purchased from Sigma-Aldrich. In brief, the precursors were dissolved in deionized water at the concentrations required to obtain molar ratios of 1/4/15 K/Mo/γ-Al₂O₃, which translated to 2 wt% potassium (K) and 20 wt% Mo loading on the γ-Al₂O₃ support. For studies with other potassium loadings, the amount of K precursor was adjusted to yield 1 – 5 wt% K. Aqueous solutions of the metal precursors were added to a beaker of γ-Al₂O₃ and dried overnight under stirring at 60 °C, then calcined in air overnight at 350 °C.

The K-Mo/γ-Al₂O₃ catalyst was then carburized in a 21% CH₄ in H₂ mixture at 600 °C for 2.5 h to form the K-Mo₂C/γ-Al₂O₃ in a procedure adopted from Hou et al.^[42] After the first 1.5 h, the CH₄ was shut off and the carbide was cooled to room temperature in H₂. At room temperature, the catalyst was passivated in 1% O₂ in N₂ for several hours. The Mo₂C/γ-Al₂O₃ catalyst was prepared by the same method with 20% Mo loading, but without the inclusion of potassium. Metallic Mo-based catalysts were used as controls and synthesized through the same procedure as above, but without CH₄ during the carburization step.

Pulse CO Chemisorption. Pulse CO chemisorption was performed using an Autochem II Chemisorption Analyzer (Micrometrics) to compare the number of active sites in each catalyst. Approximately 200 mg of catalyst was added into a U-shaped quartz reactor and reduced in 10% H₂ in Ar at 300 °C for 2.5 h. The catalyst was cooled to room temperature in He before pulsing 10% CO in He. A thermal conductivity detector was used to analyze the amount of CO adsorbed by each catalyst, which provides a means compare the number of active sites.

X-Ray Diffraction (XRD). X-ray diffraction (XRD) measurements of the reduced catalysts were performed on a Bruker D8 Advance diffractometer using Cu Kα radiation, operated at 40 kV and 40 mA over the range of 2θ = 20–80° with a 0.02° step size and 4 sec per step at room temperature.

Scanning Electron Microscopy (SEM). Scanning electron microscopy (SEM) measurements of the reduced catalysts were performed with a Carl Zeiss Supra 55 Schottky thermal field emitting microscope with a 30 μm aperture at 5–15 kV accelerating voltage. For EDS measurements, an Oxford Instruments X-Max, 80 mm silicon drift detector, at an accelerating voltage of 5 kV and working distance of 8.5 mm was inserted into the SEM chamber. The detector was calibrated with a copper standard. Data was collected on 2048 channels for 500,000 counts using a process time setting of 4 with pulse pile up correction. The quantitative analysis was unnormalized using the supplied 5 kV quantitative standard database.

Reactor Studies. To measure catalyst performance shown in Table 1, 500 mg of catalyst was loaded into a 0.25 in stainless steel reactor and reduced under 50 sccm H₂ for 2.5 h at 300 °C and 0.5 MPa. After reduction, the reactor was isolated and the bypass pressurized to 2.1 MPa with 6.3 sccm CO₂, 18.9 sccm H₂ and 5.0 sccm N₂, for a GHSV of 0.00084 L g⁻¹ s⁻¹ and H₂:CO₂ ratio of 3:1. At 2.1 MPa, concentration of the reactants in the bypass was recorded as a baseline and gases were flowed into the reactor. Reactions were run for 22 h at 300 °C and concentrations of reactants and products were analyzed by online gas chromatography equipped with a flame ionization detector (FID) and 2 thermal conductivity detectors (TCD). The concentration of each gas-phase species was calibrated by correlating the peak area of the pure compound to its concentration in a calibration gas standard.

For calculating apparent activation energies, the conversion of CO₂ was measured at 5 different temperatures from 270 °C to 330 °C, while adjusting the GHSV to maintain conversion well below the equilibrium for RWGS. For selectivity versus conversion and stability experiments, GHSV was also adjusted by varying catalyst mass and reactant flow rates to maintain GHSV between 0.00084 and 0.0042 L g⁻¹ s⁻¹.

X-Ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) measurements were performed over the fresh and spent catalysts using a commercial XPS system (Thermo

Scientific Ka) equipped with a monochromatic Al Kα source and a 180° double focusing hemispherical analyzer with 128-channel detector. The nominal XPS spot size and analyzer field of view were 400 μm². Settings for data collection were: Pass Energy = 20 eV, dwell time = 100 msec, energy step size = 0.1 eV over 35 averaged scans. Charge compensation was necessary. Calibration of the instrument was confirmed with the Cu2p_{3/2} peak of a Cu plate at 933 eV.

Density Functional Theory (DFT) Calculations. DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP).^[43] Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional^[44–45] was employed within the generalized gradient approximation (GGA) using the plane-wave projector augmented wave (PAW) pseudo-potentials.^[46] The slab model of the β-Mo₂C(001) surface had interchanging layers of C and Mo atoms, and therefore both C-terminated and Mo-terminated surfaces were inspected. The slab model of the β-Mo₂C(001) surface (both terminations) contained 4 layers, with a total of 16 C and 32 Mo atoms in one unit cell (using a 2x2 supercell with size 10.50×12.15×14.55 Å, with a vacuum space of 10 Å). For K-promoted β-Mo₂C(001), one K atom was placed on the top layer. The kinetic energy cutoff was set to 415 eV,^[26] the convergence criteria to 10⁻⁵ eV for the total electronic energy and 0.01 eV Å⁻¹ for the forces acting on atoms and the k-point mesh was 5×5×1 k-point grid, generated by Monkhorst-Pack scheme.^[47] The Climbing Image-Nudged Elastic Band (CI-NEB) method^[48] has been employed to locate transition states in the CO₂ dissociation pathway. During geometry optimization, the top two layers as well as the CO₂ molecules were fully relaxed, while the bottom two layers were fixed in their bulk positions. Vibrational frequencies on the adsorbates were performed to verify local minima (absence of imaginary mode) and transition states (presence of 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 in CO₂ adsorption. The binding energies of different CO₂ adsorption configurations are given in the Supporting Information (SI). The binding energy (BE) is calculated as: BE (adsorbate) = E(surface + adsorbate) – E(surface) – E(adsorbate), where E(surface + adsorbate) is the total electronic energy of the surface with the adsorbed CO₂, E(surface) is the corresponding energy of the clean surface (without any adsorbate), and E(adsorbate) is that of the CO₂ molecule.

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Keywords: molybdenum carbide • CO₂ conversion • heterogeneous catalysis • reverse water-gas shift • potassium promoter

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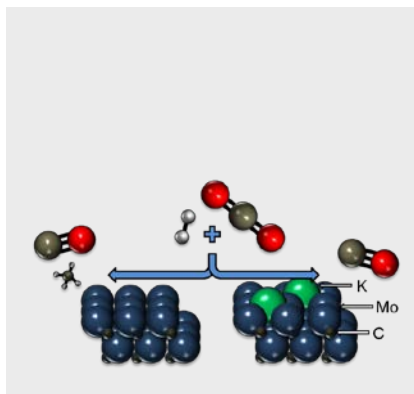
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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Modifying a molybdenum carbide catalyst supported on gamma-alumina with potassium (K) improves selectivity towards CO and catalyst stability during reverse water-gas shift. Over a broad conversion range, the selectivity to CO is maintained near 95%.



Marc D. Porosoff, Jeffrey W. Baldwin, Xi Peng, Giannis Mpourmpakis and Heather D. Willauer*

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Potassium-promoted molybdenum carbide as a highly active and selective catalyst for CO₂ conversion to CO