

CO₂ conversion through Reverse Water Gas
Shift over Molybdenum and Tungsten
Carbides: Catalytic Performance Evaluation

by

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Author's declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Mitigating climate change requires reducing CO₂ emissions and conserving energy, but current CO₂ capture and storage methods are complex and costly. An alternative is the thermocatalytic hydrogenation of CO₂ using the Reverse Water–Gas Shift (RWGS) reaction to produce value-added chemicals. Transition metal carbides (TMCs) offer significant potential in this area. This research aims to assess the catalytic performance of Molybdenum carbide (Mo₂C) and Tungsten Carbide (WC) to enhance CO₂ conversion and CO selectivity in the RWGS reaction. Using the Temperature Programmed Reduction (TPR) method (15% CH₄/H₂, 600 °C), Mo₂C, WC, and five mixed carbides (MoW_xC with x=0.25, 0.5, 0.75, 1, and 1.5) were synthesized and compared. The catalyst with the highest selectivity and good conversion was chosen to optimize the RWGS reaction.

The performance of TMCs was assessed in terms of both conversion and selectivity by varying four parameters such as Temperature (500 °C – 350 °C), Pressure (1 to 9 bar), GHSV (20,000 to 400,000 ml/(g h) , H₂:CO₂ Feed Ratio (1:1 to 5:1). To evaluate the catalyst resilience, stability tests have been also performed. Moreover, the structure of pre and post reaction catalyst has been investigated. The resulting reaction products were monitored using an in-line Infrared Analyzer to identify the concentration of CO, CH₄, and CO₂.

The results indicated that at 500 °C, CO₂ conversions approaching equilibrium for most carbide samples, categorized into three main groups. Absence of W (Mo₂C) resulted in higher conversion but lower selectivity (Group 1). Higher W concentrations in MoW_{1.5}C and WC led to higher selectivity but lower CO₂ conversion (Group 3). In Group 2, MoW_xC

($x=0.25, 0.5, 0.75$, and 1) showed better conversion and selectivity, with $\text{MoW}_{0.25}\text{C}$ and $\text{MoW}_{0.5}\text{C}$ exhibiting higher CO_2 conversion and CO selectivity than $\text{MoW}_{0.75}\text{C}$ and MoWC . WC was chosen for its high CO selectivity and good CO_2 conversion for optimizing the RWGS reaction. Under optimized conditions ($500\text{ }^\circ\text{C}$, $\text{GHSV} = 20,000\text{ ml}/(\text{g h})$, $\text{Feed Ratio} = 5:1$, atmospheric pressure), WC showed 100% selectivity and 33% conversion, maintaining stability for 100 hours with full CO selectivity and stable CO_2 conversion. Increasing the feed ratio for WC increased conversion with full CO selectivity, while for Mo_2C , more hydrogen led to more methane formation.

This study serves as a foundation for the optimization of Mo_2C and WC , aiming to convert the global challenge of CO_2 into an opportunity by producing renewable value-added chemicals and feedstock.

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List of Abbreviations

BET	Brunauer–Emmett–Teller
CB	carbon balance
CCS	carbon capture and storage
CCU	carbon capture and utilization
FTIR	Fourier transform infrared spectroscopy
GHSV	greenhouse gas
GHSV	gas hourly space velocity
IR	infrared
RWGS	reverse water gas shift
SSA	specific surface area
TGA	thermo-gravimetric analysis
TOF	turnover frequency, s ⁻¹
TPD	temperature programmed desorption
TPR	temperature programmed reduction
XRD	X-ray diffraction

Nomenclature

A	pre-exponential factor, mol/(s kg)
D	dispersion of catalyst
$d(SSA)$	SSA-based particle size, nm
$d(XRD)$	XRD-based particle size, nm
E_a	activation energy, kJ/mol
$E_{a,des}$	activation energy of desorption, kJ/mol
$E_{a,rxn}$	activation energy of reaction, kJ/mol
F_i	input flow rate (i stands for either CO ₂ , CO, or CH ₄), mol/s
f_1	CO ₂ conversion to CO
f_2	CO ₂ conversion to CH ₄
ΔH_{298}°	reaction enthalpy, kJ/mol
K	Scherrer equation shape factor
N_a	Avogadro's number
P	pressure, bar
R_g	gas constant, J/(K mol)
R	CO ₂ conversion rate, mmol/(g s)
R_{max}	maximum CO ₂ conversion rate, mmol/(g s)
R_{CO}	CO generation rate, mol/(s kg)
S_{CO}	CO selectivity
T	temperature, °C (K in Arrhenius equation)
T_{max}	peak temperature from TPD, °C
W_c	catalyst weight, kg
X_{CO_2}	CO ₂ conversion
x	weight fraction, wt%
y_i	mole fraction (i stands for either CO ₂ , CO, or CH ₄)

Greek letters

α	H ₂ :CO ₂ ratio in the feed
θ	diffraction angle, °
λ	X-ray wavelength, nm
ρ_i	material <i>i</i> density, g/cm ³
ρ_p	particle density, g/cm ³
ρ_p	bed density, g/cm ²
ν_1	frequency factor, s ⁻¹

Chapter 1: Background

1.1 CO₂ and global emission

The severity of the effects of climate change on the entire planet makes it a phenomenon that is becoming increasingly problematic. The primary cause of this issue is greenhouse gases (GHGs), which trap heat and raise Earth's temperature. CO₂ is one of the greenhouse gases that contributes significantly to the emissions of greenhouse gases worldwide. Fossil energy has been the undisputed leader in the world's primary energy consumption since the Industrial Revolution, making up 82% of total energy consumption in 2022. Technology is a "double-edged sword" that has greatly aided in human society's development, but it has also been connected to serious and enduring environmental issues such as the lack of primary energy, smog, acid rain, the greenhouse effect, and others[1]. Specifically, the atmospheric CO₂ concentration is approximately 420 parts per million, marking a new peak in less than 4 million years. **Figure 1** describes how the concentration of CO₂ has relatively increased compared to the past two decades. This rising amount of CO₂ in the atmosphere poses many health hazards by reducing the air quality index. If CO₂ emissions continue to rise at the current rate (**Figure 2**), global temperature can exceed 1.5 °C by 2040 which will lead to increased human death, water scarcity and ecosystem disruption.[2]

Therefore, collecting, using, and storing CO₂ (CCUs) to lower atmospheric CO₂ concentration and searching for cleaner energy to improve the global energy structure are practical ways to address the current problems. Therefore, it is critical to find the primary causes of the issue and develop solutions to make sure that the climate change problem may be resolved.

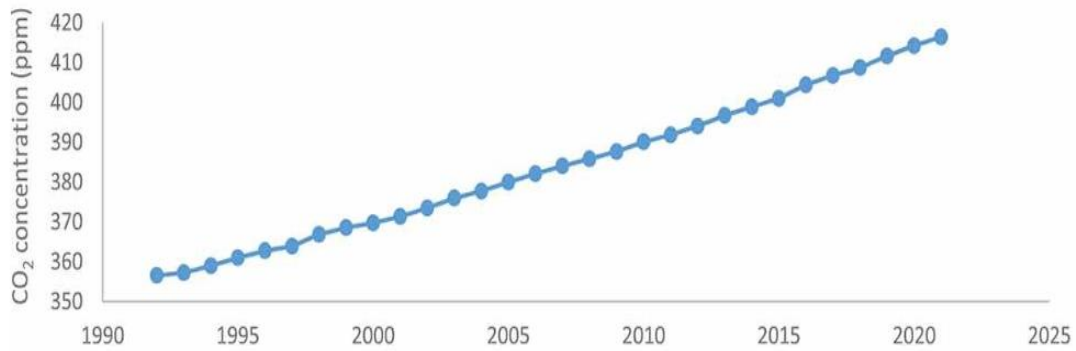


Figure 1. CO₂ concentration increment in the atmosphere since 1992 till 2021 [3]

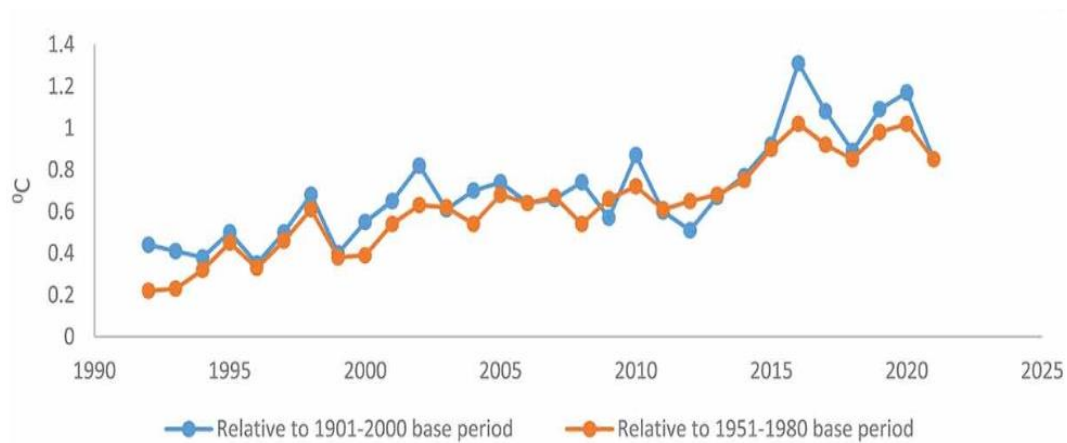


Figure 2. Changes between 1992–2021 in: global temperature anomalies relative to the 1901–2000 and 1951–1980 base periods. [3]

The trends in emissions for the top five emitters from 1995 to 2019 are displayed in Figure 3. Although Ontario is the second-highest emitting province with 39% of the population, its GHG emissions have been declining since 2005 while Alberta's have been steadily rising. The only other province where emissions are trending increasing, albeit very slightly, is Saskatchewan[4].

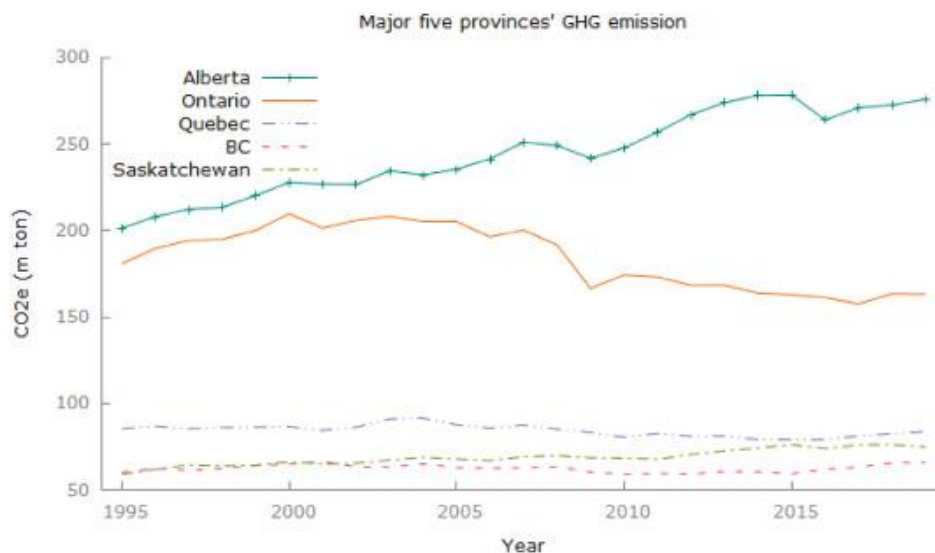


Figure 3. GHG emissions of top five emitter provinces in Canada [5]

A possible sustainable solution to tackle this problem is to close the carbon loop by converting CO₂ into valuable products, thereby reducing our dependence on fossil fuels. This transition towards sustainable alternatives will not only mitigate greenhouse gas emissions but also promote a more sustainable and environmentally friendly energy system.

1.2 Reaction pathways for CO₂

Reaction pathways for CO₂ encompass a diverse array of processes aimed at mitigating its environmental impact. These pathways involve converting CO₂ into useful products or benign compounds through chemical, thermocatalytic or electrochemical means[5]. One approach involves utilizing catalysts to facilitate the conversion of CO₂ into valuable chemicals like methanol or formic acid. Thermocatalytic conversions for CO₂ utilize both heat and catalysts to drive chemical reactions, converting CO₂ into valuable products such as methane or syngas. Electrochemical pathways use renewable energy sources to drive the reduction of CO₂ into fuels or other value-added chemicals[6]. By leveraging these

pathways, CO₂ emissions can be mitigated while simultaneously producing useful fuels and chemicals, contributing to a more sustainable carbon cycle.

H₂ is used as a reactant in thermocatalytic conversion, which transforms CO₂ into chemicals and fuels. The commercial processes used to produce H₂ today, such as steam reforming natural gas, produce greenhouse gases. Nonetheless, the overall emissions for this process will go down if H₂ can be generated by electrolysis that is driven by renewable energy. Furthermore, it will be more sustainable if the CO₂ is extracted straight from the source of the emissions, creating an artificial carbon cycle.

Figure 4 shows three typical ways for conversion of CO₂ utilizing renewable hydrogen to form multiple valuable feedstock chemicals that can be combined in other processes[7]. First is the direct CO₂ Fischer Tropsch synthesis for light hydrocarbon production. Second is the production of methanol which can be directed in two ways either direct methanol synthesis or by Carbon Monoxide hydrogenation. The third pathway for CO₂ utilization is the thermocatalytic conversion of CO₂ using Reverse Water Gas Shift reaction (RWGS). RWGS consumes CO₂ and H₂ to produce syn gas.

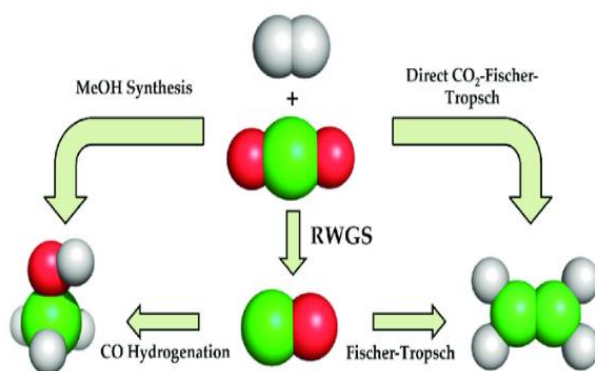


Figure 4. Simplified scheme about different CO₂ hydrogenation pathways [8]

Syngas is an important chemical because it can be used as a precursor for many different products, such as solvents and fuels. There are numerous potentials uses for syngas, including the Fischer-Tropsch process for turning it into gasoline and the methanol synthesis for turning it into acetic acid.

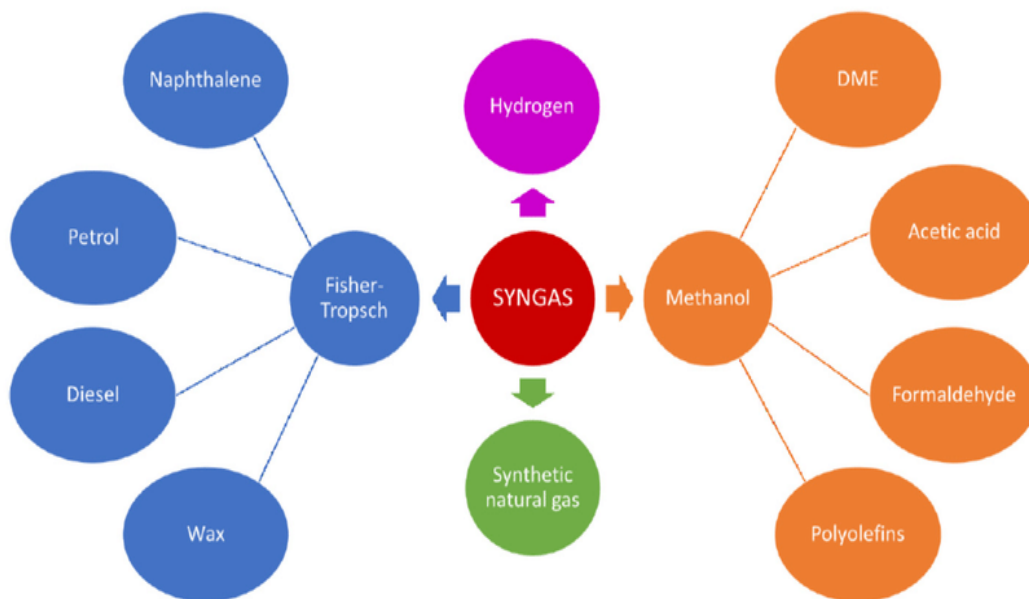
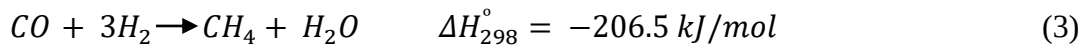
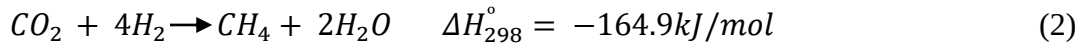
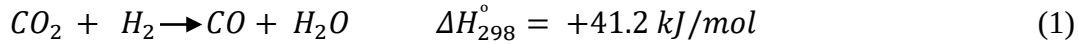


Figure 5. Application of Syngas [9]

The adaptability of syngas and its potential to enable sustainable manufacture of a variety of valuable goods (figure 9) are the driving forces behind the project's focus on the reverse water gas shift (RWGS) reaction[8]. The ability to convert CO₂ into syngas creates possibilities for the green synthesis of numerous important chemicals.

1.3 Reverse Water Gas Shift

The reverse water gas shift (RWGS) reaction plays a pivotal role in thermo-catalytic hydrogenation, as the resulting syngas mixture serves as a versatile feedstock for numerous other reactions. RWGS, being an endothermic process (Eq. (1)), is often coupled with the Sabatier reaction (Eq. (2)) and CO methanation (Eq. (3)), both contributing to CH₄ formation.



The main advantage of using RWGS is its product formation flexibility[9]. CO₂ can be easily reduced to CO under excess supply of H₂, provided proximate temperature and catalyst.

RWGS reaction is an endothermic and is operational at higher temperatures which may lead to catalyst degradation or deactivation[10]. Therefore, the need to synthesize a suitable catalyst that can convert CO₂ to CO in lower temperatures (< 600 °C) and reaction conditions for longer hours of use is a must. Also, there is a necessity to identify the proper

reaction conditions that can work for lower temperatures providing higher CO₂ conversion rates and aids the longevity of the catalyst.

1.4 Project Objectives

Main Goal:

The main goal of this thesis is to investigate the performance of Molybdenum carbide (Mo_2C) and Tungsten carbide (WC) catalyst over Reverse Water Gas Shift reaction. Moreover, different material characterization techniques have also been employed for the analysis of the structure and performance of the catalyst under different conditions. These examinations aim to provide detailed insights into the optimal use of the catalyst and to confirm the use of Tungsten Carbide as a potential RWGS catalyst. The precise objective of this project is:

1. To optimize the catalytic performance of Mo_2C and WC over RWGS reaction under various reaction conditions such as Temperature Ranges, Gas Hourly Space Velocity, H_2/CO_2 Feed Ratios and Pressure ranges (bar).
2. To understand the effect of W concentration in bimetallic TMC (MoW_xC ; $x = 0.25, 0.5, 0.75, 1, 1.5$) and precedingly to identify WC as a potential RWGS catalyst with full selectivity to CO .

1.5 Thesis Outline

Chapter 2 summarizes literature review for RWGS catalyst which includes noble metal, transition metal and activity of TMC towards CO₂ conversion and CO selectivity.

Chapter 3 identifies the catalyst used for this project, along with the synthesis method used for this project. Chapter 3 also illustrates the characterization method used in this project to evaluate all the catalysts. This includes a brief schematic and explanation of characterization techniques like X-Ray diffraction, Fourier Transform Infrared Analyzer and Temperature Programmed Desorption. Additionally, a detailed schematic of the flow system utilized for the reaction test is also provided.

Chapter 4 deals with the optimization of catalytic performance over RWGS. It explains the structure, composition, and strength of fresh and spent catalysts.

Chapter 5 briefly concludes the results presented and provides some overview on how this investigation can be further improvised.

Chapter 2: Literature review

2.1 Noble metal catalyst

The use of noble metals in the reverse water gas shift (RWGS) reaction has been extensively studied in the literature due to their catalytic activity in this process. Noble metals, i.e., platinum (Pt), palladium (Pd), ruthenium (Ru), silver (Ag), iridium (Ir), and gold (Au) are the most frequently used metal-based catalysts, which have shown outstanding performances in RWGS reactions with promising corrosion resistance and strong activity in H₂ dispersions [Liu et al., 2019, Su et al., 2017, Chen et al., 2022a][11-14]. The Ru and Rh have demonstrated excellent catalytic activities in CO₂ methanation via RWGS intermediates. The synthesis of CO depends on promoters, catalytic supports, and particle size/distribution [Su et al., 2017][13].

Research on Pt-based catalysts for the Reverse Water Gas Shift (RWGS) reaction aims to improve CO₂ conversion rates and CO selectivity. Zhao et al. (2021) achieved up to 45% CO₂ conversion at 450 °C with 32% CO selectivity using 5Pt/CeO₂-IMP-350 (4.8 wt% Pt loading, 21.7 wt% Pt dispersion)[15]. Liu et al. (2022b) found Pt-Re/SiO₂ catalysts synergistically improved RWGS reactions, and Liang et al. (2017) reported K@Pt/mullite with 7 times higher turnover frequency (TOF) than Pt/mullite at 340 °C[16, 17]. Xing et al. (2021) synthesized single atomic Pt on SrTiO₃ with 45% CO₂ conversion rate, 100% CO selectivity, and TOF of 0.643 s⁻¹ at 500 °C[18].

In investigating the performance of the Reverse Water Gas Shift (RWGS) reaction, the addition of Pd has garnered attention for its superior activity and selectivity. Yan et al., 2022 developed a novel nano-catalyst, CP-CoO_xVPd, which demonstrated a CO

production yield of approximately 3314 $\mu\text{mol g}^{-1}$ with a CO selectivity of 99% at 523 K in a $\text{CO}_2/\text{H}_2=1/3$ atmosphere[19]. Ma et al. (2020) examined Pd as single-atom catalysts (SACs) with a 5% loading, achieving >98% CO_2 conversion to CO and showing thermal stability up to 400 °C[20]. Szanyi et al. (2020) found that combining Pd/TiO₂ with fresh TiO₂ enhanced thermal stability and effective CO_2 conversion due to oxygen vacancies and a large active surface area[21]. Li et al. (2021) prepared Zr-based MOF catalysts, with Pd/PtNCs/UIO-66 exhibiting the highest CO_2 conversion (19.6%) and CO selectivity (72.3%) at 400 °C, 20 bar, and 3:1 CO_2/H_2 ratio[22]. Li et al., (2019) explored Cu/Pd/HyWO_(3-x) for photocatalytic RWGS, observing a significant rise in CO generation rate (up to 300%–500%)[23]. This metal anchoring approach presents an alternative surface modification for metal oxide (MO_x) nanomaterials in catalytic applications.

Significant advancements have been achieved in hydrogenation processes with Rh-based catalysts, particularly in the Reverse Water Gas Shift (RWGS) reaction, aiming for outstanding CO selectivity. Tang et al. (2019) investigated Rh as surface activated carbon (SAC) on TiO₂ under various operating conditions, revealing the transition of local coordination in single-atom catalysts and optimizing CO_2 conversions[24]. Mathew et al., (2021) explored various support materials, including MOFs, ZrO₂, Fe₂O₃, Al₂O₃, MgO, CeO₂, and zeolites, in combination with noble metal NPs for improved catalytic performance, achieving high CO selectivity[25]. Enhanced H_2 dissociation activity and CO_2 conversions close to equilibrium, with thermal stability surpassing 500 °C, were linked to distinct metal–metal oxide structures. Heyl et al. (2016) examined the impact of Ni-Rh/Al₂O₃ and K-Rh/Al₂O₃ catalyst dispersion on CO production performance at low temperatures (250–350 °C), demonstrating CO_2 adsorption onto K-support and conversion

to carbonate[26]. This led to the production of CO along with highly reactive formate species, facilitating a chain reaction intermediate for CO generation (**Figure 6**).

Gold nanoparticles (NPs) have shown remarkable efficacy in catalyzing CO oxidation and the water-gas shift reaction (WGSR) due to their exceptional hydrogenation capability. Chen et al., 2016 and Wang et al., 2013 utilized Au's dispersion attributes on Al_2O_3 and CeO_2 surfaces, respectively, achieving high CO selectivity of up to 99% [27, 28]. Rabee et al. (2023) found that Au/TiO_2 exhibited 10-fold higher catalytic activity than Au/ZrO_2 due to interfacial $\text{Au}-\text{Ov}-\text{Ti}^{3+}$ sites[29]. Zhao et al. (2018) developed a microporous MOF based on $\text{Au}@\text{Pd}$ core-shell encapsulation, yielding 18.2% CO_2 conversion and 96.1% CO selectivity at 400 °C with Pt addition[30]. Strategies like localized surface plasmon resonance (LSPR) and MoO_x phase deposition were employed to address issues (Su et al., 2017)[13].

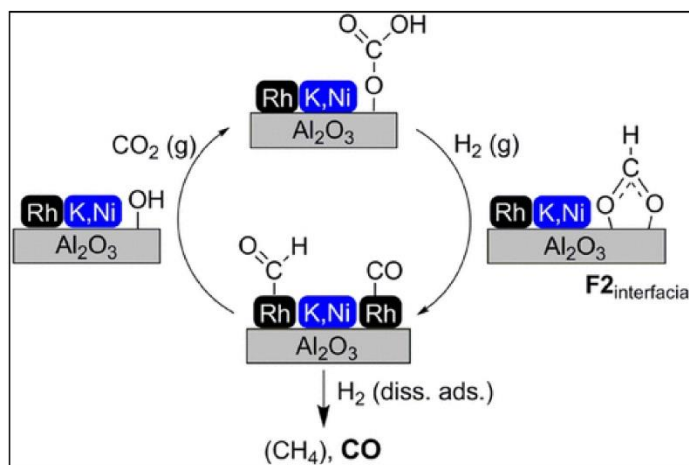


Figure 6. A formate-based mechanism over $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts (Heyl et al., 2016) [27]

Overall, the application of noble metal has delivered convincing results towards CO_2 hydrogenation to CO . The high cost and competing activity towards CO_2 methanation

make it challenging and restricting its use in industrial scale operations for higher CO₂ conversion to CO.

2.2 Transition Metal carbides

Molybdenum carbide (Mo₂C) and tungsten carbide (WC) are two examples of transition metal carbides that are highly valued catalysts for the RWGS process. TMC's seem to be a viable answer to the issues listed above, especially since Levy and Boudart discovered a noble metal-like behavior in transition metal carbides[31]. Several things make them appropriate for this approach. First off, because of their advantageous electrical structures and surface qualities, Mo₂C and WC have exceptional catalytic activity, effectively converting CO₂ and H₂ into carbon monoxide CO and H₂O. These carbides also have outstanding thermal stability, which allows them to endure the high temperatures seen in RWGS processes without suffering appreciable deterioration. Moreover, Mo₂C and WC provide sustained catalytic activity because they are resistant to classic catalyst deactivation mechanisms such carbon deposition and sintering (Qi Zhang et al., 2020)[32]. Furthermore, they exhibit remarkable selectivity in RWGS reactions, promoting CO production while reducing undesirable by products.

2.2.1 Molybdenum Carbide (Mo₂C)

The twin functions of Mo₂C for CO₂ scission and H₂ dissociation make it a particularly interesting material as reported by M.D. Porosoff et al., 2014[28]. Recent research has examined Mo₂C as a catalyst for the RWGS reaction (M.D. Porosoff et al., 2014, J Gao et al., 2016, B Yan et al., 2017) [28-30]. M.D. Porosoff et al., (2014) discovered that the Mo₂C catalyst, which was made by carburizing in C₂H₄ at 700 K, performed better in the RWGS reaction than Pt and Pd in terms of conversion and selectivity[33]. In a different study

Mo₂C nanowires produced by calcining the co-precipitate of ammonium heptamolydate and aniline yielded GHSV of 36,000 ml/ (g h) and CO₂ conversion of more than 60% at 873 K. At a molar ratio of H₂:CO₂ as 4:1, the catalyst exhibited 100% selectivity towards CO. The CO production selectivity, discussed by J Gao et al., (2016), was sustained for 20 hours at 873 K and a space velocity of 240,000 ml/(g h) and H₂:CO₂ molar ratio of 1, although conversion dropped to 28%[34].

Mo₂C catalyst demonstrated 58% CO₂ conversion with 62% CO selectivity at 450 vC, 20,000 ml/(g h) space velocity, and 3:1 H₂:CO₂ feed ratio (Kasala P. et al., 2019)[35]. According to Quingshan R. et al. (2023), carbonized molybdenum/CNTs exhibit a feed ratio of 1:2 CO₂:H₂ and a CO₂ conversion of about 40% at 500 °C and 36,000 ml/(g h) space velocity[36]. In 2024, Milad A. et al. published α -Mo₂C, which demonstrated equilibrium CO₂ conversion at 600 °C, 100,000 ml/ (g h) space velocity, and a molar ratio of 3 for H₂:CO₂. α -Mo₂C exhibits 100% selectivity towards CO and is stable for more than 500 hours when reacting on stream[37]

Although these latest findings are encouraging, more research is necessary to determine whether Mo₂C is a feasible catalyst for the RWGS reaction. More thorough research is specifically required to understand the Mo₂C-catalyzed RWGS reaction at high CO₂ conversion rates, as these reactions are more pertinent to industrial uses. The majority of current research focuses on lower temperature ranges where the CO₂ conversion stays below 30%, B Yan et al., 2017[38]. Furthermore, it is imperative to investigate the catalytic performance over a wider range of space velocities and assess the degree of catalyst deactivation at high temperatures and extended operation times.

2.2.2 Tungsten Carbide (WC)

When it comes to the catalytic characteristics of the TMC family, WC and Mo₂C are commonly contrasted. This is because similar activities have been discovered for deoxygenation (M.M. Sullivan et al., 2016) and hydrogenation (S. Ramanathan et al., 1995 and S.Y. Wu et al., 2012) [39-41]. Oxygen binding energy is a measure of activity, according to a recent assessment of the RWGS activity of different bulk TMC catalysts, with WC and Mo₂C showing the highest CO₂ conversions, M.D. Pososoff et al., 2015[42]. These patterns imply that WC can be tuned to work similarly to Mo₂C as an efficient low-temperature RWGS catalyst, M.D. Porosoff et al., 2017[43]. For the low-temperature RWGS reaction, unpromoted and alkali metal promoted WC supported on high surface area γ -Al₂O₃ (WC/ γ -Al₂O₃) are investigated as low-cost catalysts. Alkali metals improve CO selectivity, according to reactor experiments; the K promoter shows the largest increase in total CO production nearly 20.3% (James R. et al., 2020)[44]. In 2022, Mitchell J et. al., reported WC carburized at 1000 °C as an active catalyst for CO₂ hydrogenation at a GHSV of 27 000 mL h⁻¹ g⁻¹ with a 3 : 1 H₂ : CO₂ reactant ratio at 350 °C and 2.1 MPa yielding 13.9% conversion with 95.6% CO selectivity[45].

Table 1. Summarizes the CO₂ conversion and CO selectivity for Mo₂C and WC under varied reaction conditions

Catalyst composition (wt. %)	Material Synthesis	Temperature, pressure (°C, Bar)	H ₂ : CO ₂	GHSV ml/(g h)	CO ₂ Con. %	CO Sel. %	Reference
α-MoC_{1-x}	TPR	600, 1	4	36,000	60	100	J Gao et al., 2016
α-MoC_{1-x}	TPR	600, 1	1	240,000	28	99	J Gao et al., 2016
Mo₂C	Co-precipitation/ Carburization 600 °C	300, 20	3	3,636	19.9	73.5	M.D. Porosoff et al., 2017
Mo₂C	Direct Carburization/ TPR	450, 1	3	20,000	58	62	Kasala P. et al., 2019
Carbonized Mo/CNTs	TPR	500, 1	2	36,000	36	97	Quingshan R. et al. 2023
α-Mo₂C	Carburization /TPR	600, 1	3	100,000	60	100	Milad A. et al., 2024
Unpromoted WC	Co-precipitation/ Carburization 825 °C	300, 20	3	3636	8.8	89.9	James R. et al., 2020
Unpromoted WC	Co-precipitation/ Carburization 825 °C	350, 20	3	3,636	24.3	88	James R. et al., 2020
W_xC	Co-precipitation/ Carburization 600 °C	350, 21	3	27000	2.5	96.5	Mitchell J et. al., 2022

WC is potentially seen as a major catalyst for dry reforming of methane and has shown higher CO₂ conversion as reported in many literatures and not many have reported WC as a RWGS catalyst. Therefore, this study investigates the use of WC over RWGS reaction and how it can be compared to Mo₂C which serves as a traditional RWGS catalyst delivering higher CO₂ conversion and improved selectivity.

Table 1 provides a summary of Mo₂C and WC as reverse water gas shift catalyst under various reaction conditions such as Temperature, Pressure, Feed ratio and GHSV, underlining their capability to convert CO₂ and their affinity towards CO formation. The selected catalysts from the literature are chosen which closely resembles the preparation methodology used in this study to determine the best activity of the material under reaction conditions.

Furthermore, further research is necessary to fully understand the processes behind the RWGS reaction that Mo₂C facilitates. WC is potentially seen as a suitable catalyst for dry reforming of methane as recorded in many literatures. The full potential of WC as a RWGS catalyst is necessary and would provide new insights into enhancing CO formation, thereby increasing CO₂ conversion up to equilibrium.

Chapter 3: Methodology

3.1 Catalyst Synthesis

All carbides were prepared by the temperature programmed reduction (TPR) method[46]. Two grams of ammonium molybdate tetrahydrate and two grams of ammonium metatungstate hydrate, respectively, were dissolved in 20 to 25 ml of distilled water for two hours, or until the molybdenum/tungsten salt was completely dissolved, to create monometallic molybdenum carbide and tungsten carbide. After that, the resulting solution was put onto a petri dish and allowed to evaporate for 24 h at 55 °C. Before carburization, the resulting solid was crushed into a fine powder and dried at 100 °C for 18 h. Changes in the molar ratio of Mo:W were used to make bimetallic MoWC by varying the tungsten to molybdenum ratio. For example, the planned tungsten to molybdenum atomic ratios were 0.25, 0.5, 0.75, 1, and 1.5. To adhere to the same preparation technique as for the monometallic molybdenum carbide, all precursors were dissolved in the appropriate volume of distilled water. After that, each grounded sample was put into a tubular reactor made of stainless steel to undergo carburization. The reactor was purged with nitrogen at a rate of 100 ml/min for a minimum of 10 minutes in order to eliminate ambient oxygen before carburization. Subsequently, a 15% CH₄/H₂ flow rate of 100 ml/min was applied to all samples, and the temperature was increased by 5 °C/min to 40 °C for two hours, then to 600 °C (2 °C/min) and maintained there for four hours. Following carburization and reactor cooling to room temperature, the catalysts were passivated for an entire night at a flow rate of 25 ml/min of 0.4% O₂/N₂. The obtained black powder was stored in a vial until use.

3.2 Analytical Instruments

This section provides a brief explanation of each analytical technique utilized in the study, along with any related schematics and underlying principles. These techniques are employed to assess the shape, performance, and composition of the catalyst.

3.2.1 X-Ray Diffraction

The crystal structure and chemical components of the phases that are now present in XRD can be determined using X-ray diffraction (XRD), a nondestructive analytical technique. A radiation beam is diffracted as it travels through an atom's crystal phase. The pattern produced by the diffracted X-ray indicates the structural orientation of every atom in a particular molecule.

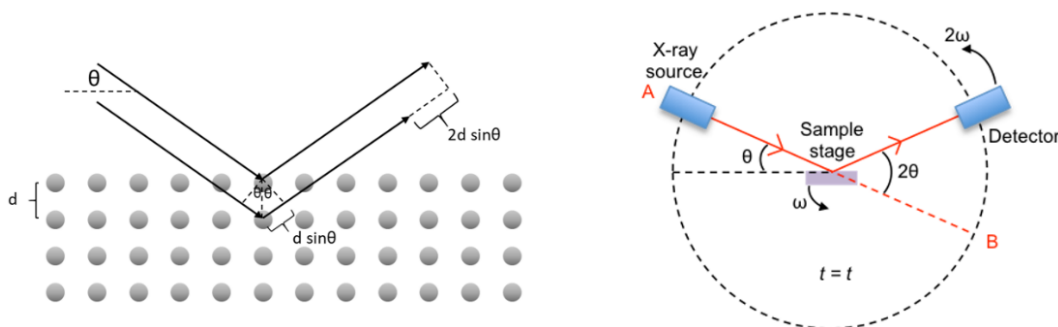


Figure 7 (left) Bragg's law, (right) schematic of a typical XRD measurement

XRD depends on the interplay of constructive and destructive interference of monochromatic X-rays as they pass through a crystalline sample. Monochromatic X-rays are produced and filtered to emit radiation of a single wavelength using a cathode ray tube. These X-rays are next focused and aimed at the sample. The detector and sample stage both move at a constant circular speed in order to always meet the 2θ angle required by Bragg's

law. When the criteria are met for Bragg's law ($2d\sin\theta = n\lambda$, with λ as the X-ray wavelength, n as a positive integer, d as the distance between planes, and θ as the grazing angle), the sample interacts with the incoming rays to create constructive interference (**Figure 7**). Examining the diffraction pattern captured on a photographic film enables the identification of the crystal's structure. When X-rays fulfill the requirements stated in the above equation, a superimposition can be seen in the reflection direction. This indicates that every crystal plane will exhibit unique peak positions and intensities, allowing for comparison with existing literature to determine the composition of the sample. Initially measuring the diffraction angle (θ) of a known crystal allows the calculation of the X-ray wavelength, thus identifying the element that produced the characteristic X-ray.

Rigaku MiniFlex II was used to obtain X-ray diffraction (XRD) patterns, which were then analyzed with Bruker EVA software. The size of the crystal grains was determined by utilizing the Scherrer equation in the Bruker EVA software, Eq (4).

$$D_{XRD} = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

3.2.2 Brunauer Emmett Teller (BET) Specific Surface Area (SSA)

The surface area of a catalyst is a critical factor in determining its performance, making accurate measurement essential. The Brunauer-Emmett-Teller (BET) method is commonly used for this purpose. It measures the adsorption isotherms, which plot the amount of gas adsorbed on the solid against the equilibrium pressure. This method relies on the adsorption of non-reactive gas molecules to form a monolayer coverage on the catalyst's surface[47].

The BET model, described by **Equation 5**, involves several important parameters: p (the equilibrium pressure), p_0 (the saturated vapor pressure of the adsorbate at the specified temperature), V_m (the volume of gas needed to form a monolayer on the surface), V (the quantity of gas adsorbed at pressure p), and C (a constant related to the enthalpy of adsorption)[48].

A plot of $p/V(p_0-p)$ against p/p_0 can be created by obtaining a set of p and V values, and this will produce a linear relationship. This line's slope and intercept both equal $(C-1) / CV_m$ and $1 / CV_m$, respectively, making it possible to calculate V_m and the constant C . The specific surface area can be computed by applying **Equation 6**, which deals with surface area. The formula includes the following variables: V (molar volume of the adsorbed species), a (quality of the adsorbent material), s (adsorption cross-sectional area of the adsorbed species), and N_A (Avogadro constant)[48].

$$\frac{p}{V(p_0-p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{p}{p_0} \quad (5)$$

$$S_{BET} = \frac{(V_m N_A s)}{V} \quad (6)$$

Liquid nitrogen is used to lower the temperature because the adsorption isotherms are measured at lower temperatures to avoid any chemical adsorption on the catalyst surface. To remove a volatile substance, a standard BET operation involves heating the sample to 300 °C while an inert gas is present. After removing the volatile materials, liquid nitrogen is used to cool the sample to a temperature of about -190 °C. The samples undergo N_2 flow during this step, where they are exposed to varying pressures. By adjusting the amount of gas adsorbed on the catalyst's surface, the variable pressure is produced. The resulting isotherm is then plotted using **Eq (6)**. SSA was determined AMI-300Lite, Altamira Instruments using 10% N_2/He as adsorbing gas.

3.2.3 Thermogravimetric analysis (TGA)

One helpful analytical technique for researching material stability, breakdown kinetics, and product lifespan is thermogravimetric analysis (TGA). By heating the sample at a steady pace, TGA determines the connection between the sample's mass and temperature. Due to the extremely high precision balance of TGA, information about thermal stability and product generation on a sample may be obtained by examining the thermogravimetric curve (weight vs. temperature).

For this study, TGA is used to evaluate the material stability of fresh sample over a range of high temperatures, giving us insights of how oxidation can lead to increase or decrease in weight of the sample under air flow at specific temperatures. Also, TGA is employed to examine the coke formation on the surface of samples post RWGS reaction. TGA in this case is integrated with Fourier Transform Infrared Analyzer (FTIR) to analyze and measure the off gases concentration majorly CO₂, CO, and H₂O. **Figure 8** illustrates a brief schematic of the TGA instrument used for the analysis[49]. The sample weighing 15-20 mg was placed in a platinum pan and was introduced to air flow at 25 ml/min in a closed furnace. The furnace temperature starting from 25 °C, at the first stage, rises to 150 °C at the rate of 10 °C/min and holding for 1 minute. Second stage the temperature of the furnace is programmed to increase at 5 °C/min until 800 °C which is the maximum we go for our samples. Following the outlet line of TGA instrument is connected the inlet of FTIR to analyze and measure the off gases, focusing CO₂, CO and H₂O, that are produced during the burning of sample under the whole range of temperature i.e. from 25 °C to 800 °C. Thermal gravimetric analysis (TGA) was conducted on TGA 55 (TA Instruments),

using the continuous flow FTIR analyzer (MultiGas™ 2030, MKS Instruments) for off-gas analysis.

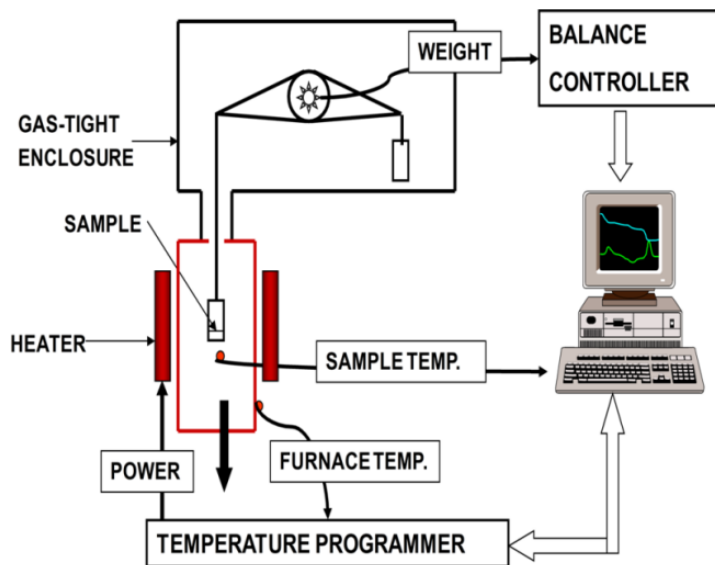


Figure 8. TGA Apparatus schematic [50]

3.2.4 CO₂ Temperature programmed desorption (TPD)

TPD, or temperature-programmed desorption, is a helpful method for assessing the interaction between CO₂ and the catalyst surface. TPD can assist in determining the quantity and intensity of active sites. The activation energy of a catalyst's desorption may also be determined using the TPD peaks. A standard TPD experiment involves flushing low concentration CO₂ at room temperature for surface adsorption, balanced with an inert gas (e.g., 5% CO₂/He). The sample bed is then heated to 800 °C at a steady rate of increase. When the thermal energy surpasses the adsorption energy, the adsorbed species desorb as the temperature rises. The desorbed gas is found and examined using a Thermal Conductivity Detector (TCD). The TPD curve with desorption peaks is produced by the

TCD, which also makes it possible to monitor the desorption events. The type of active sites on the catalyst's surface may be evaluated using this data.

In this study, 0.1 g of catalyst was reduced in 10% H₂/Ar for two hours at 500 °C. Helium (He) was used to flush the sample until it reached room temperature. After an hour of exposure to 5% CO₂/He, the catalyst was flushed with He for 1 h. The TPD analysis was performed by heating at a rate of 5 °C/min under He from 25 °C to 800 °C. An in-line FTIR was also connected to the outlet of the TPD instrument to analyze and measure off gases like CO₂, CO, CH₄ and water. **Figure 9** displays a typical schematic for a TPD instrument.

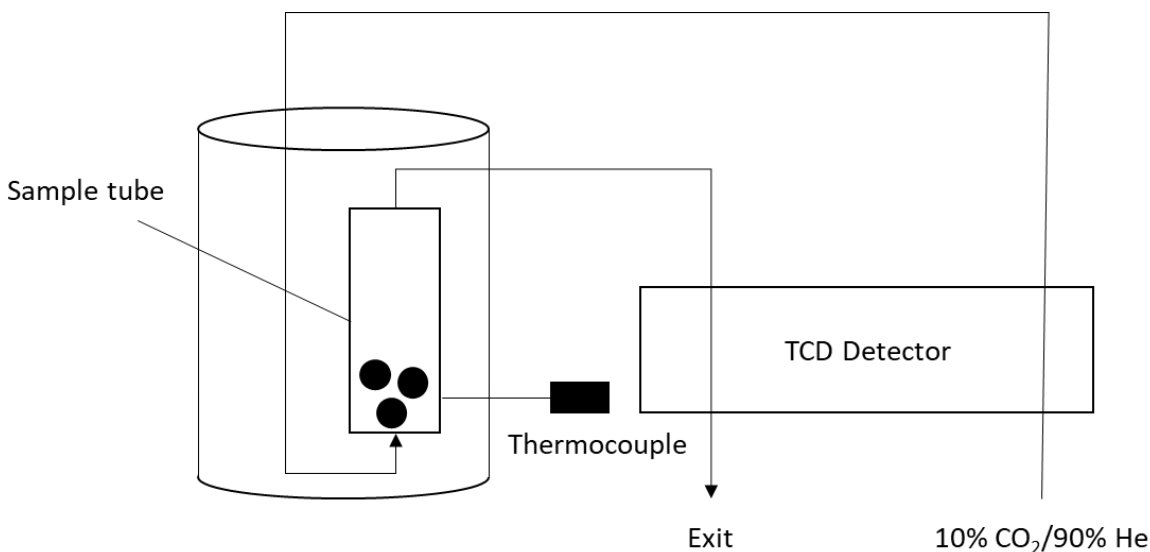


Figure 9. CO₂-TPD schematic

3.2.5 In-situ FTIR (Reaction Mechanism studies)

Infrared spectroscopy is a type of absorption spectroscopy that relies on the assumption that the vibrations of compound molecules are responsible for the absorption of certain infrared wavelengths[50]. The chemical link and atomic weight of the atoms connected at both ends determine the wavelength of the absorbed infrared radiation. This serves as the theoretical foundation for using infrared spectroscopy to determine a compound's structure. A common "molecular fingerprint" for analyzing molecule structure and chemical composition is infrared spectroscopy.

A certain group or bond exists in the molecule based on the correlation between the position, intensity, shape, and absorption band of the peaks formed by the absorption of infrared light. The FTIR instrument employed in this study is a transmission type. The source's infrared signal passes through the sample pellet and the KBr windows on each side of it before reaching the detector (**figure 10**). To examine the adsorbed species during the reaction, spectra are acquired at various reaction durations and temperatures.

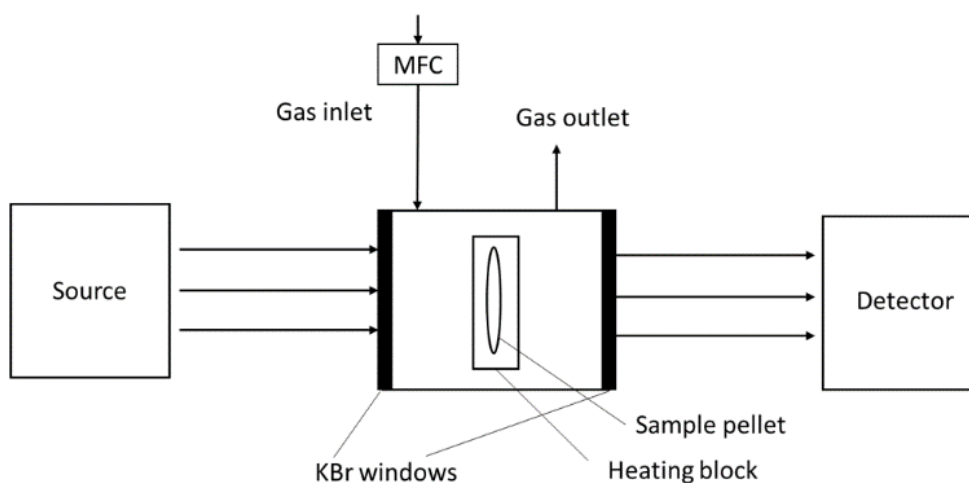


Figure 10. In-situ FTIR schematic

3.3 Flow system and reaction test

3.3.1 Flow system configuration

The reactor system (**Figure 10**) consists of the reactor installed inside a programmable tube furnace (TF55035A-1, Tube Furnace, Lindberg/Blue M). The catalyst bed was in contact with the thermocouple tip of a K type thermocouple (1/8", Omega Engineering) that was placed through the output tube (**Figure 11**). Feed flow rates were regulated by mass flow controllers (EL-FLOW select mass flow controllers, HOSKIN SCIENTIFIC LIMITED), and pressure was managed by a electrical back pressure regulator (EL-PRESS pressure meter/controllers, HOSKIN SCIENTIFIC LIMITED) and mechanical back pressure regulator (Stainless Steel BP Regulator, Swagelok). SMC AFM40-N02-Z-A, a mist trap, and Agilent Technologies, 5182-9411, a silica gel column (filled with silica gel orange, Fisher Scientific) were used to extract water. The IR analyzer (IR-208, Infrared Industries, Inc., USA) was used to measure the dry basis concentrations of CO, CO₂, and CH₄ in the outflow stream. LabVIEW (National Instruments) was used to operate the complete flow system. Analog-to-digital converters (NI 9215, NI 9263, National Instruments) were used to continually monitor and record the flow rates, pressure, temperature, and gas concentrations.

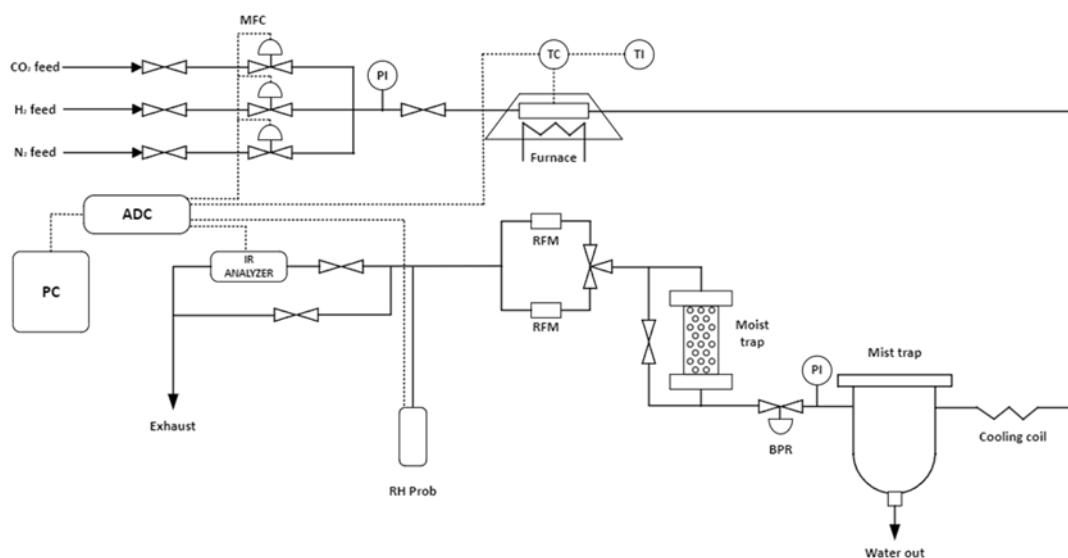


Figure 11. Flow system setup for conducting catalytic performance evaluation. Abbreviations: ADC, analog-to-digital converter; BPR, back pressure regulator; RFM, Rotor flow meter; IR, infrared; MFC, mass flow controller; PI, pressure indicator; PC, personal computer; TC, thermocouple; TI, temperature indicator.

catalyst is placed), and the outlet (where the thermocouple is placed). The inlet is 3/4" SS tubing attached to the 3/4" to 1/4" union which is followed by a 1/4" SS tubing. The union serves as a catalyst holder on which the catalyst is sandwiched between two quartz wool pieces over a fine mesh to avoid floating wool or catalyst inside the flow system.

sketch of the kinetic reactor

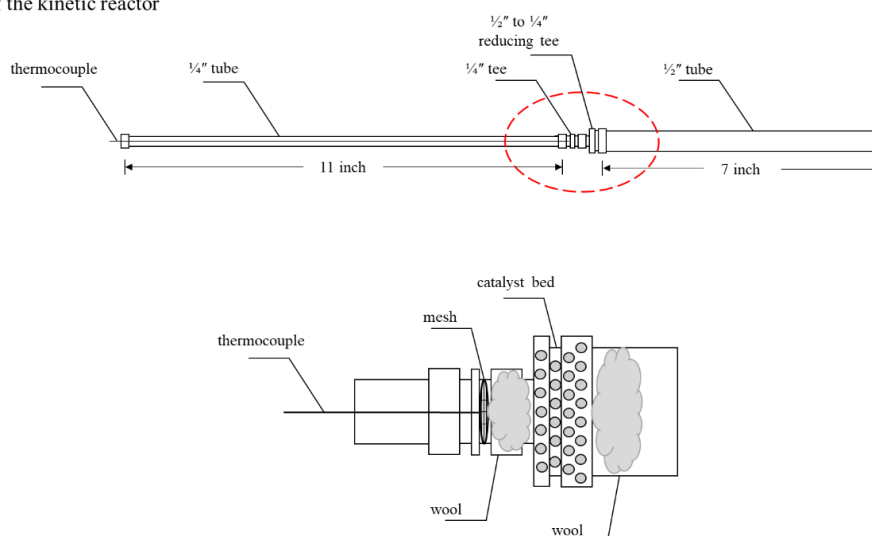


Figure 12. Reactor configuration and catalyst placement.

The powdered catalyst obtained after synthesis was pelletized and sieved (425-250 μm particle size) before loading it inside the reactor. For stability test, a quartz U-tube was used as a reactor and the pelletized and sieved catalyst was placed inside the U-tube and sandwiched by two quartz wool pieces from both ends. 300 mg of pelletized and sieved catalyst was used in each reaction test including stability test as well. Post reaction the catalyst was taken out removing the quartz wool from the inlet end and was used for characterization.

3.3.3 RWGS reaction tests

All the carbide samples that were loaded into the reactor were reduced under H_2 gas flow at 100 ml/min and 500 $^\circ\text{C}$ for 2 h. Post reduction, at the same temperature, the catalyst was introduced with a feed mixture of H_2 and CO_2 in the ratio 3:1 under atmospheric pressure and GHSV of 20,000 ml/g-h. The temperature of the furnace was programmed to step down by 25 $^\circ\text{C}$ after every 2 h (after complete stabilization) of reaction until 350 $^\circ\text{C}$ under similar pressure and feed conditions. All the conversions and selectivity's were calculated at steady state conditions and reported in a similar way except the stability test whose data is presented as transient.

CO_2 conversion and selectivity to CO were calculated according to Eqs. (7, 8) (y_{CO} , y_{CH_4} , and y_{CO_2} are mole fractions on dry basis, after removal of condensed water and humidity).

$$X_{CO_2} = \frac{y_{CO} + y_{CH_4}}{y_{CO_2} + y_{CO} + y_{CH_4}} \quad (7)$$

$$S_{CO} = \frac{y_{CO}}{y_{CO} + y_{CH_4}} \quad (8)$$

Carbon balance of the system is given by **Eq. (9)**. Where, α is the ratio of H_2/CO_2 in the feed, f_1 and f_2 are the conversion to CO and CH_4 respectively, $F_{C,out}$ is the outlet molar flow rate[51].

$$CB = (y_{CO_2} + y_{CO} + y_{CH_4})(1 + \alpha - f_1 - 4f_2) \quad (9)$$

$$\alpha = \frac{F_{H_2,f}}{F_{CO_2,f}} \quad (10)$$

$$f_1 = \frac{y_{CO}}{y_{CO_2} + y_{CO} + y_{CH_4}} \equiv \frac{F_{CO,out}}{F_{C,out}} = \frac{F_{CO,out}}{F_{CO_2,f}} \quad (11)$$

$$f_2 = \frac{y_{CH_4}}{y_{CO_2} + y_{CO} + y_{CH_4}} \equiv \frac{F_{CH_4,out}}{F_{C,out}} = \frac{F_{CH_4,out}}{F_{CO_2,f}} \quad (12)$$

Chapter 4: Catalytic Performance Evaluation – Mo₂C and WC for RWGS

To understand the impact of various reaction parameters on the carbide samples prepared over RWGS reaction various reaction tests were conducted underlining parameters such as effect of temperature, GHSV, feed ratio, and pressure and to further understand the durability of the catalyst's stability tests were also done. Below sections briefly discuss the effect of each factor over RWGS reaction on metal carbides synthesized for this study.

4.1 Effect of Temperature

Mo₂C, MoW_xC (x= 0.25, 0.5, 0.75, 1 and 1.5) and WC synthesized were analyzed over a range of temperature from 350 °C to 500 °C under a hydrogen to carbon dioxide feed ratio 3:1 with gas hourly space velocity fixed at 20,000 (ml/(g h)) and atmospheric pressure. Most of the carbides showed high CO₂ conversion throughout the temperature range reaching closer to equilibrium conversion ranges. The temperature test performed gave insights of the catalytic behavior of metal carbides, prepared for this study, towards RWGS reaction and for a competing side reaction, the Sabatier Reaction forming minute amount of CH₄. As temperature increased CO selectivity and CO₂ conversion also increased as Sabatier reaction slows down for it operates at lower temperature and while RWGS works best at higher temperatures leading to highest CO selectivity and CO₂ conversion at 500 °C. At lower temperatures, except MoW_{1.5}C and WC, all carbides favored CH₄ and CO formation leading to higher conversion rates.

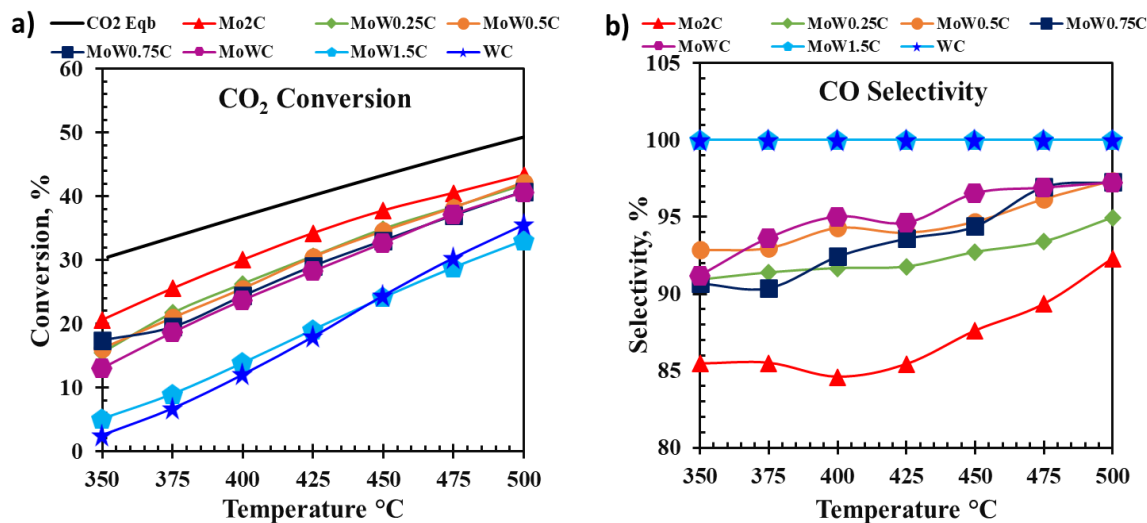


Figure 13. Catalytic performance evaluation conversion (a) and selectivity (b) as a function of temperature (350 °C to 500 °C) on Mo₂C, MoW_xC (x= 0.25, 0.5, 0.75, 1 and 1.5) and WC. The black solid line represents RWGS equilibrium. Parameters: GHSV – 20,000 ml/(g h), H₂/CO₂ – 3/1 and Pressure – 0 bar.

Mo₂C showed the highest CO₂ conversion (Figure 12) as compared to other carbides analyzed over the temperature range, but its CO selectivity (RWGS reaction) was the lowest among all other carbides. This was because Mo₂C was relatively active for Sabatier reaction as well showing high CH₄ formation, at lower temperatures up to 425 °C, with targeted CO from RWGS reaction. For mixed metal carbides an interesting shift in conversion and selectivity was observed. As we increased tungsten molar concentration from 0.25 to 1 in the mixed carbide samples the CO selectivity increased but CO₂ concentration went down relatively as there was no significantly high side reaction take place for CH₄ formation and the mixed carbides were more active for RWGS reaction. MoW_{1.5}C and WC were 100% selective to CO, no sign of Sabatier reaction, but the CO₂ conversion was relatively lower than the rest of the samples analyzed. This clearly indicates that WC is fully selective towards reverse water gas shift reaction with high CO₂ conversion

to CO. Overall, below 425 °C all carbides, except MoW_{1.5}C and WC, favored both RWGS and Sabatier reaction leading to higher CO₂ conversions but CO selectivity below 95%. Above 450 °C carbides favored RWGS reaction majorly and increased CO₂ conversion as well as CO selectivity above 95% was observed.

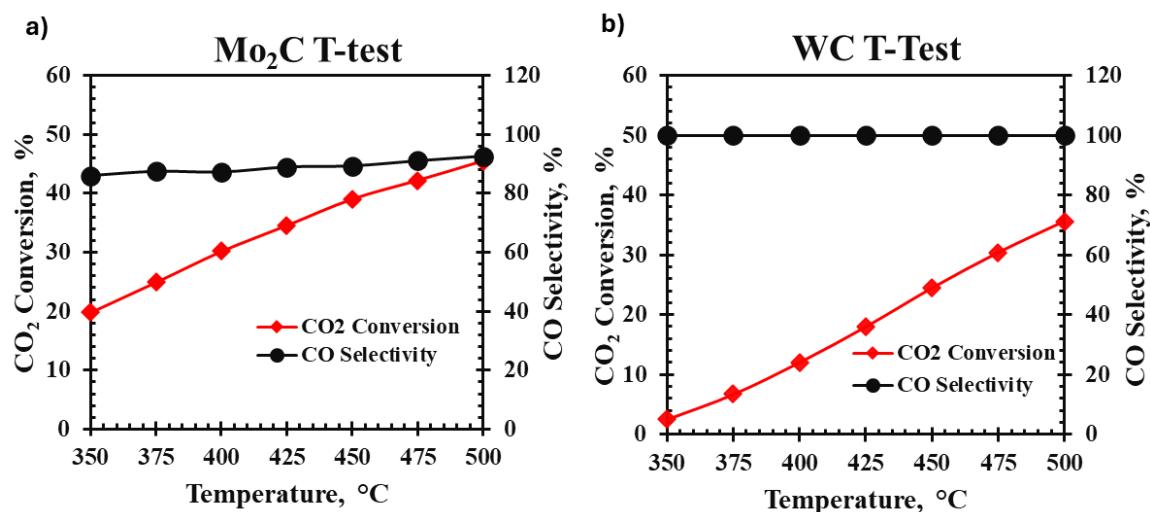


Figure 14. Catalytic performance evaluation as a function of temperature (350 °C to 500 °C) on Mo₂C (a) and WC (b). Parameters: GHSV – 20,000 ml/(g h), H₂/CO₂ – 3/1 and Pressure – 0 bar

Mixed carbides clearly give an indication of the effect of increasing W concentration on CO selectivity and CO₂ conversions. Therefore, Mo₂C and WC were selected for further evaluation for RWGS reaction under various reaction parameters. Figure 13 shows the temperature-based performance of Mo₂C and WC under given reaction conditions, explanation to which is discussed earlier in this section.

4.2 Effect of GHSV

Varying the gas hourly space velocity for Mo₂C (**figure 14**) showed improved CO selectivity but the CO₂ conversion went down to higher values. During the temperature test conducted at GHSV of 20,000 ml/(g h) CH₄ formation was significant up to 4% at lower temperatures. All the GHSV tests were conducted at 500 °C as the CO selectivity was highest and RWGS is best operational at higher temperatures. As GHSV was increased a clear drop in CH₄ formation, nearly 1.8%, was observed indicating that at higher GHSVs Mo₂C is highly active for RWGS reaction than Sabatier reaction. It is observed that although Mo₂C is active for RWGS reaction at higher GHSVs the CO₂ conversion is significantly lower. At 20,000 ml/(g h), CO₂ conversion was nearly 42% which decreased to around 36% at GHSV of 70,000 ml/(g h) and eventually dropped to 24% at an hourly velocity of 400,000 ml/(g h).

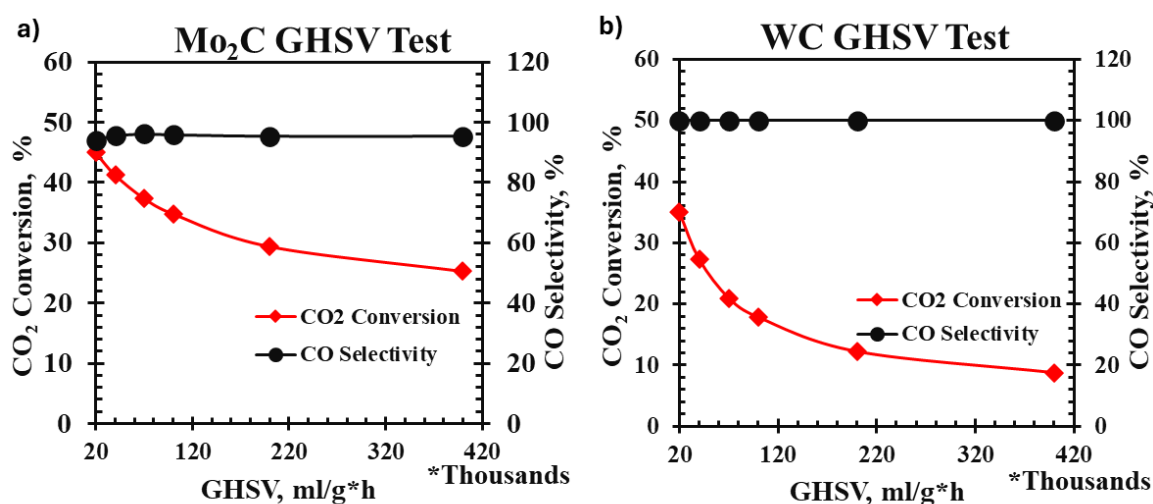


Figure 15. Catalytic performance evaluation as a function of GHSV (20,000 to 400,000) ml/(g h) on Mo₂C (a) and WC (b). Parameters: Temperature – 500 °C, H₂/CO₂ – 3/1 and Pressure – 0 bar

A relatively high conversion drop was observed in WC as GHSV was increased with no loss in CO selectivity throughout the test showing that WC is highly active for RWGS reaction. At 20,000 ml/(g h), CO₂ conversion was around 35% which reduced to nearly 20% at a GHSV of 70,000 ml/(g h). As further GHSV was increased CO₂ conversion decreased more to below 10% at an hourly space velocity of 400,000 ml/(g h).

It is interesting that as GHSV was increased from 20,000 to 100,000 ml/(g h), CO₂ conversion for Mo₂C decreased to only around 10% from its initial value but for WC the conversion went down to nearly 17%, which is almost half of initial CO₂ conversion for WC. Also, the CO selectivity for Mo₂C in the GHSV test range was almost constant after 70,000 ml/(g h) and conversion did not drop significantly, whereas for WC the CO selectivity was 100% during the whole test but with higher CO₂ concentration decrement. This behavior of Mo₂C and WC shows that increasing gas velocity hinders the property of catalyst to participate in the reaction as the surface of both carbides will have less gas residence time.

4.3 Effect of Feed ratio

The effect of increasing hydrogen in the feed mixture results in higher CO₂ conversion. Both Mo₂C and WC showed significant increase in CO₂ conversion (**figure 15**) with CO selectivity for Mo₂C going down whereas for WC, selectivity towards CO remains 100%.

At H₂/CO₂ feed ratio 1:1, Mo₂C was completely selective towards CO with around 20% CO₂ conversion to CO. Increasing the feed ratio to 2:1 and 3:1, below 2% methane formation was observed leading to increasing CO₂ conversion and thereby decreasing CO selectivity. When H₂/CO₂ feed was changed to 4:1 higher methane formation around 4%

was observed which increased to above 5% at H_2/CO_2 feed ratio 5:1. Higher CO_2 conversions were observed reaching up to 55%. This indicated that excess hydrogen combines with the carbon molecules, from CO_2 , which are strongly adsorbed over the catalytic surface and aids CH_4 formation.

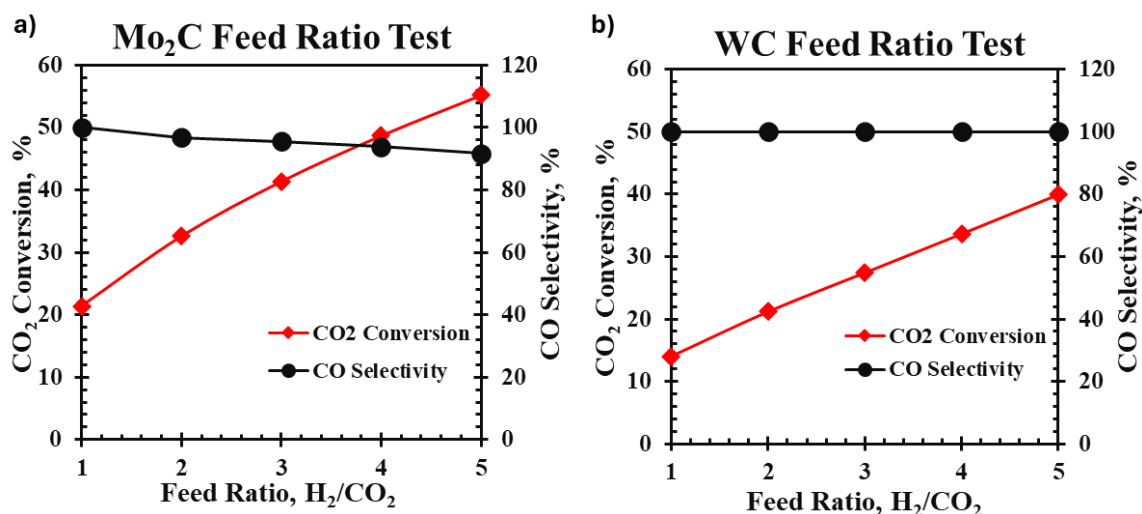


Figure 16. Catalytic performance evaluation as a function of Feed Ratio H_2/CO_2

(1/1 to 5/1) on Mo_2C (a) and WC (b). Parameters: Temperature – 500 °C, GHSV

40,000 ml/(g h) and Pressure – 0 bar.

WC on the other hand did not show any methane formation throughout the test. The excess hydrogen for WC favors RWGS reaction and a sharp increase in the CO_2 conversion to CO was observed, leading to 100% CO selectivity. At feed ratio 1:1, CO_2 conversion was relatively lower than Mo_2C , around 15% which substantially increased to 27% at feed ratio of 3:1. As hydrogen was increased further in the feed to 5:1 H_2/CO_2 , CO_2 conversion went up to 40%.

4.4 Effect of Pressure

Increasing pressure shifts RWGS reaction towards Sabatier reaction for both Mo₂C and WC. At atmospheric pressure or 1 bar absolute pressure Mo₂C shows little methane formation around 2.6% and nearly 42% carbon monoxide formation. As we increase pressure to 3 bar absolute CH₄ formation increases sharply to 17% lowering CO formation close to 31%. Further increment in pressure to 5 bar absolute results in higher methane formation nearly 30% lowering CO formation to 24%. Moving to 7 bar and 9 bar absolute pressure, Mo₂C becomes highly active for Sabatier reaction increasing CH₄ formation to around 38% and 42%, respectively with lower CO formation below 20%.

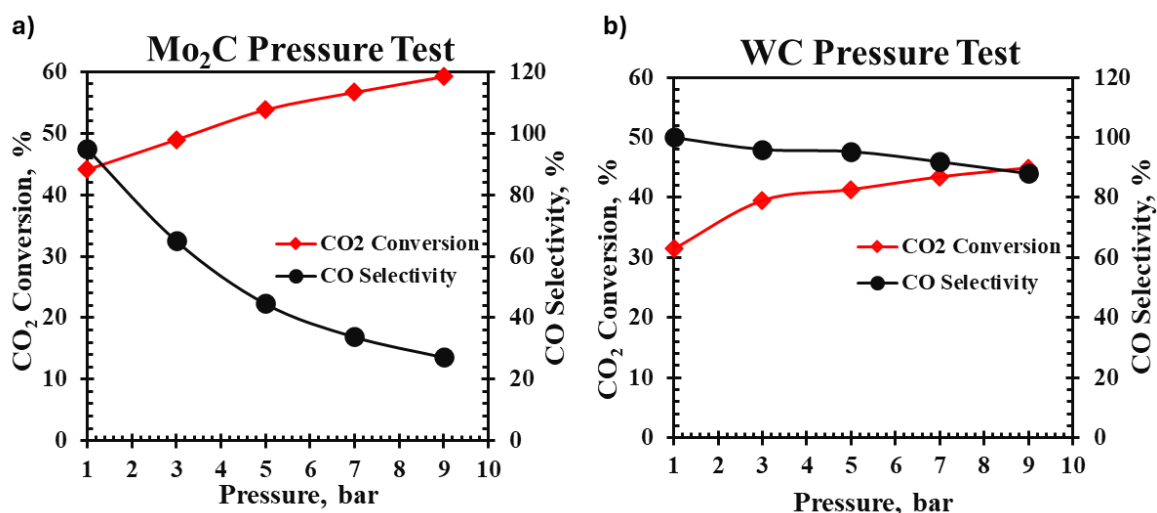


Figure 17. Catalytic performance evaluation as a function of Pressure (1 to 9 bar absolute) on Mo₂C (a) and WC (b). Parameters: Temperature – 500 °C, GHSV 20,000 ml/(g h) and Feed Ratio H₂/CO₂ - 3/1 to 5/1.

WC showed similar behavior as for Mo₂C when pressure was increased, resulting in formation of methane. At 1 bar absolute pressure, WC was 100% selective towards CO

with close to 31% CO₂ conversion to CO. As pressure was raised to 3 bar absolute slight methane formation, around 1.5%, was observed with an interesting point that CO formation also increased simultaneously near to 38%. Increasing pressure to 5 and 7 bar absolute increased CH₄ formation close to 2% and 3.5%, respectively, but CO formation remained constant for both pressure changes i.e. around 40%. When reached 9 bar absolute pressure, relatively higher, around 5%, methane formation was observed while CO formation was still stable at nearly 40%.

Overall, increasing pressure increased CO₂ conversion for both carbide samples. Mo₂C at higher pressures increased CH₄ formation and decreased CO production, whereas WC was stable for CO formation at higher pressures producing less than 5% CH₄. In terms of CO selectivity, Mo₂C is much less selective towards CO, which is seen in figure 16, as it decreased to 10% at 9 bar absolute. WC is highly selective towards CO at higher absolute pressures up to 5 bar with 95% CO selectivity and at elevated pressures like 9 bar absolute, delivering nearly 88% CO selectivity.

4.5 Stability Tests

To understand the carbides strength and reusability stability tests for 100 h were conducted. **Figure 17** shows the performance of Mo₂C and WC under specific reaction conditions for 100 h time on stream. Both samples were very stable for duration of the study and did not show any deviation in the conversion rates as time passed by. Two temperatures were tested for the stability tests, first at 500 °C for 24 h followed by 600 °C or next 76 h of reaction. The stability test determined that the structure and composition of both samples remains intact and does not degrade over the reaction period. The pelletized

catalysts loaded into the reactor were collected as in the form and further TGA-FTIR analysis was done to see the coke formation on the surface of Mo₂C and WC.

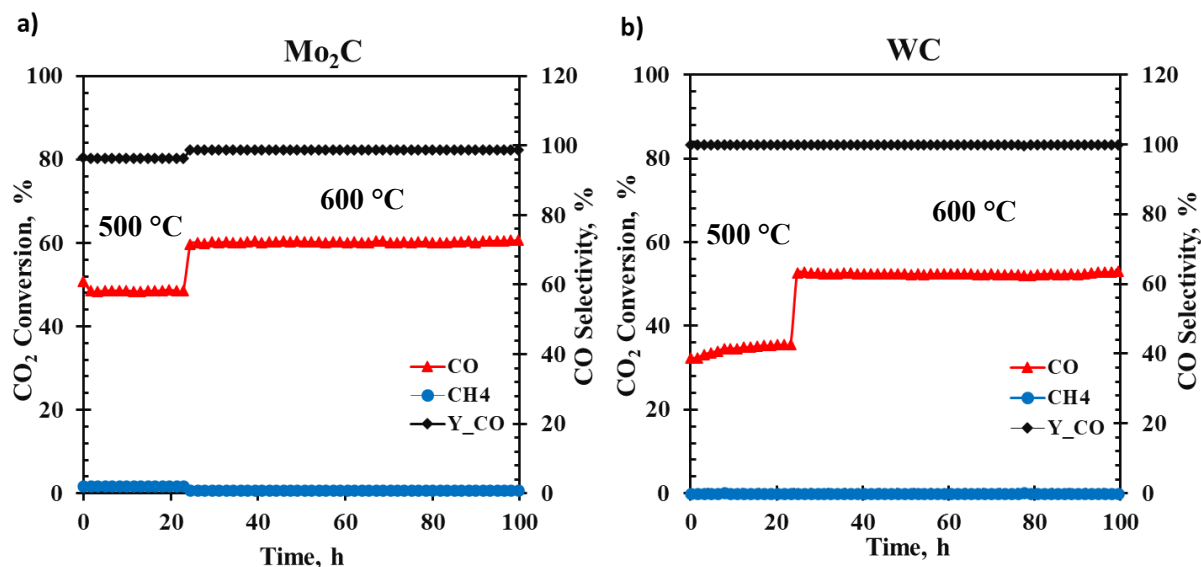


Figure 18. Stability Test for Mo₂C (a) and WC (b). Parameters: Temperature – 500 °C, GHSV 20,000 ml/(g h), Feed Ratio H₂/CO₂ - 3/1, Pressure – 0 bar and Time – 100 h.

Mo₂C at the initial stage of the stability test at 500 °C showed slight methane formation below 2% and therefore reduced CO selectivity to around 96%. Mo₂C did not lose its structure and composition for the first 24 hours of reaction and no loss in conversion of CO₂ to CO and CH₄ was observed. Further increasing the temperature to 600 °C, CH₄ formation went down to negligible and CO formation increased to around 60% which is almost equilibrium at this temperature. Mo₂C at higher temperature was highly stable and as shown in figure 17(a) CO₂ conversion did not change over the course of next 76 h after increasing the temperature.

WC showed similar activity as of Mo₂C with the fact that it did not have any CH₄ formation throughout the stability test. WC was fully selective towards CO at both lower

and higher temperatures showing an increase in conversion to CO at the later stage. Initially at 500 °C, CO₂ conversion to CO was stable around 35% with 100% CO selectivity, moving to 600 °C the conversion increased sharply to nearly 52% which was stable throughout. WC, like Mo₂C was highly stable in its structure and did not lose its strength over the 100 h of reaction. Both carbides, Mo₂C and WC, had higher coke formation on the surface which is later discussed in chapter 5.

Chapter 5: Catalyst Characterization & Reaction Mechanisms – Mo₂C and WC for RWGS

5.1 Structure and composition of Fresh Catalysts

The distinctive β -Mo₂C peaks were visible in the monometallic Mo₂C XRD pattern at roughly 34.6, 38.2, 39.6, 52.3, 61.8, 69.7, 74.9, and 75.9°. A minor peak at $2\theta=26.2^\circ$ is attributed to MoO₃[52]. In contrast, the catalyst pattern showed prominent oxide phase peaks of either Mo or W when tungsten was added to molybdenum carbide. The XRD patterns of tungsten and molybdenum oxides, as well as the two carbides, are identical. Therefore, even though tungsten carbide formation demands a greater carburization temperature than its molybdenum counterpart, it is challenging to determine with certainty from XRD patterns whether the tungsten was in the oxide phase or the inverse of the molybdenum. Using carbothermal hydrogen reduction, Wang et al., for example, generated Mo₂C and W₂C supported on activated carbon at various temperatures (600, 700, 800, and 900 °C) for two hours[53]. The scientists discovered that while tungsten required temperatures above 800 °C to develop its carbide phase, molybdenum showed signs of carbide phase formation at 700 °C carburization temperature. To keep some tungsten in its metallic condition, we kept the carburization temperature low in our investigation—600 °C. The temperature ramp was then lowered to 2 °C/min while the carburization was kept at 600 °C for four hours to extract the molybdenum/tungsten oxide phase from the catalyst. A significant oxide phase is present in the resulting bimetallic MoWC, as evidenced by its XRD pattern. Moreover, the carburization period was extended to 5 hours at 600 °C (ramp of 3 °C/min), and traces of tungsten and molybdenum were still present in the oxide phase. Two temperature plateaus were used: the first at 400 °C (5 °C/min) for two hours, and the

second at 600 °C (2 °C/min) for four hours, in order to completely remove the oxide phase from the catalyst. The XRD pattern reveals that the bimetallic MoW was completely carburized, devoid of any oxide phase-related peaks. The approximate locations of the metallic W peaks were 40.26, 58.3, and 73.25°.

Different MoW-based catalysts were created by altering the atomic ratio of the tungsten added to the molybdenum once the right catalyst carburization conditions were identified. The molybdenum to tungsten atomic ratios were 0, 0.25, 0.5, 0.75, 1, and 1.5. **Figure 18** shows the XRD profiles of Mo₂C and catalyst produced with varying molar ratios of Mo:W. The β -Mo₂C characteristic peaks were seen in the monometallic Mo₂C XRD pattern. Tungsten ratios up to 0.75 demonstrate a similar pattern, suggesting the creation of a Mo₂C (W₂C) mixed catalyst. The addition of tungsten (sample MoW0.25C) was seen to reduce the sharpness of the original Mo₂C peaks, with no movement in peak positions observed. It's interesting to note that the XRD pattern of equimolar Mo:W shows that W₂C and Mo₂C coexist with a metallic tungsten state. The delayed phase shift of tungsten during carburization from the oxide to the carbide equivalent can be attributed to the existence of metallic tungsten at this ratio. As tungsten exceeded molybdenum, in fact, a strong oxide phase peak at $2\theta=26.2^\circ$ and a metallic tungsten-attributed peak at $2\theta=40.4^\circ$ occurred. Tungsten was added to molybdenum carbide to lower the temperature at which carburization occurred. For example, Tran et al. reported that they tried to prepare monometallic tungsten carbide at 600 °C and 15% CH₄/H₂ flow but found by XRD that it was only in the metallic phase and that they needed to reach higher temperatures to reach the carbide phase. However, the carburization temperature of molybdenum dropped to 600 °C when tungsten was added[54]. Therefore, the formation of strong Mo-W alloying in the

bimetallic catalyst may be indicated by a decrease in the tungsten carbide carburization temperature following the addition of molybdenum. This process makes it easier for tungsten oxide to change into metallic tungsten and then tungsten carbide. Nevertheless, this type of transformation was not seen at higher W:Mo molar ratios, which could be attributed to more "isolated" tungsten clusters from the mixed Mo-W alloy that did not carburize at 600 °C. Consequently, to completely convert tungsten oxide into the metallic and subsequently the carbide phases, higher tungsten to molybdenum ratios necessitates higher carburization temperatures and/or times. To achieve a rich tungsten carbide surface over molybdenum carbide, the carburization temperature for the sample MoW_{1.5}C was raised to 700 °C for four hours. The XRD pattern is shown in and shows that no metallic tungsten peak is present, indicating that the oxide phase has been effectively eliminated. Additionally, two phases of tungsten carbide, W₂C and WC, were detected in this catalyst. The XRD diffractogram revealed several distinctive peaks of WC at 31.6, 35.9, and 48.6°, indicating that different tungsten phases are susceptible to variations in carburization temperature and duration.

Table 2 lists the average crystallite sizes that were determined using the Scherrer equation. The crystallite sizes of all mixed carbides were significantly smaller than those of the Mo₂C sample. In fact, the molybdenum carbide crystallite size was 11.4 nm, and it dropped to a minimum of 4.5 nm upon the addition of tungsten. These findings may indicate the formation of a Mo-W alloy, which may cause a lattice strain effect as a result of tensile or compressive forces[55]. This strain may inhibit the development of larger crystallites, favoring the formation of smaller ones instead. According to Gioria et al., the crystallite sizes of the copper-based catalyst dropped dramatically from 18.8 to 1.9 nm

upon the addition of nickel[56]. Similar results were also reported by Oezaslan et al. when comparing Cu and PtCu based catalysts[57].

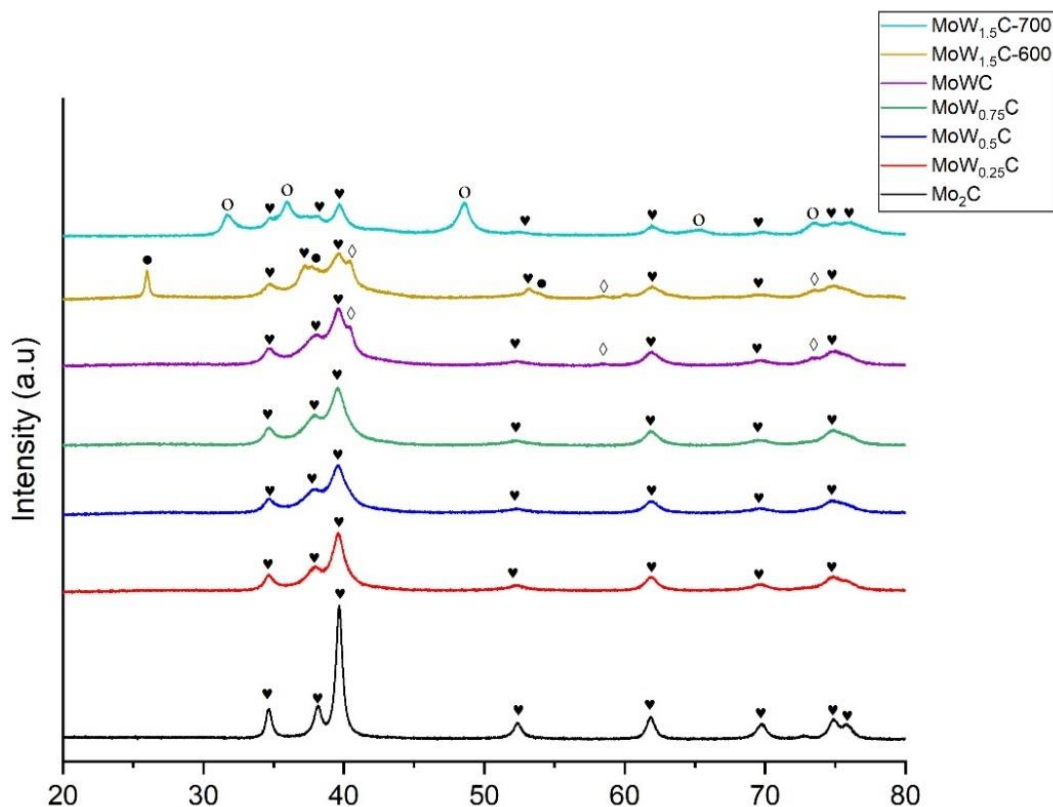


Figure 19. The XRD patterns of the Mo/W catalysts synthesized with different Mo: W molar ratios. ♥: β - $\text{Mo}_2\text{C}(\text{W}_2\text{C})$; ○: WC; ◇: W; ●: $\text{Mo}_2\text{O}(\text{W}_2\text{O})$.

Figure 19 shows the XRD pattern of spent Mo_2C , $\text{MoW}_{0.5}\text{C}$, $\text{MoW}_{1.5}\text{C}$ and WC after temperature test on the carbides. The catalyst has maintained its crystalline structure and phase composition throughout the reaction process. This suggests that the catalyst did not undergo significant structural changes, such as phase transformations, crystallite size changes, or amorphization. The carbides' active phase did not undergo chemical degradation or react to generate new phases. The catalyst composition stayed stable as there were no new peaks or variations in peak intensity. Since there was no structural change and

no new species formation, it can be suggested that the metal carbides are durable and can be used for longer periods. For all the spent samples no oxide phase was observed to be present after their evaluation over a temperature range 350 to 500 °C.

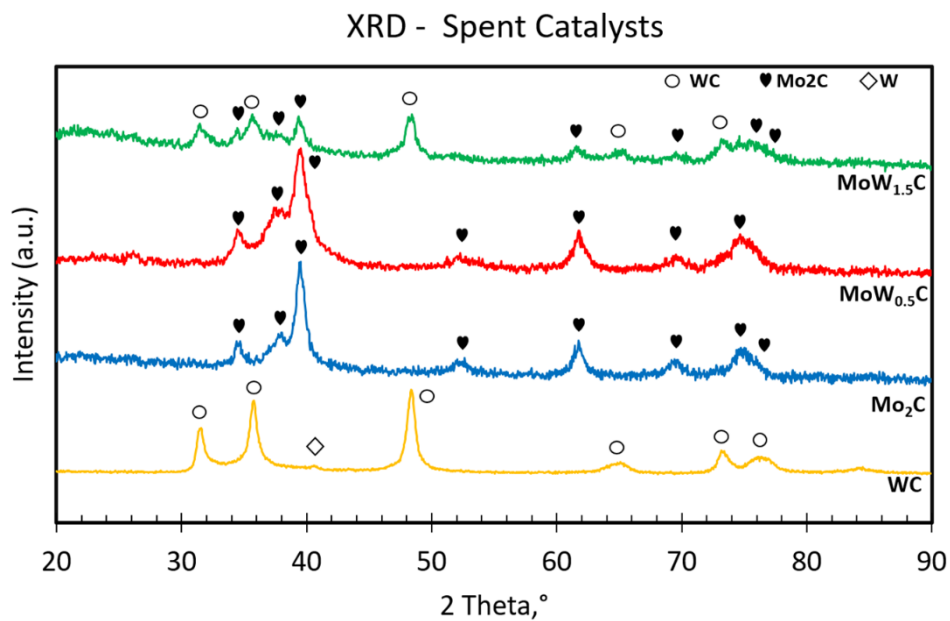


Figure 20. The XRD patterns of the spent Mo₂C, MoW_{0.5}C, MoW_{1.5}C and WC catalysts. ♥: β -Mo₂C(W₂C); o: WC; ◇: W; ●: Mo₂O(W₂O).

Table 2. Properties of the mixed carbide catalysts

Catalyst	Phases	BET surface area ^a (m ² . g ⁻¹)	Crystallite size ^b (nm)
Mo ₂ C	β-Mo ₂ C	61.5	11.4
MoW _{0.25} C	β-Mo ₂ C, W ₂ C	46.9	4.5
MoW _{0.5} C	β-Mo ₂ C, W ₂ C	29.0	5.2
MoW _{0.75} C	β-Mo ₂ C, W ₂ C	26.4	5.1
MoWC	β-Mo ₂ C, W ₂ C, W	16.3	5.9
MoW _{1.5} C-600	β-Mo ₂ C, W ₂ C, W, WO ₂	53.7	-
MoW _{1.5} C-700	β-Mo ₂ C, W ₂ C, WC	25.5	5.4
WC-700	WC, W	17.8	

a: calculated from the BET plot, b: calculated from XRD line width using Scherrer equation.

5.2 CO₂ TPD adsorption strength analysis

To study the CO₂ adsorption strength and dissociation to CO, TPD technique was employed with an in-line FTIR for selected fresh and spent carbide samples discussed in this study. Based on the catalytic performance of carbide samples over a range of temperature from 350 to 50°C (discussed above in **section 4.3**) it was clear that the seven samples studied in the temperature test can be categorized in three groups. Among these three groups four samples were selected for further characterization and experiments.

All the four samples selected, Mo₂C, MoW_{0.5}C, MoW_{1.5}C and WC, were reduced under hydrogen gas flow prior to starting adsorption for one hour with 5%CO₂/He gas mixture.

Temperature was ramped from 25 °C to 800 °C at 10 °C/min to observe and measure desorption of gases, its concentration and TCD intensity.

All fresh carbides showed stronger adsorption of CO₂ (**Figure 20**) and desorbed at temperatures higher than 500 °C for three samples except WC in which desorption started around 350 °C.

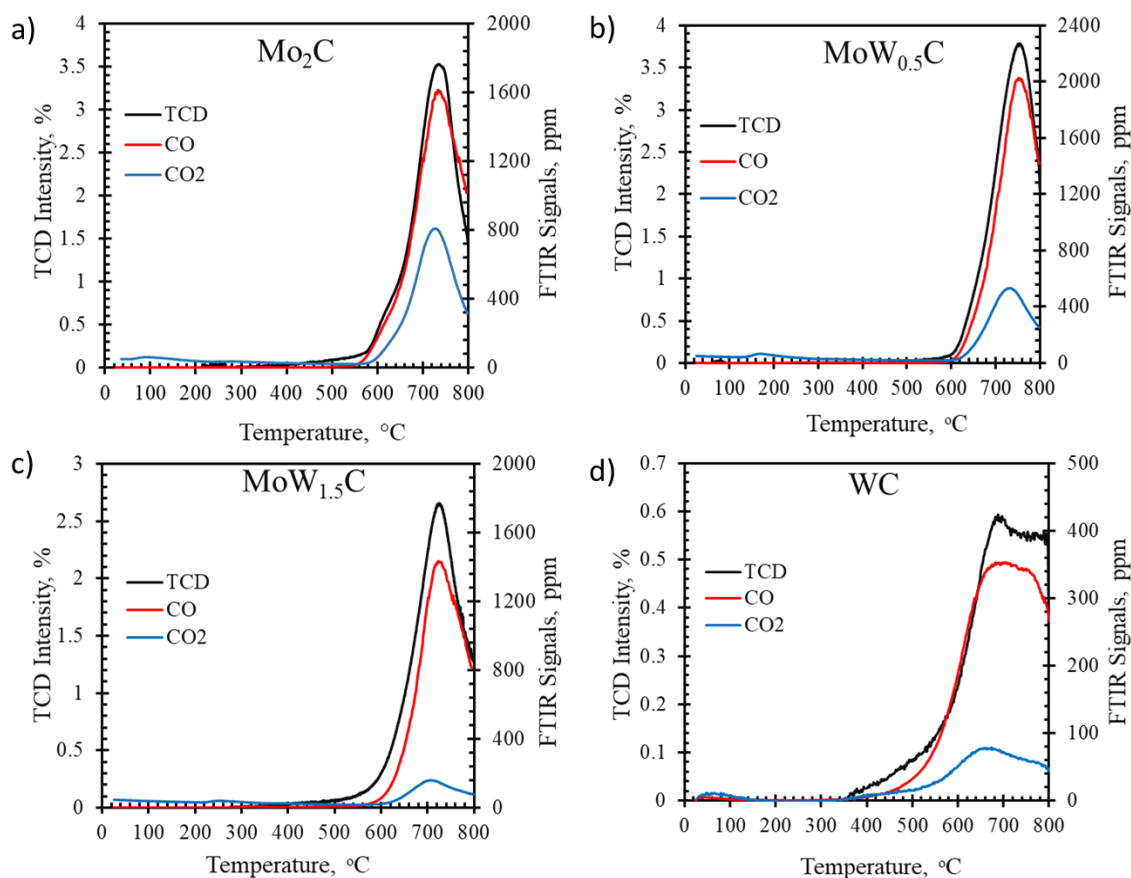


Figure 21. CO₂ TPD-FTIR analysis on fresh carbide samples (post reduction)

It is clear from the analysis that most of the CO₂ adsorbed on the surface of the carbides are dissociated to CO and only limited amount of CO₂ undissociated desorbed as temperature increased. This behavior of the carbides makes them more useful in RWGS process as more CO₂ is converted to CO. Moreover, it appears that addition of Tungsten

leads to lower TCD intensity as observed with lower molar ratios of W in bimetallic carbides. For $\text{MoW}_{0.5}\text{C}$ and $\text{MoW}_{1.5}\text{C}$ the TCD peaks appear at similar temperatures, nearly 720 °C. The intensity of TCD signals for both mixed carbides were relatively higher and better peak formation was observed in $\text{MoW}_{0.5}\text{C}$ than $\text{MoW}_{1.5}\text{C}$. Since increasing W leads to lower CO_2 desorption and relatively higher CO formation leading us to our target in considering WC as a potential RWGS catalyst, $\text{MoW}_{0.5}\text{C}$ and $\text{MoW}_{1.5}\text{C}$ were not selected only Mo_2C and WC for further reaction test and characterization to optimize the catalytic performance over RWGS reaction.

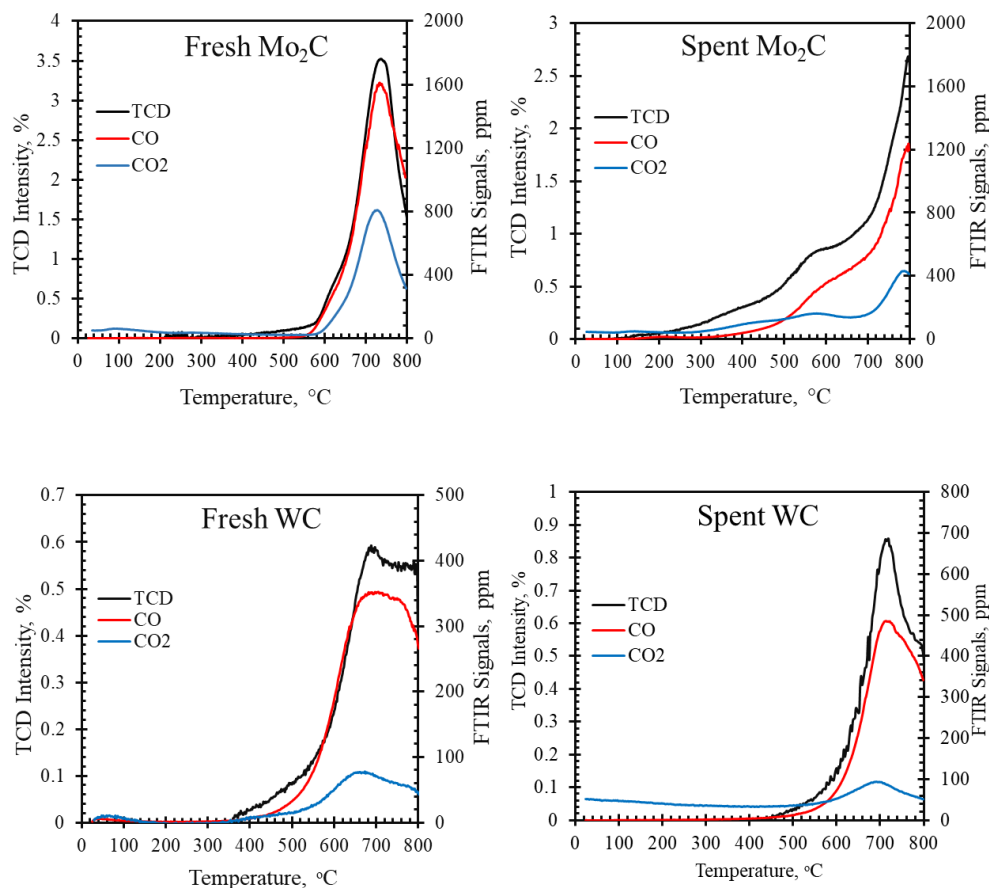


Figure 22. CO_2 TPD-FTIR analysis on fresh and Spent Mo_2C and WC samples

The spent carbide samples showed similar results in comparison to fresh samples. There was higher CO desorption from the surface was observed with lower amount of CO₂ desorption (**Figure 21**). The TCD intensities for both Mo₂C and WC were slightly higher than fresh samples because of coke formation on the catalyst surface, which will be discussed in section 4.6 later. Significant shift in the TCD signals formation for spent Mo₂C which started appearing after 250 °C while for fresh Mo₂C the TCD signals start appearing after 500 °C. There was clear peak formation for fresh Mo₂C around 720 °C while on spent Mo₂C the peak did not form at all until 800 °C and appears to be increasing. This indicates that the carbon deposition on the surface of post reaction Mo₂C is in higher quantity but loosely adhered to the surface and was easily desorbed starting around 250 °C. On a contrary, for spent WC the TCD signals appeared after 45°C which was observed at 350 °C on fresh WC, indicating that on spent WC carbon deposition is much stronger than spent Mo₂C. On spent WC better peak formation was observed while for fresh WC the peak didn't form fully until 800 °C which was totally different for spent Mo₂C.

5.3 Thermal Stability and off gas analysis: TGA-FTIR

Thermogravimetric analysis of Mo₂C and WC displayed their characteristics of oxidizing at different temperatures and showed an increase in their weight during the analysis (**Figure 22**). Both fresh and spent carbides were analyzed under the temperature range 25 to 800 °C and the off gases were measured with an integrated FTIR.

Fresh Mo₂C was stable until 230 °C, with nominal weight loss from evaporation of adsorbed water, after which it started to oxidize, gain weight and simultaneously releasing CO₂ indicating the loss of carbon from its surface and forming molybdenum trioxide (MoO₃). There were two oxidation stages which led to an increase in weight of fresh Mo₂C

sample. First 10% weight gain between 250 °C and 350 °C during which higher amount of CO₂ was released, which is basically carbon from the carbide phase converted to CO₂ resulting in formation of a protective oxide layer of MoO₃ that prevented further oxidation until 420 °C and second between 425 °C and 500 °C again followed by forming oxide layer and releasing CO₂, limiting further weight gain by oxidation. Reaching to nearly 500 °C, Mo₂C was thoroughly oxidized and the MoO₃ layer was strong enough to limit further oxidation therefore, the weight gains up to 25% remains almost constant on the TGA curve within the temperature range of about 500 °C to 700 °C. When the temperature exceeds 710 °C, the curve of the Mo₂C sample suddenly declined accounting for a weight loss around 80% after oxide formation, which lead by MoO₃ breakdown and evaporating at higher temperature of around 770 °C. Chen et al., in 2011 reported similar TGA analysis of Mo₂C underlining the significant increase in weight as followed by MoO₃ formation[58]. A very minute amount of CO or H₂O was produced in duration of the TGA analysis of both fresh and spent Mo₂C.

Similar oxidation, forming MoO₃ layer and weight gain up to 30% was observed for spent Mo₂C sample with higher CO₂ release because of coke formation on the sample after 100 h TOS stability test. The temperatures of CO₂ desorption from the surface of spent Mo₂C was like that of fresh sample.

Both fresh and spent WC showed notable stability under high temperature up to 40°C with negligible weight loss, CO₂, CO, and water measured by FTIR analyzer. After 42°C, oxidation of WC began until 500 °C resulting in weight gain around 20%, formation of WO₃ and thereby releasing carbon in the form of CO₂. The amount of carbon dioxide released from fresh WC sample is relatively higher than in spent WC and lower amount of

CO₂ release from the spent carbide surface. Weight gain in spent WC is found to be similar to fresh WC around 15%. Both fresh and spent WC after first oxidation and formation of WO₃ did not undergo further oxidation as Mo₂C as the temperature increased from 500 °C to 800 °C. Compared to fresh and spent Mo₂C, WC did not lose its weight at all after 700 °C and was stable throughout the experiment. This indicates that the WO₃ layer formed after initial oxidation is strong enough to limit further oxidation and to withstand higher temperatures.

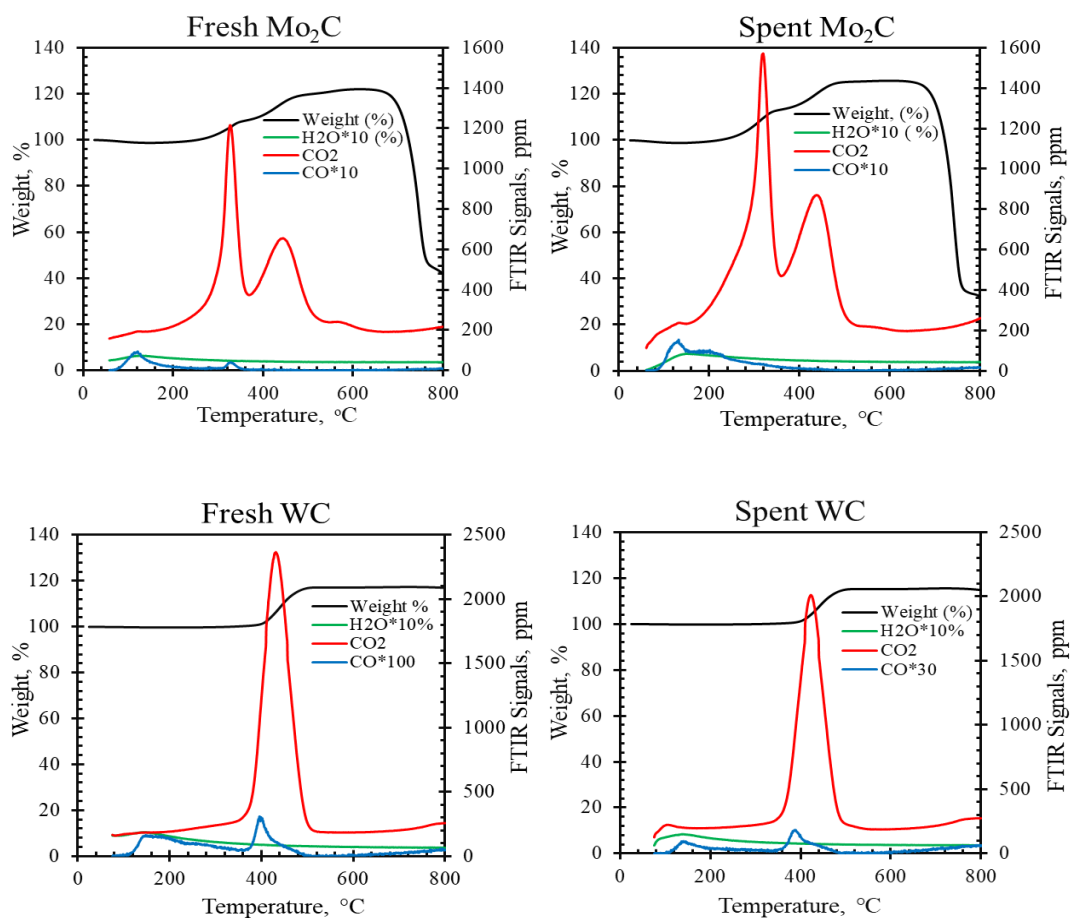


Figure 23. TGA-FTIR Analysis of Fresh and Spent Mo₂C and WC after 100 h stability test.

Formation of WO_3 is confirmed by change in color of WC post TGA (Figure 23)[59]. At room temperature, the color of WO_3 is light yellow and similar was observed in our analysis.

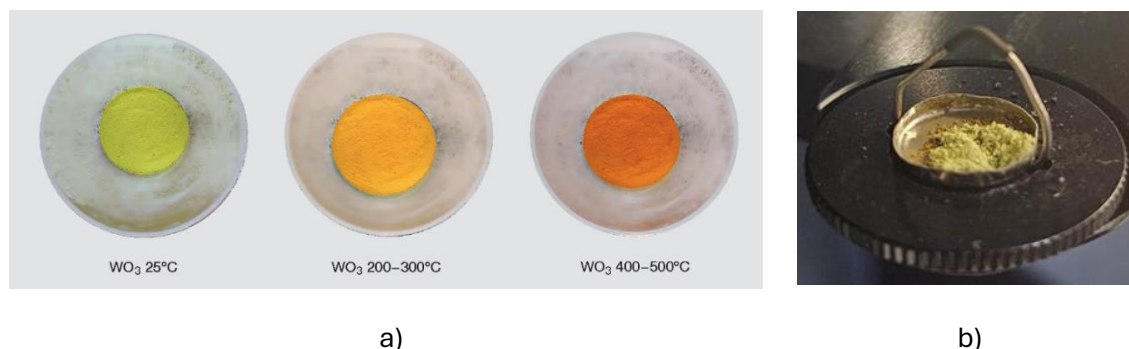


Figure 24. a) Color transition of WO_3 with temperature increment [58] and b) WO_3 at 25 °C post TGA

5.4 In-situ FTIR (reaction mechanism)

In-situ FTIR analysis of spent Mo_2C and WC gave insights on the reaction pathways for RWGS. It was clear that at lower temperatures Mo_2C had formates as well as carbonates and bicarbonates species during adsorption and reaction stages. While for WC, most of the species were carbonates and bicarbonates with little peaks for formate species.

Figure 25(a) shows the CO_2 adsorption peaks at 300 °C on spent Mo_2C . During adsorption, for the first 2 minutes no significant peaks were observed but after 3 minutes of stabilization peaks start to appear with lower intensities. All the peaks remained intact during time increment and only changed in their intensities delivering stronger peaks. The peaks of adsorbed CO_2 , which were associated with surface carbonate and bicarbonate centered at 1620 cm^{-1} , 1368 cm^{-1} and 1332 cm^{-1} [60], weaker peaks of gas phase CO are observed at 2100 cm^{-1} [61], and at wavelengths 1540 cm^{-1} , 1510 cm^{-1} and 1450 cm^{-1} [62] shows formate species as an indication of CO_2 reduction reaction. During the reaction

(figure 25(b)), peaks started to appear after 1 minute of stabilization as CO in gas phase can be observed at 2100 cm^{-1} . Carbon Monoxide peaks were very strong and kept getting stronger in intensity as the reaction progressed with time. The peak centered at 1620 cm^{-1} , linked to bicarbonate species, disappeared and peak observed during adsorption at 1450 cm^{-1} shifted to 1488 cm^{-1} with higher intensity during the reaction, which is associate with formate species.

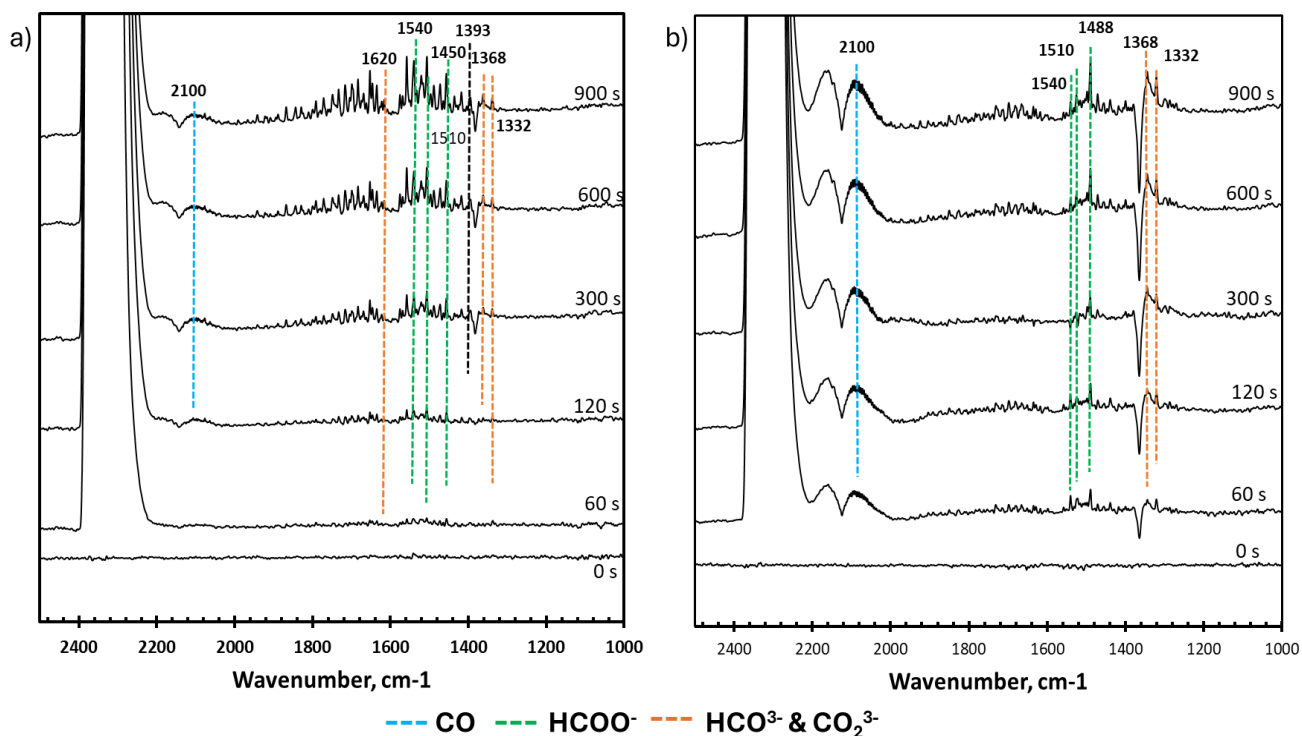


Figure 25. Transient in situ FTIR spectra for Spent Mo_2C recorded at $300\text{ }^\circ\text{C}$ (a) CO_2 Adsorption and (b) under reaction conditions (2% CO_2 , 8% H_2 , balanced by Ar).

The steady state spectra at different temperatures (figure 26) for both CO_2 adsorption and reaction conditions indicates that majority of the peaks did not appear at $100\text{ }^\circ\text{C}$. During adsorption, only CO peaks at 2100 cm^{-1} and bicarbonate species at 1368 cm^{-1} appear at this temperature while at the reaction stage CO peak disappear and only weak bicarbonate

species appear at 100 °C. This indicates that at lower temperature CO₂ reduction did not take place. At 200 °C during adsorption, CO₂ reduction reaction starts, and formate species centered at 1540 cm⁻¹, 1510 cm⁻¹, and 1450 cm⁻¹ appeared and bicarbonate and carbonate species were present with weaker signals. It is interesting to note that CO peak did not appear at this temperature. Reaction at 200 °C did not serve much the purpose for peaks to appear, only bicarbonate and CO gas phase peaks are detected at this temperature. Majority of the peaks appear at 300 °C, during both adsorption and reaction, as the catalyst was designed to work at higher temperatures, various peaks were identified. Strong formate species centered at 1540 cm⁻¹, 1510 cm⁻¹, and 1450 cm⁻¹ with lower intensities of bicarbonate and carbonate species. Adsorbed CO₂ appeared at 1620cm⁻¹ during adsorption which disappeared during reaction at 300 °C. CO gas phase peaks were detected at both 200 °C and 300 °C.

It can be concluded that first, CO₂ is adsorbed on the surface as carbonate, which is hydrogenated to bicarbonate with the participation of surface hydrogen. Bicarbonate is then transformed to surface formate species. CH₄ is produced by successive hydrogenation of formate species. CO can be produced by direct CO₂ reduction as a by-product, with this pathway being slightly suppressed on the molybdenum carbide surface at lower temperature, resulting in higher CH₄ generation. Since the final temperature for In-situ FTIR was 300 °C, therefore dominant peaks for formates have been observed for Mo₂C. At higher temperature the reaction pathway changes to produce CO.

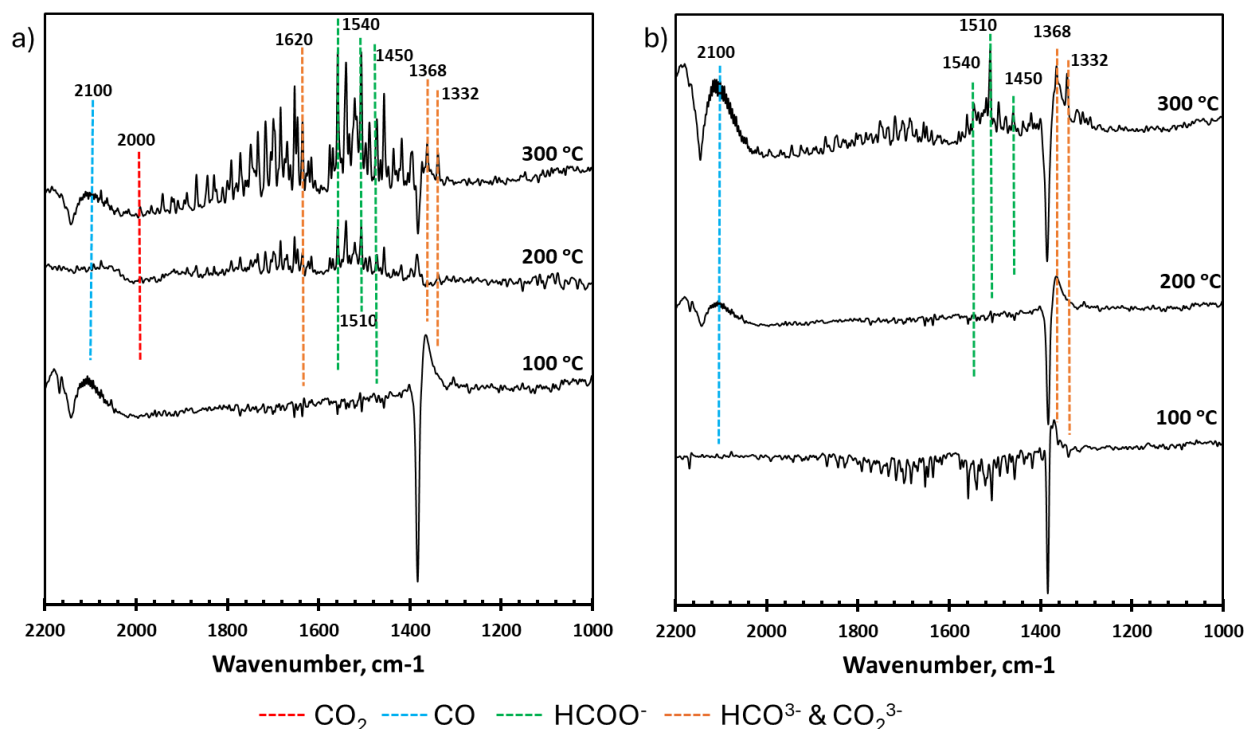


Figure 26. Steady (after 15 min stabilization) in situ FTIR spectra recorded for Spent Mo_2C at different temperatures (a) CO_2 adsorption and (b) under reaction conditions (2% CO_2 , 8% H_2 , balanced by Ar)

For WC, adsorption and reaction showed similar results (**figure 27 (a) and (b)**). During CO_2 adsorption, peaks appear for both formates and bicarbonates and carbonates with varying intensities indicating the reaction pathway followed over the catalyst's surface. At 300 °C, weaker gas phase CO peaks appeared after 2 minutes of stabilization along with bicarbonate species at 2100 cm^{-1} and 1368 cm^{-1} , respectively. Over the course of adsorption until 15 minutes, it is clearly observed that very weak peaks of formates corresponding to 1554 cm^{-1} and 1540 cm^{-1} appeared and increasing intensities of peaks associated to carbonates and bicarbonates were detected to be centered at 1368 cm^{-1} and 1332 cm^{-1} . Adsorbed CO_2 peaks were observed at 2000 cm^{-1} after 5 minutes of adsorption, which were very weak. During reaction, strong CO peaks appeared immediately after 1 minute at 2100 cm^{-1} along with weaker peaks of bicarbonates centered at 1368 cm^{-1} . As reaction

progressed, bicarbonates and carbonates peaks got stronger at 1368 cm^{-1} and 1332 cm^{-1} with weaker intensities of formate species at 1540 cm^{-1} and 1510 cm^{-1} .

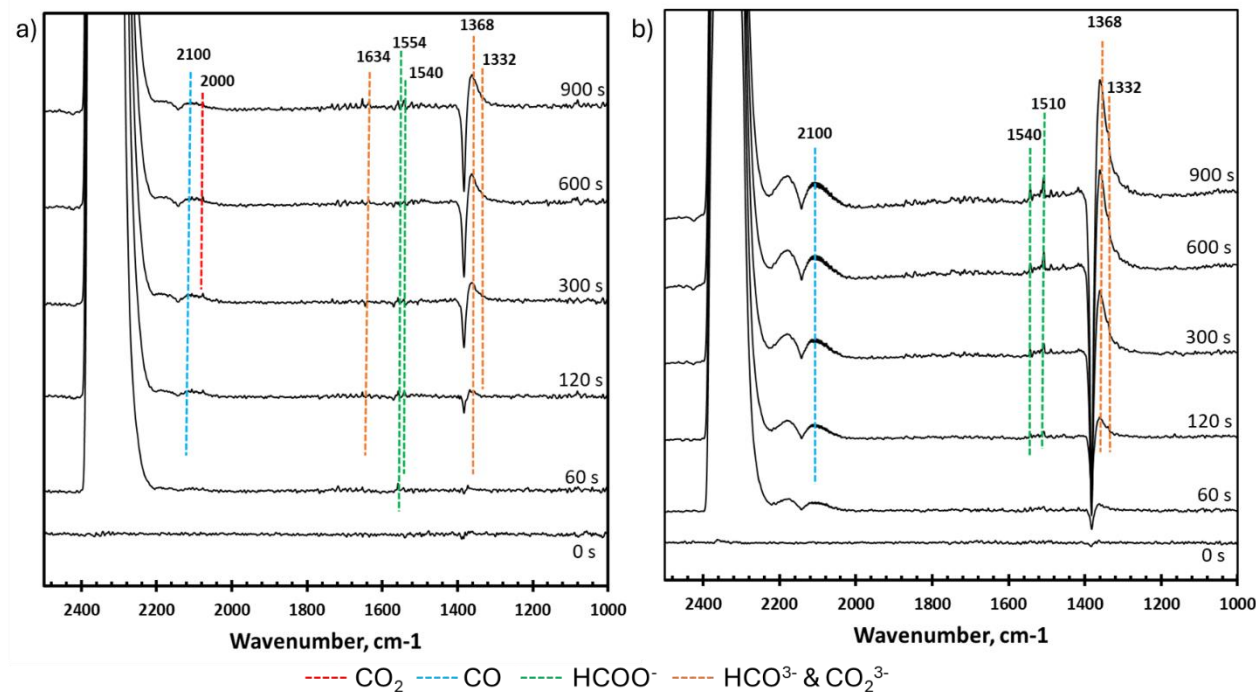


Figure 27. Transient in situ FTIR spectra for Spent WC recorded at 300 °C (a) CO₂ Adsorption and (b) under reaction conditions (2% CO₂, 8% H₂, balanced by Ar).

Steady state spectra at different temperatures (**figure 28 (a) and (b)**) clearly defines the reaction pathway for WC. At 100 vC, during both adsorption and reaction, no significant peak formation takes place, except bicarbonate species at 1368 cm^{-1} indicating CO₂ reduction to surface bicarbonates. At 200 °C, during adsorption, weaker formate species along centered at 1540 cm^{-1} , 1510 cm^{-1} , and 1450 cm^{-1} appeared with established peaks of bicarbonates. Strong CO peaks also appear at this temperature at 2100 cm^{-1} . Conversely, during reaction at 200 vC only bicarbonate species were detected indicating further breakdown of formates. Similarly at 300 vC, formate species, during adsorption, appear

with weaker signals at same location and bicarbonate and carbonate species appeared with stronger intensities. CO in gas phase, at 2100 cm^{-1} , also appeared to be more strong at higher temperatures. At reaction conditions at $300\text{ }^{\circ}\text{C}$, high intensities of bicarbonates and carbonates, at 1368 cm^{-1} and 1332 cm^{-1} , appear with weaker peaks of formates at their residing locations. Weak CO and CO_2 peaks also appear at $300\text{ }^{\circ}\text{C}$ during the reaction period.

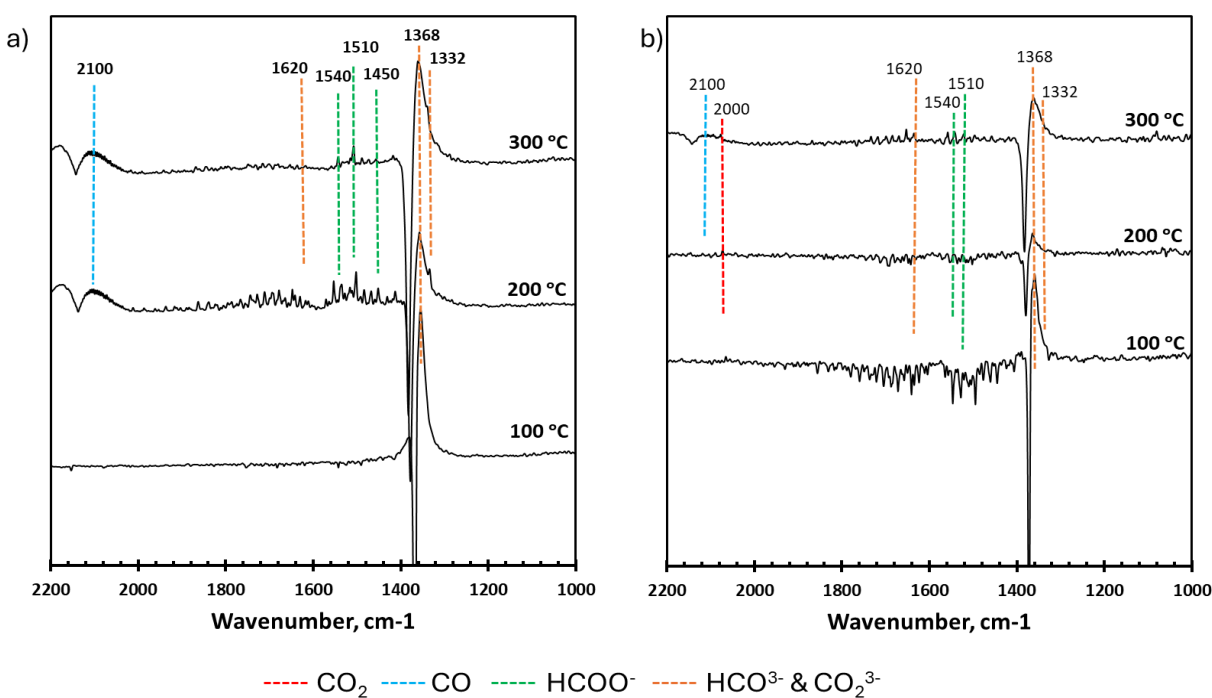


Figure 28. Steady (after 15 min stabilization) in situ FTIR spectra recorded for Spent WC at different temperatures (a) CO_2 adsorption and (b) under reaction conditions (2% CO_2 , 8% H_2 , balanced by Ar)

Overall, it can be concluded that the absence of formate species on the surface of WC explains its full selective nature towards CO as observed in the temperature tests. CO produced over WC is by direct reduction of CO_2 to bicarbonate and carbonates. Since the reaction conditions of tests conducted were at higher temperatures and methanation

reaction takes place at lower temperatures the formation of formate species at 200 °C and getting decreased as temperature increased to 300 °C makes the reaction pathway clear for WC. Since Mo₂C was active for both Sabatier reaction and RWGS reaction, therefore formate species leading to CH₄ formation are observed at lower temperature of 300 °C.

Chapter 6: Conclusion and future work

6.1 Conclusion

The successful evaluation for thermocatalytic conversion of CO₂ via Reverse Water Gas Shift over molybdenum and tungsten carbide was carried out. Catalyst performance evaluation through series of reaction tests and material characterization was completed to analyze the performance of the catalyst synthesized.

Molybdenum carbide, a series of mixed metal carbides (Molybdenum and Tungsten) MoW_xC ($x = 0.25, 0.5, 0.75, 1 \text{ \& } 1.5$) and WC were prepared to study their performance over RWGS reaction to produce CO via thermocatalytic conversion of CO₂. Various reaction tests including scans over temperature ranges, space velocity, feed ratio and pressure tests were done to evaluate the best conversions rates at different conditions. To analyze the strength of the material stability tests for 100 h was done. Surface area analysis, XRD, CO₂-TPD-FTIR, TGA-FTIR and In-situ FTIR was carried out to investigate the structural properties for both fresh and spent samples.

Over the temperature test Mo₂C outperformed every other catalyst synthesized for this study to convert CO₂ but the CO selectivity was the lowest among all other carbides prepared. As W concentration was increased an improvement in CO selectivity was observed with decreasing conversion rates, since there was no CH₄ formation to add to the CO₂ conversion which was the case for pure Mo₂C and lower W concentration carbides. For MoW_{1.5}C and WC CO selectivity was 100% throughout the temperature scan. The best temperature for the study was 500 °C at which highest conversions with full CO selectivity was observed. Since the focus of the study was to see the performance of Mo₂C and WC over RWGS reaction other mixed carbides served the purpose of proving WC as a potential catalyst for RWGS. Since the focus of the study was to

see the performance of Mo₂C and WC over RWGS reaction other mixed carbides served the purpose of proving WC as a potential catalyst for RWGS. Henceforth both abovementioned catalysts were chosen to further evaluate their performance for thermocatalytic conversion.

Increasing Space velocity clearly indicates the improvement for CO selectivity for Mo₂C decreasing the formation of methane and promoting CO production. WC did not show higher conversion upon increasing space velocity but was fully selective to CO. Feed ratio test showed increased conversion for both Mo₂C and WC, while the CO selectivity decreased with increasing CO₂ conversions for Mo₂C, WC unlike showed full selectivity to CO in addition to increased conversions. Pressuring the reaction served for improved conversion for Mo₂C but higher decrement in CO selectivity, similarly WC showed increased conversion, but the CO selectivity as compared to Mo₂C decreased to a lower extent. The stability test proved to be very useful in analyzing the durability of both Mo₂C and WC. Catalysts remained undegraded during 100 h reaction with stable conversions at 500 °C for first 24 h and increased conversion when temperature increased to 600 °C.

TPD analysis showed that CO₂ was strongly adsorbed on to the material's surface and dissociates majorly in the form of CO with little CO₂ at higher temperatures. WC desorbed CO at lower temperature around 350 °C and rest all carbides desorbed CO₂ and CO at temperatures above 500 °C. TGA-FTIR analysis for fresh and post stability samples displayed the oxidizing properties of Mo₂C and WC. Both materials turned to MoO₃ and WO₃ respectively after their thermal degradation in air at 800 °C. It was clear that a higher amount of coke formation was present onto the catalyst surface after stability which desorbed at higher temperatures during TGA. Mo₂C after converting to MoO₃ lost its weight after 700 °C to nearly 80% while WC

increased in its weight after forming WO_3 , stating that the oxide layer on W is strong enough to undergo further oxidation of reduction.

Reaction mechanism studies prove that the reaction pathway on the surface of Mo_2C is dominated by formats which undergo further hydrogenation to form methane at lower temperature of 300 °C. Conversely, for WC at 300 °C the carbonate and bicarbonate species dominate the reaction pathway and by direct conversion of CO_2 to carbonate and bicarbonate it produces CO and H_2O . Lower temperature is favored by methanation and hence the formate pathway observed on Mo_2C explains its less selective nature towards CO which is opposite in the case of WC which have less formats and higher CO selectivity.

6.2 Future Work

WC has served as a potential catalyst for RWGS reaction with full selectivity towards CO although with lower conversions of CO_2 . Future actions may include the change in the synthesis process of WC to enhance its conversion capability. Same could be done for Mo_2C as it serves the purpose of higher CO_2 conversions reaching equilibrium. Density functional theory analysis (DFT Analysis), which is in progress could explain more on the reaction mechanism and pathways for Mo_2C and WC on their CO_2 converting properties.

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