Tunable Syn Gas Ratio via Bireforming Over Coke-Resistant Ni/Mo₂C Catalyst

Adrianne Brush,^a Edward J. Evans Jr.,^b Gregory M. Mullen,^a Karalee Jarvis,^c and C. Buddie Mullins^{*abcd}

**Corresponding author; e-mail: mullins@che.utexas.edu*

^a McKetta Department of Chemical Engineering, University of Texas at Austin, 1 University Station, C0400 Austin, USA

^b Department of Chemistry, University of Texas at Austin, 1 University Station, C0400 Austin, USA

^c Texas Materials Institute and Center for Nano- and Molecular Science, University of Texas at Austin, 1 University Station, C0400 Austin, USA

^d Center for Electrochemistry, University of Texas at Austin, 1 University Station, C0400 Austin, USA

Graphical Abstract

Abstract

This study demonstrates the ability of $\text{Ni}/\text{Mo}_2\text{C}$ to catalyze the Methane Bireforming Reaction (combined Dry Methane Reforming Reaction, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$, and Steam Methane Reforming Reaction, $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$). By varying the ratio of $\text{CO}_2:\text{H}_2\text{O}$, the resulting $\text{H}_2:\text{CO}$ ratio could be tuned from 0.91 to 3.0, covering a wide range of Syn Gas ($\text{H}_2 + \text{CO}$) ratios relevant to various hydrocarbon syntheses. We also document the unusual deactivation behavior of $\text{Ni}/\text{Mo}_2\text{C}$ in this system. The catalytic activity would change from very high (greater than 50% conversion) to very low (less than 10% conversion) within 10 minutes. Despite running under conditions typically favorable for coking with a Ni catalyst (high temperature, 950°C , and excess methane), XRD, TGA, TEM, SEM, and EDX results clearly show no evidence of coking during the reaction or after deactivation. In addition, the changes to the $\text{Ni}/\text{Mo}_2\text{C}$ catalyst seen after deactivation (oxidation of Mo_2C to MoO_2 , Ni-phase changes, and catalyst morphology changes) could not be seen in the catalyst subjected to reaction conditions that were halted before deactivation could occur. This suggests a sudden, rapid deactivation “event” occurs in this catalytic system as opposed to gradual catalyst deactivation, a behavior more typically seen with catalysts.

Keywords: Nickel Molybdenum Carbide Bireforming Coke-resistant

Research Highlights:

$\text{Ni}/\text{Mo}_2\text{C}$ catalyzes methane bireforming without coking to produce 0.9:1-3:1 $\text{H}_2:\text{CO}$.

1 Introduction

Since Levy and Boudart demonstrated that tungsten carbide (WC) exhibited catalytic activity similar to Pt[1], metal carbide based catalysts have attracted a significant amount of attention due to their catalytic similarity to noble metal catalysts[2–5]. Along with WC, molybdenum carbide (Mo_2C) catalysts have been one of the primary carbides studied, particularly for reactions involving hydrocarbons[6–11]. After Green and coworkers demonstrated that WC and Mo_2C catalyzed methane reforming reactions with activities comparable to Ir and Ru[12–17], studies of methane and hydrocarbon reforming catalyzed by Mo_2C have become a popular vein of research[18–20].

Part of the interest in carbide based catalysts is due to their unusual mechanisms, especially for methane reforming reactions. While the actual catalytic mechanism(s) are still unclear, Mo_2C -based catalysts appear to balance competing oxidation and carburization reactions. This is supported by the fact that Mo_2C deactivates via oxidation to MoO_2 [12,14,17,19,21–23], and that C^{13} labeling studies have demonstrated carbon exchange between Mo_2C and CH_4 [16,22]. LaMont and Thomson [24] proposed the following as the possible competing carburization and oxidation reactions for Dry Methane Reforming (DMR):

where the catalytic cycle is represented by reactions 1-3, with (3) being the rate determining step. The first step in the deactivation of the catalyst via oxidation to MoO_2 is represented by reaction 4, with the stability of the catalyst determined by the relative rate of (4) versus (1). A mechanism for Steam Methane Reforming (SMR) was not proposed, but likely also consists of competing carburization and oxidation reactions, since Mo_2C shows similar catalytic and deactivation behavior for the SMR reaction as the DMR reaction[21]. Additionally, Darujati, Lamont and Thomson demonstrated that H_2 and CO inhibited catalyst oxidation under methane reforming

conditions and that a “carburizing ratio” (defined as: $R_s = \frac{P_{\text{H}_2} + P_{\text{CO}}}{P_{\text{CO}_2} + P_{\text{H}_2\text{O}}}$) of 0.8 or higher

stabilizes the Mo_2C catalyst at atmospheric conditions[21]. Lamont and Thomson later demonstrated that this ratio could be obtained by including H_2 or CO in the reactant stream, recycling the product stream, or operating under mass-transfer limited, high conversion conditions that give a high R_s at the catalyst surface[25].

One branch of this research has been to incorporate other metals that catalyze methane reforming into Mo_2C . In particular, the addition of Ni or Co to Mo_2C during catalyst synthesis has demonstrated an increased reactivity and stability compared to pure Mo_2C for methane reforming reactions[26–31]. Ni-based catalysts are the most commonly used in methane reforming reactions[32], where Ni is often responsible for the methane decomposition step[33]. It is likely that Ni performs a similar function in Ni/ Mo_2C catalysts. This is supported by the findings of Shi et al[27] who found that Ni/ Mo_2C with a Ni:Mo ratio of 1:2 showed high, stable activity for the DMR reaction. However, a lower Ni:Mo ratio of 1:3 oxidized to Ni/ MoO_2 with deactivation,

similar to Mo₂C catalysts, but a higher Ni:Mo ratio of 1:1 showed carbon formation, interpreted as coking, but no oxidation to MoO₃, with deactivation, a mechanism more typical of Ni-based methane reforming catalysts[34–36].

These findings demonstrate the potential benefit of using Ni/Mo₂C as a catalyst for certain methane reforming applications. A major issue in Ni-based catalysts is preventing coking, which causes catalyst deactivation and the potentially dangerous phenomenon of “whiskering,” where formation of carbon filaments can plug the reactor or destroy the catalyst[37–39]. This is particularly true for reactions run at high temperature, where coking becomes an even greater issue for Ni-based catalysts, and much work in finding coke-resistant catalysts has been done[40]. As a result, a majority of research on methane reforming over Ni/Mo₂C has focused on Dry Methane Reforming (Reaction 5)[26–28,41], which is notorious for causing coking in Ni-based catalysts. Partial Oxidation (Reaction 6)[42] and Water-Gas Shift (Reaction 7)[43] reactions have also been studied, but to a lesser degree, and, to our knowledge, Steam Methane Reforming (Reaction 8) has not been previously studied at all on Ni/Mo₂C.

Dry Methane Reforming: $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$ (5)

Partial Oxidation: $\frac{1}{2}\text{O}_2 + \text{CH}_4 \rightarrow \text{CO} + 2\text{H}_2$ (6)

Water-Gas Shift Reaction: $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$ (7)

Steam Methane Reforming: $\text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{CO} + 3\text{H}_2$ (8)

Dry Methane Reforming is attractive in situations where the methane feed is rich in CO₂, as can be the case with natural gas or biogas, or a cheap source of CO₂ is available, such as a waste CO₂ stream. One issue with Dry Methane Reforming is that the synthesis gas (“Syn Gas”: H₂ + CO) ratio produced is 1:1 H₂:CO. However, one of the most common ratios of Syn Gas used in industry is ~2:1 H₂:CO, typically used in industry to make most hydrocarbons, such as methanol, via the Fischer-Tropsch reaction[34,36,44,45]. In order to achieve the desired H₂:CO ratio, steam can be added as a reactant in order to simultaneously perform the dry reforming and steam reforming reaction, a process known as bireforming. However, bireforming is not as widely used due to the easy formation of carbon on the Ni-based catalysts at the high temperatures (up to 960°C) required for high conversion, as covered in a review by Mortensen and Dybkjaer[46]. One potential benefit of bireforming, however, is that the H₂:CO ratio can be adjusted based on the reactant mixture, allowing a range of Syn Gas ratios to be produced in one reactor. Since capital costs tend to be the most significant costs typically associated with a methane reforming process[32,47], finding a versatile methane reforming process that utilizes one reactor is highly desirable.

In this study, we demonstrate that Ni/Mo₂C can catalyze the dry methane reforming reaction, the steam methane reforming reaction, and bireforming reaction at 950°C. In addition, by varying the ratio of CO₂:H₂O that is used to reform CH₄, we can tune the resulting H₂:CO ratio of the Syn Gas product. Additionally, we document an unusual catalyst behavior in this reaction. All reactions exhibit high conversion for a certain period of time (100-300 minutes) followed by a rapid (less than 10 minutes) drop in conversion. During the period of high conversion, the catalyst exhibits no signs of coking, oxidation or other indications of any degree of deactivation. Yet, immediately after the sharp drop in conversion, the catalyst shows a significant degree of Mo₂C oxidation to MoO₃ as well as a noticeable change in the Ni phase. Further exposure to the

reaction conditions after deactivation showed increases in the degree of oxidation of the catalyst as well as no rebound in catalytic activity. Most strikingly, we find no evidence of coking in this reaction, either when the catalyst is active or deactivated. This is especially significant considering that the reaction conditions used (high temperature of 950°C and excess CH₄) are favorable for coke formation on Ni-based catalysts[48].

2 Experimental

2.1 Catalyst Synthesis

The Ni/Mo₂C catalyst was synthesized in two distinct steps: synthesis of NiMoO₄/MoO₃, and carburization of Ni/MoO₄/MoO₃ to Ni/Mo₂C. NiMoO₄/MoO₃ was synthesized similar to the process described by Shi et al.[27]. Ni(NO₃)₂·6H₂O (Alfa Aesar, 99.9985%, metals basis) and (NH₄)₆Mo₇O₂₄·4H₂O (Sigma Aldrich, 99.98%, metals basis) in quantities to make a molar ratio of 3:10 Ni:Mo were dissolved in 18MΩ Deionized (DI) H₂O. The solution was stirred and heated to 80°C for 4 hours, allowing ~80% of the H₂O to vaporize off in the process. The resulting slurry was then vacuum filtered, and the solid was dried at 120°C for 12 hours. The dried solid was then calcined in air by ramping to 550°C at 5°C/min, holding at 550°C for 4 hours, and letting cool overnight. The resulting solid, determined to be NiMoO₄/MoO₃, was then stored.

The catalysts were synthesized and subjected to reaction conditions by first loading 0.4g of the NiMoO₄/MoO₃ on top of acid-washed quartz wool in a vertical 7mm ID quartz tube reactor, heated by a furnace (Applied Test Systems Model 3210). Up to 4 gases, controlled by electronic mass flow controllers, could be flowed through the reactor simultaneously. Steam (H₂O) was introduced into the system by means of a syringe pump and heated tubing immediately upstream from the quartz tube reactor. The NiMoO₄/MoO₃ was carburized to Ni/Mo₂C in 10 standard cubic centimeters per minute (SCCM) of flowing CH₄ and 40 SCCM H₂ by ramping from 300°C to 700°C at 1°C/min, and then holding at 700°C for 2 hours. The synthesis was stopped by turning off the furnace and flowing 50 SCCM of pure nitrogen overnight.

2.2 Bireforming Reaction Runs

For reaction run samples, the catalyst was kept in the quartz tube reactor under nitrogen without exposure to atmosphere and the reaction was performed the day after the synthesis. The catalyst was heated to 950°C at 10°C/min while flowing 36 SCCM N₂. Once the reactor reached 950°C, a mixture of 48 SCCM CH₄, 36 SCCM N₂ and 36 SCCM combined H₂O and CO₂ (amounts of each varied based on experiment) was flowed to begin the reaction run. This corresponds to 120 SCCM total flow of reactants and inert, consisting of 40% CH₄, 30% N₂, and 30% combined H₂O and CO₂. A reaction run was stopped by halting flow of all species except nitrogen. The reactor's furnace was turned off, and 36 SCCM N₂ flowed through reactor while the system cooled. The samples were removed from the reactor the following day, and ground with a mortar and pestle before post-reaction characterization. Most carbide studies indicate a need to "passivate" samples in a low-oxygen environment prior to exposure to atmosphere to prevent "deep oxidation." However, duplicates of NiMo-AsSyn and NiMo-30/0-AtDeact were each performed, but given a passivation treatment of 14 hours of 100SCCM 0.5% O₂/99.5% Ar at room temperature prior to removal from the reactor. The post-reaction characterization results

were identical to those made without the passivation step, indicating that, at least for this study, passivation was not necessary.

Conversion data during the reaction was determined via injection of a continuously replenished sample loop every 10 minutes into a HP 5890 gas chromatograph (GC) using a Carboxene 1000 packed GC column and a thermal conductivity detector (TCD). Standardization injections were performed before each reaction run by performing GC injections of a stream of CH₄, N₂, and CO₂ with flowrates the same as the reaction run for that day. N₂ was utilized as an internal standard, and a comparison of the CH₄:N₂ and CO₂:N₂ peak area ratios of each injection to that found in the standardization injections was used to calculate CH₄ conversion (X_{CH₄}) and CO₂ conversion (X_{CO₂}), respectively. Calibration curves of H₂ and CO, in conjunction with the N₂ internal standard, were used to determine the effluent flowrates of H₂ and CO. The 95% confidence interval of each measurement was determined to be no more than $\pm 1.1\%$, and this uncertainty was propagated through the calculations of conversion, H₂:CO ratios, and H₂ and CO yields. Although this is discussed in more detail in section 3.1, all reaction runs at some point exhibited a sharp drop in CH₄ conversion (typically from X_{CH₄} > 50% to X_{CH₄} < 10%) between two consecutive GC injections, which was used to designate the point of catalyst deactivation. Carbon balances were performed for each data point using the equation:

$$\% \text{ Difference} = \frac{(CH_{4,out} + CO_{2,out} + CO_{out}) - (CH_{4,in} + CO_{2,in})}{(CH_{4,in} + CO_{2,in})}$$

All data points fell within $\pm 10\%$, and more than 80% of our data points fell within $\pm 5\%$.

“Snapshots” of the catalyst at various timepoints in the reaction were taken so that catalyst characterization via X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), and electron microscopy could provide insight into the catalyst before and after deactivation. Each sample was created by allowing the reaction run to progress to the timepoint desired, then stopping the reaction as described above. For the “as synthesized” (“AsSyn”) timepoint sample, the catalyst was removed from the reactor the day after synthesis without any further heating or exposure to reaction conditions. The “heated to 950°C” (“950C”) timepoint sample was heated to 950°C in 36 SCCM flowing N₂, then cooled overnight in 36 SCCM flowing N₂. The “mid-reaction” (“MidRxn”) timepoint samples were exposed to reaction conditions for 100 minutes before the reaction run was stopped. The “at deactivation” (“AtDeact”) timepoint samples were stopped 10 minutes after the first Gas Chromatography (GC) injection that showed signs of deactivation was taken. Similarly, the reaction runs for the “1 hour after deactivation” (“1hrDeact”) timepoint samples were stopped 1 hour after the first GC injection to show signs of deactivation.

The format for sample names throughout this manuscript is: “NiMo-“ (or “Mo₂C-“ for pure Mo₂C samples without Ni) %CO₂/%H₂O – Timepoint. For example, “NiMo-20/10-AtDeact” refers to Ni/Mo₂C subjected to 120 SCCM total flow of reactants, composed of 40% CH₄, 30% N₂, 20% CO₂, and 10% H₂O, until deactivation was detected from the GC and the reaction was stopped. “MidRxn” and “1hrDeact” timepoints were taken only for 3 conditions: 0% CO₂, 30% H₂O; 15% CO₂, 15% H₂O; and 30% CO₂, 0% H₂O. Mo₂C samples were handled identically to Ni/Mo₂C samples, except that commercial MoO₃ (Acros Organics, 99+%), was used as the oxide precursor due to the inability to form MoO₃ using the same process as was used to synthesize NiMoO₄/MoO₃. Due to lack of reactivity, the only Mo₂C samples are “Mo₂C-AsSyn” and

“1hrDeact” for 3 conditions: 0% CO₂, 30% H₂O; 15% CO₂, 15% H₂O; and 30% CO₂, 0% H₂O. Table 1 summarizes the various samples with their reaction conditions and analytical results.

2.3 Catalyst Characterization

BET surface area analysis was performed using a Quantachrome Instruments NOVA 2000 high-speed surface area BET analyzer at a temperature of 77 K. The data was analyzed by Quantachrome Autosorb1 software, using multipoint BET analysis from P/P₀ 0.1 to 0.3 and achieving a minimum correlation coefficient of 0.995 and a C value greater than 20. Due to the small sample sizes used in the reaction tests, surface area analysis could not be reported for the specific samples discussed in this study. However, a larger sample equivalent to “NiMo-950C” was created in a 2” tube furnace using the same flowing gases and temperature program as used to create the NiMo-950C sample. 20 SCCM CH₄ and 80 SCCM H₂ were flowed through the tube furnace while the temperature was ramped from 300°C to 700°C at 1°C/min, held at 700°C for 2 hours while the CH₄/H₂ mixture flowed, then allowed to cool overnight while 100 SCCM N₂ flowed. The next day, the sample was ramped from 25°C to 950°C at 10°C/min, then allowed to cool overnight, all while 100 SCCM N₂ flowed through the tube furnace. The sample was removed the following day and not subjected to grinding with a mortar and pestle before BET analysis in order to more closely measure the surface area seen by the reaction.

XRD analysis was performed using a Bruker D8, using a KFL Cu 2K X-ray source operated at 40kV and 40mA and utilizing a Lynx Eye detector. Quantitative Rietveld analysis was performed with TOPAZ 4.2 software, and used a refined MoO₂ structure (spacegroup: P121/c1; lattice parameters: *a*: 5.5397198 Å, *b*: 4.8527199 Å, *c*: 5.6234565 Å, β : 119.6132°) and a refined Mo₂C structure (spacegroup: pbcn; lattice parameters: *a*: 4.7346397 Å, *b*: 6.0146343 Å, *c*: 5.2192023 Å). Ni phase was not included in fit. All analysis obtained a goodness of fit (*G*) of 2 or less.

A field emission JEOL 2010F high resolution transmission electron microscope (HRTEM) operated at 200 kV was used to obtain TEM and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images and conduct analysis on the nanometer scale. The TEM is equipped with an Oxford energy dispersive spectroscopy (EDS) instrument with a SiLi detector for elemental analysis. The transmission electron microscopy (TEM) grids were prepared by sonicating a small amount of catalyst sample in toluene. A few drops of the suspended catalyst were placed on lacey carbon coated copper grids. The TEM grid was then placed in a vacuum oven and heated to 100 °C overnight to remove excess solvent.

Thermo-gravimetric analysis was performed using a Mettler TGA/DSC 1. Air was used as the ambient gas, and the sample was ramped from 25°C to 1000°C at 10°C/min.

SEM and EDS analysis were performed on a JOEL JSM-6490LV SEM in high vacuum mode, unless otherwise noted. For stand-alone SEM images, the sample was coated with gold to improve sample conductivity for higher magnification imaging. All SEM images were taken using the SEI detector, 20kV accelerating voltage, 15mm working distance, and 30nm spot size. No coating was used when performing EDS analysis. All EDS analysis was taken using 20kV accelerating voltage, 11mm working distance, and 50nm spot size. 64 scans were averaged together for the EDS maps of Mo, Ni, C, and O.

It should be noted that these analytical techniques were performed on most samples, leading to a significant amount of data to report. In the main text of this manuscript, a representative set of conditions are presented for each analytical technique, and similar figures for the remaining conditions are reported in the Supplemental Information. In most cases, the data reported in the Supplemental Information follows the same trends as the representative data reported in the main body of the manuscript, and any differences are noted.

3 Results and Discussion

Below is a table of all samples referenced in this manuscript along with select analytical results for easy comparison.

Identifiers		Oxidant Mix		Reaction Run Results			TGA	XRD Phases	
Sample Name	Timepoint	%CO ₂	%H ₂ O	Deactivation Time (min)	Total Run Time (min)	Average H ₂ :CO*	Max Wt %	%Mo ₂ C	%MoO ₂
NiMo-AsSyn	As Synthesized	N/A	N/A	N/A	N/A	N/A	129%	100%	0%
NiMo-950C	Heated to 950C	N/A	N/A	N/A	N/A	N/A	130%	100%	0%
NiMo-0/30-MidRxn	100 min Reaction	0	30	N/A	100	2.9(8)	132%	93%	7%
NiMo-15/15-MidRxn	100 min Reaction	15	15	N/A	100	1.5(7)	137%	99%	1%
NiMo-30/0-MidRxn	100 min Reaction	30	0	N/A	103	0.9(5)	136%	100%	0%
NiMo-0/30-AtDeact	At Deactivation	0	30	110	118	3.0(0)	124%	31%	69%
NiMo-5/25-AtDeact	At Deactivation	5	25	190	200	2.3(8)	129%	55%	45%
NiMo-10/20-AtDeact	At Deactivation	10	20	100	110	1.8(9)	126%	45%	55%
NiMo-15/15-AtDeact	At Deactivation	15	15	230	243	1.5(7)	127%	48%	52%
NiMo-20/10-AtDeact	At Deactivation	20	10	220	230	1.3(0)	127%	46%	54%
NiMo-25/5-AtDeact	At Deactivation	25	5	290	300	1.1(1)	128%	53%	47%
NiMo-30/0-AtDeact	At Deactivation	30	0	190	198	0.9(1)	126%	48%	52%
NiMo-0/30-1hrDeact	1hr Deactivated	0	30	100	160	3.0(0)	122%	28%	72%
NiMo-15/15-1hrDeact	1hr Deactivated	15	15	360	440	1.6(7)	120%	23%	77%
NiMo-30/0-1hrDeact	1hr Deactivated	30	0	270	330	0.9(6)	122%	28%	72%
Mo2C-AsSyn	As Synthesized	N/A	N/A	N/A	N/A	N/A	131%	100%	0%
Mo2C-0/30-1hrDeact	1hr Deactivated	0	30	0	60	N/A	119%	20%	80%
Mo2C-15/15-1hrDeact	1hr Deactivated	15	15	0	60	N/A	126%	51%	49%
Mo2C-30/0-1hrDeact	1hr Deactivated	30	0	0	60	N/A	122%	35%	65%

Table 1: Ni/Mo₂C and Mo₂C samples with their respective oxidant mixtures, time to deactivation, total time exposed to reaction conditions, average H₂:CO ratio during period of

high conversion, maximum weight % during Air-TGA, and %Mo₂C and MoO₂ as determined by Quantitative Rietveld Analysis of XRD spectra.

**All average H₂:CO ratios have a maximum 95% confidence interval of $\pm 2\%$ (± 0.08). Values for TGA and XRD analysis are reported to illustrate trends across timepoints, and are not necessarily meant to represent absolute, quantitative values.*

3.1 Bireforming Reaction Runs

Figure 1 depicts the CH₄ conversion, X_{CH₄}, (Figure 1a), CO₂ conversion, X_{CO₂}, (Figure 1b) and H₂:CO ratio (Figure 1c) versus reaction time for the various ratios of CO₂:H₂O oxidants. H₂O conversion could not be reported, as we could not effectively measure H₂O in the product stream with our setup. All conditions exhibit a similar reaction progression: each run reaches X_{CH₄} > 70% and X_{CO₂} ≈ 100% within the first 30 minutes of reaction, close to the maximum possible CH₄ and CO₂ conversions of 75% and 100%, respectively, due to excess CH₄. All runs then show a gradual decrease in X_{CH₄} and X_{CO₂} to no less than 45% and 65%, respectively, until exhibiting a rapid decrease in X_{CH₄} and X_{CO₂} to <10% and < 20%, respectively, within 10-20 minutes. This sudden decrease in conversion is considered to be an indication of the catalyst deactivation point. Designating this phenomenon as the point of deactivation is supported by the fact that no signs of reaction recovery were seen in the hour after deactivation for our “1hrDeact” samples.

As can be seen in Figure 1, the time required for the catalyst to deactivate ranged from 100 to 300 minutes, and does not seem to follow any discernable pattern with respect to CO₂:H₂O ratios. Several replicates of some conditions were performed and we found that no set of conditions had a consistent time required for catalyst deactivation. In fact, each condition showed a range of times between 100 and 300 minutes, similar to the range seen between the conditions seen in Figure 1. This suggests that the time to catalyst deactivation is likely due to some other phenomenon or catalyst property, and may not be affected significantly by the H₂O:CO₂ ratio.

Figure 1c demonstrates that the average H₂:CO ratio for pure steam reforming (0% CO₂, 30% H₂O; black curve) is 3.0 while the catalyst is active, exactly as expected for steam reforming. The pure dry reforming (30% CO₂, 0% H₂O; purple curve) results in a H₂:CO ratio of 0.91 while the catalyst is active, slightly less than the expected value of 1.0 for dry reforming. For reaction conditions containing a mixture of H₂O and CO₂, the subsequent H₂:CO ratios decrease from 2.38 to 1.11 as less H₂O and more CO₂ is used in the oxidant mixture, as can be seen in Table 1. In fact, the H₂:CO ratios for all conditions are close (<0.12 difference) to the values expected, assuming complete conversion of H₂O and CO₂. However, the H₂:CO ratios are all slightly less than expected. This is likely due to the Water Gas Shift Reaction (WGSR, H₂O + CO → H₂ + CO₂), which has a K_{eq} of 0.68 at 950°C[49], favoring H₂O + CO, but could also indicate some degree of oxidation of carbon in the catalyst to produce CO.

The absolute molar yields of H₂ and CO per mole of CH₄ consumed were calculated and are plotted in Figures S1a and S1b, respectively. The values for each run closely match what would be expected from each set of conditions, indicating that the methane reforming reactions are the dominant reactions in this system. Additionally, after deactivation, increases in H₂ molar yield and decreases in CO molar yield are seen with H₂O rich conditions, while the opposite

(decreases in H₂ molar yields and increases in CO molar yields) is seen with CO₂ rich conditions. This phenomenon is mirrored in the H₂:CO ratio, plotted in Figure 1c, where the H₂:CO ratio increases in H₂O-rich conditions and decreases in CO₂-rich conditions after catalyst deactivation. This is consistent with contributions from the Water Gas Shift Reaction due to an increase in H₂O and/or CO₂ with deactivation. However, it is likely that the oxidants also oxidize the catalyst after deactivation, as indicated by increases in both H₂ and CO yield in the first data point after deactivation for many of the conditions.

Using BET surface area analysis, Ni/Mo₂C heated to 950°C was determined to have a specific surface area of 5.9 m²/g. This is less than the 9 – 35 m²/g range seen in other Ni/Mo₂C catalysts reported by Shi et al.[27] and Cheng and Huang[26]. Based on the reactant flowrates, Ni/Mo₂C catalyst mass of 0.3g, and a methane conversion of 50%-75% while active, the areal reaction rate of this system is calculated to be $2.3 \times 10^{-5} - 3.5 \times 10^{-5}$ (moles CH₄ reacted)m⁻²sec⁻¹. However, since the active sites of the catalyst are unknown in this system, it is difficult to compare to more traditional catalysts, where activity is most commonly described in terms of turnover frequency (TOF).

Samples of Mo₂C without Ni were also subjected to the three major reaction conditions (0% CO₂/30% H₂O, 15% CO₂/15% H₂O, and 30% CO₂/0% H₂O), and the CH₄ conversion data is shown in Figure S2. As can be seen in Figure S2, all of the Mo₂C catalysts show very little activity for methane reforming (<5% X_{CH₄}), especially when compared to the corresponding Ni/Mo₂C catalysts. The steam reforming run appeared to show higher initial activity (as high as 25% X_{CH₄}), but that may be caused by experimental error due to excess H₂O that can occur at the beginning of a reaction run from priming the syringe pump and heated steam lines. All reaction runs were allowed to run for 1 hour to confirm the persistently low activity.

Figure 1: CH_4 Conversion (a), CO_2 Conversion (b), and $H_2:CO$ production ratio (c) for various amounts of CO_2 and H_2O oxidants. Error bars represent the 95% confidence interval for each measurement.

3.2 XRD Analysis

Figure 2 depicts the XRD spectra for the Ni/Mo₂C catalyst at different timepoints during a representative dry reforming reaction run (40% CH_4 , 30% N_2 , 30% CO_2 and 0% H_2O). From bottom to top in Figure 2, the spectra represent: 1) NiMo-AsSyn; 2) NiMo-950C; 3) NiMo-30/0-MidRxn; 4) NiMo-30/0-AtDeact; and 5) NiMo-30/0-1hrDeact. Similar progressions are shown for pure steam reforming (0% CO_2 , 30% H_2O) and 50/50 dry/steam reforming (15% CO_2 , 15% H_2O) in Figures S3 and S4, respectively, and follow the same trends as Figure 2. XRD of the catalyst oxide precursor confirming it to be composed of NiMoO₄/MoO₃ can be found in Figure S5.

Carburization of the NiMoO₄/MoO₃ precursor causes the MoO₃ phase to carburize to Mo₂C, as seen in Figure 2. However, after carburization, the Ni is no longer in a NiMoO₄ phase. Instead, the Ni appears to be part of a Ni⁰-rich phase with some Mo incorporated into it, as will be discussed in more detail below. With heating to 950°C, the Ni-rich phase and Mo₂C phases both stay chemically unchanged, but appear to sinter into larger crystallites, indicated by the sharper

XRD peaks compared to “NiMo-AsSyn”. Quantitative Rietveld analysis suggests the crystallite size increases from ~40nm to ~150nm with heating to 950°C. 100 minutes into the dry reforming reaction run, the Ni-rich phase and the Mo₂C phase are both still present and unchanged compared to “NiMo-950C”. Most surprisingly, though, is a lack of peaks corresponding to MoO₂ or graphite, which would indicate deactivation due to oxidation or coking, respectively. However, the catalyst immediately after deactivation shows clear peaks corresponding to MoO₂. Running reaction conditions for 1 hour after deactivation results in more oxidation, as seen by the increase in the main MoO₂ peak at $2\theta=26.0^\circ$ relative to the main Mo₂C peak at $2\theta=39.3^\circ$ compared to the spectra for “NiMo-30/0-AtDeact”. Figure S6, which displays the XRD spectra for the Ni/Mo₂C catalyst “at deactivation” for the remaining oxidant mixtures, demonstrates that this behavior is common to all tested mixtures of CO₂ and H₂O. It is unclear, however, if the oxidation of the catalyst itself is responsible for catalyst deactivation or is merely a byproduct of exposure to a more oxidizing reactant stream once deactivation occurs.

XRD spectra of the Mo₂C catalysts are shown in Figure S7. Similar to “Ni/Mo₂C-AsSyn”, “Mo₂C-AsSyn” showed broad Mo₂C features, indicative of small crystallite size (on the order of ~20nm, according to Quantitative Rietveld Analysis), but no MoO₂ features. All three of the deactivated catalysts exhibited peaks for both Mo₂C and MoO₂. In addition, the Mo₂C peaks in the deactivated catalysts were sharper than for “Mo₂C-AsSyn”, indicating sintering of Mo₂C into larger crystallites during heating to 950°C in N₂ and one hour of reaction conditions.

Quantitative Rietveld analysis was performed on the XRD spectra for every sample, and the normalized %MoO₂ and %Mo₂C are reported in Table 1. The Rietveld analysis confirms what a qualitative inspection of the XRD spectra suggests: the %MoO₂ relative to %Mo₂C increases with prolonged exposure to the reaction conditions after deactivation. The lack of a MoO₂ feature through the reaction, the sudden appearance of MoO₂ at deactivation, and the growth of the MoO₂ feature with continued exposure to reaction conditions after deactivation show definitively that the onset of oxidation occurs at deactivation and the catalyst continues to oxidize after deactivation. The fact that MoO₂ accounts for ~50% of the catalyst immediately after deactivation for all reaction conditions indicates a high degree of oxidation within a short span, mirroring the rapid decline in conversion.

XRD of Catalyst Through Synthesis and Dry Reforming Reaction

Figure 2: a) XRD of catalyst at various timepoints during synthesis and dry reforming reaction; b) Reference spectra with dashed lines extending into 2a for ease of phase identification.

The Nickel-containing phase also undergoes a transformation during synthesis and after deactivation, as can be seen in Figure 3, a close-up of the Ni-region in XRD for the dry reforming reaction progression spectra shown in Figure 2. Similar close-ups for the steam reforming reaction, 50/50 dry/steam reaction, and all of the “at deactivation” samples can be seen in Figures S8, S9, and S10, respectively. As discussed above, and seen in Figure S5, the Ni in the catalyst precursor seems to be present as part of a NiMoO₄ phase. After synthesis and through the first 100 minutes of the reaction, peaks appear in the XRD pattern at $2\theta=44.2^\circ$ and $2\theta=51.4^\circ$, in between the expected positions for Ni⁰ and Mo_{0.09}Ni_{0.91}. Since Mo can incorporate into the Ni phase up to ~10% Mo[50], this Ni-rich phase is likely pure Ni⁰ with up to 9% Mo incorporated into it.

After deactivation, however, the Ni-rich peaks shift lower, to $2\theta=43.0^\circ$, $2\theta=43.6^\circ$ and $2\theta=50.8^\circ$. The features at $2\theta=43.0^\circ$ and $2\theta=43.6^\circ$ appear to be at least two distinct peaks, which can be seen more clearly in Figure S10. The most likely match to these peaks is a mixture of NiO, which has a major peak at $2\theta=43.1^\circ$, MoNi₄, which has a major peak at $\sim 43.5^\circ$ and minor peaks at $2\theta=50.4^\circ$ (larger) and 51.2° (smaller), and Mo_{1.08}Ni_{2.92}, which has a major peak at 43.0° and a minor peak at 50.1° . However, none of the minor peaks of the MoNi_x phases line up well with the small, broad peak at 50.8° . The one other major peak for NiO, at $2\theta=37.1^\circ$, would be obscured by MoO₂ features at the same angle, and cannot be seen. In addition, a peak at $2\theta=40.6^\circ$ in the deactivated catalyst is consistent with Mo⁰, possibly formed during the oxidation of Mo₂C to MoO₂ or the oxidation of Mo_{0.09}Ni_{0.91} to NiO. The slight shift to higher 2θ relative to the reference spectra may be indicative of some Ni incorporation into the Mo phase. Overall, these results suggest that, during catalyst deactivation, some of the Ni is oxidized, while other Ni regions incorporated more Mo, and some Ni possibly incorporated into a Mo phase created during deactivation. Interestingly, the Mo₂C samples do not have the same Mo⁰ feature in their

spectra, indicating that the presence of Ni may be involved in the formation of the Mo^0 phase during deactivation. Similar to the oxidation of Mo_2C to MoO_2 , it is unclear whether the changes in the Ni phase are responsible for catalyst deactivation, or merely a byproduct of exposure to a more oxidizing reactant stream after catalyst deactivation.

Close-up of Ni region in XRD - Dry Reforming Reaction Progression

Figure 3: a) Close-up of Ni-region in XRD of catalyst at various timepoints during synthesis and dry reforming reaction; b) Reference spectra with dashed lines extending into 3a for ease of phase identification.

3.3 TEM

Figure 4 displays high magnification TEM images of the Ni/Mo₂C at four points in the mixed methane reforming reaction process: immediately after synthesis (4a), 100 minutes into the reaction (“mid-reaction”; 4b), at deactivation (4c), and 1 hour after deactivation (4d). Graphitic layers of carbon surrounding the bulk material can be seen for the as-synthesized and mid-reaction catalyst sample (Figure 4a and 4b). The spacing between the graphitic layers was measured to be 3.4Å using the Gatan Digital Micrograph program, which is consistent with the distance between the planes of graphitic layers. However, once the catalyst deactivates, these carbon layers are no longer found, as shown in Figures 4c and 4d. This suggests that the catalyst does not coke with deactivation, but rather excess carbon in the catalyst is actually consumed during this reaction, despite operating at conditions that would normally cause coking in Ni-based catalysts.

Figure 4: HRTEM images showing the disappearance of the graphitic layers on $\text{Ni}/\text{Mo}_2\text{C}$ particles over the course of the 50/50 Dry/Steam reforming reaction: a) NiMo-AsSyn , b) NiMo-15/15-MidRxn , c) $\text{NiMo-15/15-AtDeact}$, d) $\text{NiMo-15/15-1hrDeact}$.

Figure 5 displays an HAADF-STEM image of the lacey carbon support of the “ $\text{NiMo-15/15-AtDeact}$ ” sample. Small nanoparticles 1-10nm in size can be seen on the carbon support film as bright white dots, indicating the particles are composed of elements with high atomic mass. An image of these small particles alongside of a larger particle can be seen in Figure S11. This phenomenon is seen with the “at deactivation” and “1 hour deactivated” catalyst samples but is not present in the “as-synthesized” and “mid-reaction” catalyst samples. When conducting EDS on the carbon film of the TEM grid (Figure S12), we see very little to no molybdenum or nickel signal at their major characteristic energies of 2.3 keV and 7.4 keV, respectively, for the as-synthesized and mid-reaction samples (Figures S12a and S12b). However, molybdenum and nickel peaks are readily seen on the carbon support film in the at-deactivation (Figure S12c) and 1 hour deactivated (Figure S12d) samples. This suggests that the shedding of these small nanoparticles likely coincides with catalyst deactivation and are rich in nickel and molybdenum.

Figure 5: HAADF-STEM of NiMo-15/15-AtDeact. The small particles ranging from 1 to 10nm in size observed on the TEM grid carbon film appear as white dots. EDS indicates that they are likely composed of Ni and Mo.

3.4 TGA Analysis

Figure 6 shows the weight % (Figure 6a) and mass-normalized heat flow (Figure 6b) versus temperature for the Air-TGA analysis of the Ni/Mo₂C catalyst at various timepoints in the pure dry reforming (30% CO₂, 0% H₂O) reaction. Similar Air-TGA plots of the Ni/Mo₂C catalyst for pure steam reforming (0% CO₂, 30% H₂O) and the 15% CO₂/15% H₂O condition, are shown in Figures S13 and S14, respectively. Air-TGA plots of the Ni/Mo₂C catalyst “at deactivation” for the remaining reaction conditions (5/25, 10/20, 20/10, and 25/5 of CO₂/H₂O) are shown in Figure S15. All conditions show similar behavior to the Air-TGA plots about to be discussed. Additionally, Air-TGA plots of commercial MoO₃, commercial Mo₂C, synthesized Mo₂C, and synthesized Mo₂C subjected to 1 hour of 15% CO₂/15% H₂O reaction conditions are shown in Figure S16 for comparison to the Ni/Mo₂C samples.

Figure 6: Air-TGA plots of sample weight percent (a) and heat flow (b) for Ni/Mo₂C at various timepoints during the dry reforming reaction.

In Figure 6, the plot of NiMoO₄/MoO₃ (gray) shows no change in weight % until ~790°C, where there is also a large negative spike in heat flow, as seen in Figure 6b. The negative spike in heat flow at 790°C, indicative of an endothermic process, is most likely the transition of a MoO₃ solid phase to the liquid phase.[51] The decline in weight % above 790°C for MoO₃ is most likely due to the subsequent greater incorporation of oxygen to the point that the Mo/O system can exist in the gas phase and is slowly evaporated off.[51] These interpretations are further confirmed by the fact that pure MoO₃ exhibits the same behavior, as can be seen in Figure S16. However, in the case of pure MoO₃, the weight % eventually reaches zero by 980°C, while the NiMoO₄/MoO₃ decreased to only ~24% by 1000°C. This indicates that some or all of the Ni phase(s) in the NiMoO₄/MoO₃ sample do not evaporate off.

The Ni/Mo₂C samples from different reaction timepoints all exhibit a common behavior: no change in weight % until ~400-500°C, when each sample increases in weight % to some maximum weight %, then followed by a decline in weight % starting at ~790°C and continuing until the end of the analysis at 1000°C. The increase in weight % for each sample coincides with a large positive amount of heat flow, indicative of an exothermic process. This suggests that the Mo₂C in the Ni/Mo₂C samples is oxidizing to MoO₃ in the region. This assertion is supported by a few pieces of evidence. First, this same behavior is characteristic of pure Mo₂C samples, as can be seen in Figure S16. Second, the maximum weight % of commercial Mo₂C is 140%, almost exactly the theoretical increase in weight % of 141% expected by the Mo₂C to MoO₃ transformation. Finally, both the Mo₂C and Ni/Mo₂C samples exhibit the same endothermic spike at 790°C and decline in weight % starting at 790°C as seen in the MoO₃ and NiMoO₄/MoO₃ samples.

A closer inspection of the maximum weight % of the Ni/Mo₂C samples provides an insight into the catalyst at different timepoints in the reaction. The maximum weight percent measured for “NiMo-AsSyn,” “NiMo-30/0-MidRxn,” “NiMo-30/0-AtDeact,” and “NiMo-30/0-1hrDeact” samples are 130%, 136%, 126% and 121%, respectively. This trend is consistent across conditions, as can be seen in Table 1: The “MidRxn” samples have the highest maximum weight %, followed by the “AsSyn” and “950C” samples, the “AtDeact” samples, and finally the “1hrDeact” samples.

The theoretical maximum weight % for pure Ni/Mo₂C samples, assuming complete oxidation to Ni/MoO₃, is 135%. There are two likely explanations for a sample that attains a maximum weight % less than 135%. First, there could be interstitial carbon that contributes mass initially, but is combusted to gaseous CO₂ during TGA. Since none of the curves exhibit a weight % less than 100% below 800°C, this combustion likely occurs at the same time as Mo₂C oxidation (400°C – 750°C). This is likely the case for NiMo-AsSyn, since HRTEM clearly shows a carbon layer in the as-synthesized catalyst (Figure 4), and no oxide features are seen in the XRD. Additionally, NiMo-AsSyn exhibits the largest amount of exothermic heat released of all the samples, which would be consistent with some combustion.

The second explanation for a maximum weight % less than 135% would be that some of the Mo₂C has oxidized to MoO₂, since oxidation from MoO₂ to MoO₃ results in less weight gain than oxidation from Mo₂C to MoO₃. This is likely the case for the “AtDeact” and “1hrDeact” samples. This is supported by the clear presence of MoO₂ in the XRD spectra for the samples at these two timepoints. In addition, “1hrDeact” samples show smaller maximum weight % values than the “AtDeact” samples, consistent with a greater degree of MoO₂ compared to Mo₂C, as suggested by the Quantitative Rietveld XRD Analysis trends. The “1hrDeact” samples have the lowest amount of exothermic heat released, and the “AtDeact” samples have the second-to-lowest amount of exothermic heat released, consistent with partially oxidized samples instead of samples with excess carbon.

The maximum weight % of the “MidRxn” samples are all very close the theoretical maximum of 135%. These results suggest that the carbon layers seen in HRTEM images of the catalyst mid-reaction are likely not as prevalent as the carbon layers seen in the as-synthesized catalyst images. In addition, these results indicate that little, if any, oxidation of the catalyst has occurred, consistent with the Quantitative Rietveld XRD Analysis.

Overall, these TGA results give support to the proposed catalyst life progression. NiMoO₄/MoO₃ is carburized to form Ni/Mo₂C with significant interstitial carbon layers. When exposed to reaction conditions, a significant amount of the carbon layers are oxidized off, but the catalyst remains Ni/Mo₂C with little to no oxidation to MoO₂. Once deactivation occurs, however, a significant amount of Mo₂C oxidizes to MoO₂, and more Mo₂C oxidizes to MoO₂ as the catalyst is further exposed to reaction conditions after deactivation occurs. It is possible that the carbon layers are crucial to catalyst stability and, after all the excess carbon is oxidized off during the reaction, rapid catalyst deactivation occurs. Finally, these TGA results provide a clear indication that no coking of this Ni-based catalyst occurs when subjected to reaction conditions or with deactivation.

3.5 SEM-EDX

Figure 7 shows a set of SEM images of the Ni/Mo₂C catalyst exhibiting the morphological changes that occur between different timepoints in the reaction. In Figure 7a, the 1,000x image shows that the synthesized catalyst seems to be composed of particulates on the order of 1 to 20 microns in size. Upon closer inspection of the particulates at 100,000x, many features ~100nm or less in size are clearly evident. The catalyst heated to 950°C, Figure 7b, as well as the catalyst 100 minutes into the reaction, Figure 7c, show particulates of similar size as compared to the as-synthesized catalyst in the 1,000x images. However, in the 100,000x images, the features smaller than 100nm seem less prevalent in 7b and 7c than in 7a, indicating a degree of sintering during the heating and reaction processes.

The deactivated catalyst, both immediately after deactivation, Figure 7d, and 1 hour after deactivation, Figure 7e, exhibits a significant morphological change compared to the active catalyst. The particulates of the deactivated catalyst appear to be larger overall, with some particles almost 100 microns in size. In addition, the sub-100nm features seen in the active catalyst are not seen in the deactivated catalyst. Instead, there appears to be an agglomeration of several ~200-500nm sized regions. Quantitative Rietveld Analysis determined the crystallite sizes of Mo₂C and MoO₂ in the at-deactivation and 1 hour after deactivation samples to generally be between 300nm and 800nm, suggesting that these regions may be individual crystallites. Figure S17, which displays TEM images of NiMo-AsSyn, NiMo-15/15-MidRxn, NiMo-15/15-AtDeact, NiMo-15/15-1hrDeact, confirms these observations. These trends are consistent across all of the reaction conditions, as can be seen in Figures S18-S36, which depict SEM images of all the samples listed in Table 1.

Most striking in these images is the lack of any carbon filaments, indicative of “whiskering,” in the catalyst at any point during the reaction process. Whiskering is a common and dangerous problem for Ni-based catalysts, especially under conditions where carbon formation is typically seen, such as the high temperatures and excess methane conditions used in this study. While an SEM image of a small portion of catalyst sample cannot be used to make any definitive claims about the rest of the sample, the lack of any evidence of whiskering in any images taken, combined with the XRD and TGA results gives strong support to the claim that whiskering does not occur, even under conditions favorable for coking to occur.

Figure 7, SEM images at 100,000x (left images), 10,000x (middle images), and 1,000x (right images) for a) NiMo-AsSyn, b) NiMo-950C, c) NiMo-15/15-MidRxn, d) NiMo-15/15-AtDeact, e) NiMo-15/15-1hrDeact.

Figure 8 depicts an SEM image (a) with EDX mapping of Mo (b), Ni (c), O (d) and C (e) for NiMo-30/0-MidRxn at 10,000X magnification. Similar SEM/EDX images at magnifications of 2,000x and 10,000x of NiMo-AsSyn, NiMo-0/30-MidRxn, NiMo-15/15-MidRxn, NiMo-30/0-

MidRxn, NiMo-0/30-AtDeact, NiMo-15/15-AtDeact, NiMo-30/0- AtDeact, NiMo-0/30-1hrDeact, NiMo-15/15-1hr Deact, and NiMo-30/0-1hr Deact are shown in Figures S37-S56. Notice that many of the regions of high Ni concentration, indicated by bright yellow spots, have corresponding low concentrations of Mo, indicated by dark regions, as can be seen by comparing Figure 8b and Figure 8c. This suggests that the Ni is often present as a Ni-rich phase, on the order of a few microns in size, with little or no Mo incorporated in it, consistent with the XRD results. However, there are several regions of high Ni content that also exhibit some degree of Mo across all timepoints in the reaction. Similarly, the EDX picked up lower levels of Ni in each sample in regions not part of a large, distinct Ni-rich area. These phenomena can be caused by subsurface or nearby Mo or Ni, due to the ~micron-sized penetration depth of the EDX method. However, in the case of Ni, it is also possible that there are lots of very small crystallites of Ni distributed within the catalyst, as suggested by the TEM results.

The most striking aspect of this set of EDX images is the relative similarity of the element distribution, specifically the Ni regions, within the catalyst at all timepoints in the reaction run. All of the samples seem to show several distinct regions of high Ni concentration, with the sizes of these regions estimated at ~1-3 μ m. In addition, no major changes in the micron-scale Ni regions' size or distribution can be seen as the reaction progressed from "as-synthesized" to "mid-reaction" to "at deactivation" to "1 hour after deactivation." The mapping of O and C does not show any definitive trends or obvious regions of high O or C concentration within the catalyst. It is unknown whether this is due to relatively uniform distribution of C and O within the Ni/Mo₂C/MoO₂ material, or whether it is due to ambient hydrocarbons and surface oxides. It is worth noting that while there does appear to be carbon present in most of the regions where Ni is also present, there does not appear to be a higher concentration of carbon near the Ni regions. This, along with the XRD, TGA, and SEM results, indicates that there is no evidence of coking or whiskering near the Ni regions, as would be expected for a Ni-based catalyst operating under the conditions used in this study.

Figure 8: EDX mapping of NiMo-30/0-MidRxn at 10,000x. a) SEI; b) Mo; c) Ni; d) C; e) O. Image has been slightly brightened and white gridlines added for ease of visual inspection.

4 Conclusions

The Ni/Mo₂C catalyst is able to catalyze both the dry methane reforming and steam methane reforming reactions at 950°C. In addition, Ni/Mo₂C can catalyze the bireforming reaction by running CH₄, N₂, CO₂, and H₂O together. The H₂:CO ratios formed from different ratios of CO₂:H₂O follows the trend expected: the H₂:CO ratio increases from ~0.9 to ~3 as the oxidant mix goes from consisting entirely of CO₂ to consisting of a mixture of CO₂ and H₂O to consisting entirely of H₂O. This conclusively demonstrates the ability to tune the H₂:CO ratio for methane reforming by co-running the dry reforming and steam reforming reactions over Ni/Mo₂C. In every reaction condition tested, the catalyst exhibited a similar reaction progression: very high initial activity that slowly declines over a period of 1-5 hours, then a rapid decline in conversion to less than 10% within 10 minutes which indicates catalyst deactivation.

Despite running the reaction at high temperature and with excess methane, this catalyst does not show any signs of coking or whiskering during the reaction or after deactivation, as would be expected for a Ni-based catalyst. Instead, the catalyst appears to deactivate via oxidation of the Mo₂C to MoO₃, as is more typical of Mo₂C based catalysts. In addition, with deactivation, the Ni phase appears to change as well, likely oxidizing somewhat and/or incorporating Mo into the Ni⁰ phase. Future studies to determine the reaction and deactivation mechanisms would provide crucial insights into how to most effectively utilize this coke-resistant Ni-based methane reforming catalyst.

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