Fischer-Tropsch Synthesis over Early Transition Metal Carbides and Nitrides: CO Activation and Chain Growth

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Abstract

A series of transition metal carbide and nitride catalysts (Mo_2C , Mo_2N , W_2C , W_2N , VC , VN , NbC , and NbN) were prepared and evaluated for Fischer-Tropsch synthesis. The activity trend was $\text{Mo}_2\text{C} \sim \text{W}_2\text{C} \sim \text{VN} \sim \text{NbN} > \text{Mo}_2\text{N} \sim \text{W}_2\text{N} \gg \text{VC} \sim \text{NbC}$, with carbides and nitrides of the same parent metal exhibiting significantly different turnover frequencies (TOF). For example, the Mo_2C catalyst exhibited a TOF of 0.36 s^{-1} at 300°C whereas the TOF for the Mo_2N catalyst was 0.04 s^{-1} . The carbides and nitrides favored light hydrocarbons ($\text{C}_1\text{-C}_4$) exhibiting α values between $0.31 - 0.43$ at 290°C , and were active for the water-gas shift reaction. Results from temperature programmed desorption and reaction indicated that both the Mo_2N and Mo_2C catalysts are capable of direct (without H_2 assistance) CO dissociation; however, the activation barrier is much higher over Mo_2N than Mo_2C . The results also indicate that C-C coupling over the Mo_2C surface was facilitated by molecularly adsorbed CO (without H_2 pre-adsorption), suggesting the primary pathway to C_{2+} hydrocarbons was through the oxygenate mechanism.

Keywords: Fischer-Tropsch, carbide, nitride, CO dissociation, CO hydrogenation, CO insertion mechanism, oxygenate mechanism

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1. Introduction

Carbon monoxide and hydrogen, simple building blocks available in syngas, can be combined to produce hydrocarbon and oxygenate-based fuels and chemicals via a number of different pathways including methanation, methanol synthesis, mixed alcohol synthesis, Fischer-Tropsch synthesis (FTS), and Fischer-Tropsch-to-Olefins [1, 2]. All of these pathways require a catalyst that can perform some, if not all, of the following steps: (i) H_2 activation, (ii) CO adsorption and activation, (iii) C-O bond cleavage, (iv) C-C bond formation, and (v) hydrogenation. Early transition metal carbides and nitrides have been demonstrated to be active for syngas conversion reactions, catalyzing the aforementioned reaction steps, albeit to varying degrees depending upon metal/non-metal atom type, reaction conditions, and presence of promoters [3-21]. Kojima et al. were among the first to investigate the CO hydrogenation activities of early transition metal carbides [3-5]. At atmospheric pressure, they found that carbides such as TiC, TaC, Mo_2C , WC, and W_2C produced primarily CH_4 , light hydrocarbons ($\text{C}_2\text{-C}_4$), CO_2 , and H_2O ; however a small amount of higher hydrocarbons were also observed (C_{5+}). Ranhotra et al. compared the CO hydrogenation performance of Mo_2C and Mo_2N catalysts at atmospheric pressure and reported that the activity for the face centered cubic (fcc) phases were similar [6]. Kim et al. found that supported and unsupported Mo_2C catalysts exhibited CO hydrogenation rates at atmospheric pressure similar to those for Ru [7], a metal that is known to be an effective CO hydrogenation catalyst. The effects of pressure [8] and promoters such as K [12, 17, 19], Rb [20] and Ru/Co [9, 10] have also been explored. While the utility of early transition metal carbides and nitrides for syngas conversion reactions has been demonstrated, very little is known about the reaction mechanisms over these materials.

Recently, Medford et al. investigated the elementary steps of syngas reactions over Mo_2C (001) using computational tools [22]. They reported that the Mo-terminated Mo_2C (001) surface behaved similarly to Ru/Rh with regards to carbon reactivity, but acts more like Mo/W with regards to oxygen reactivity. These results are consistent with recent work exploring the deoxygenation of biomass-derived intermediates over early transition metal carbides, which demonstrated that these materials favor C-O bond cleavage due to their strong affinity for oxygen [23-25]. Medford et al. also reported that the activation energy for CO dissociation over Mo_2C was relatively low (1.43 eV), and that the hydrogenation of CO led to significantly lower CO dissociation barriers [22]. Moreover, coupling of HCO species was observed to be more favorable than coupling of CH_x species. These findings suggest that FTS over Mo_2C catalysts may follow a mechanism involving oxygenate intermediates.

The key objectives of work described in this paper were to evaluate the FTS activities and selectivities of a series of early transition metal carbides and nitrides (Mo_2C , Mo_2N , W_2C , W_2N , VC, VN, NbC, and NbN) under industrially-relevant conditions and elucidate the mechanisms for production of key products over these materials. The materials were characterized by X-ray diffraction (XRD), nitrogen physisorption, and pulse chemisorption, and their catalytic properties were evaluated for FTS at 25 bar and 200 – 320 °C. The elementary reaction steps and the interactions of these materials with H_2 and CO were probed using temperature programmed desorption (TPD) and temperature programmed reaction (TPRxn). The results provide insight into the preferred reaction pathway and the effect of the non-metal on reactivity, and can be used to guide further catalyst improvements.

2. Experimental

2.1. Catalyst Preparation and Pretreatment

High surface area carbide and nitride materials were synthesized using a temperature programmed reaction procedure [13, 26-28]. The oxide precursors (particle size of 125–250 μm) were supported in a tubular quartz reactor and placed in a vertical furnace. The synthesis conditions for the Mo, W, V, and Nb carbides and nitrides are provided in Table S1. These parent metals were chosen because they form stable carbide and nitride structures, can be synthesized at temperatures below 1000 $^{\circ}\text{C}$, and can achieve moderate to high surface areas. The synthesis conditions were developed based on previous research in our group [13, 26-30] and other references [31]. Upon completion of the temperature program, the reactor was quenched to room temperature (RT), and the sample was then passivated with 1% O_2/He mixture flowing at 20 mL min^{-1} for 6 h. This passivation step is required to prevent bulk oxidation of the catalyst upon exposure to air due to the pyrophoric nature of these materials.

The carbide and nitride catalysts were pretreated prior to FTS reaction rate measurements and chemisorption experiments. The catalysts were pretreated at atmospheric pressure in the gas used during synthesis flowing at 200 mL min^{-1} for 4 h at the maximum temperature used during synthesis (Table S1). For example, Mo_2C was pretreated at 590 $^{\circ}\text{C}$ in 15% CH_4/H_2 . These conditions were chosen to remove the oxygen deposited during the passivation step and return the catalyst to its as-synthesized state.

2.2. Materials Characterization

The bulk crystal structures of the passivated carbide and nitride catalysts were characterized using XRD. The diffraction experiments were performed using a Rigaku miniflex X-ray diffractometer with a $\text{Cu-K}\alpha$ ($\lambda = 1.54 \text{ nm}$) radiation source and a Ni filter. A range of $20^{\circ} < 2\theta < 90^{\circ}$ was scanned at a rate of 5 $^{\circ} \text{min}^{-1}$ with a 0.02 $^{\circ}$ step size.

Surface area and CO pulse chemisorption measurements were carried out using a Micromeritics 2910 AutoChem Chemisorption analyzer. Prior to these measurements, the catalysts were pretreated as described above, degassed in flowing He at a temperature 10 °C higher than the pretreatment temperature to remove any adsorbed H₂, and then cooled to RT. The BET surface areas were measured using N₂ physisorption at 77 K. The CO pulse chemisorption experiments were performed at RT by repeatedly dosing the sample with pulses containing 5% CO/He until complete saturation was achieved. The CO uptakes were determined from peak areas recorded using a thermal conductivity detector (TCD). Site densities were calculated assuming a stoichiometry of one CO molecule adsorbed per active site.

2.3. Fischer-Tropsch Synthesis Experiments

The FTS rate and selectivity measurements were carried out in a 4.6 mm I.D. stainless steel U-tube fixed bed reactor. Catalyst samples (40–200 mg) were supported on a quartz wool plug inside the reactor. The reactions conditions were 25 bar, H₂/CO = 2, gas hourly space velocity (GHSV) of 9,600–42,000 h⁻¹, and two temperature ranges: 200–250 °C and 270–320 °C. The GHSV was calculated by dividing the volumetric flow rate of the feed (mL h⁻¹) by the volume of the catalyst bed (mL). The two temperature ranges were selected to cover the typical temperatures used industrially for FTS, allow for adequate control of reaction temperature, and maintain differential reaction conditions. The amount of sample used was also adjusted to maintain CO conversions below 10% (differential conditions). The samples were diluted with low surface area SiO₂ (<1 m² g⁻¹, particle size: 125–250 μm) to maintain a constant bed height and volume as well as to prevent channeling, avoid problems with axial dispersion, and minimize temperature gradients in the bed. In addition to the carbide and nitride materials, two commercial catalysts, Fe/SiO₂ and Co/Al₂O₃, were obtained from Johnson-Matthey and used as bench-mark

catalysts. The pretreatment conditions and reaction conditions for these materials were selected based on the supplier's recommendations.

H₂, CO, and N₂ (internal standard) were introduced into the reactor using mass flow controllers and the feed lines to the reactor were heated to 150 °C. The pressure of the system was set and maintained using a back pressure regulator located downstream of the reactor. All effluent lines were maintained at 200 °C to ensure that reaction products up to C₁₀ remained in the vapor phase. Heavier products were condensed out in a trap; however, no liquids were observed after any of the 40 h time on stream (TOS) experiments. The concentrations of reactants and products in the effluent gas were analyzed using a Varian 3800 gas chromatograph equipped with two TCDs and a flame ionization detector. The GC responses for reactants and products were calibrated using gas standards (Scott Master Class) and gravimetrically-prepared liquid standards. The GC sampled the effluent gas every 45 min.

The FTS performance of the carbide and nitride catalysts was evaluated using rate and selectivity measurements. The catalysts were allowed to stabilize for 8 h before steady-state rate measurements were recorded. Rates were recorded at each temperature for 4 h, allowing for 6 samples to be taken by the GC at each temperature. An example of the rate data as a function of TOS for the Mo₂C catalyst over the temperature range of 200 – 250 °C is shown in Fig. S1. The product formation rate on a C₁ basis was calculated according to Equation 1:

$$r = \left(\frac{F_{exit}}{W_{cat}} \right) \sum_i C_i Z_i \quad \text{Eqn. 1}$$

where F_{exit} is the flow rate of the effluent gas from the reactor, W_{cat} is the weight of catalyst in the reactor, C_i is the molar concentration of component i in the effluent stream determined from GC analysis, and Z_i is the carbon number of component i . The components are the reaction products (i.e., hydrocarbons, alcohols and CO₂). The product formation rate was calculated

including and excluding the by-product CO₂. For all experiments, the carbon balance closed to within $\pm 5\%$.

The total selectivity (including CO₂) on a C₁ basis was determined using Equation 2:

$$S_j = \frac{C_j Z_j}{\sum_i C_i Z_i} \quad \text{Eqn. 2}$$

where S_j is the total selectivity to component(s) j . Component(s) j can be one compound (e.g., CH₄) or a series of compounds such as C₂–C₄ hydrocarbons, C₅₊ hydrocarbons, or alcohols. The hydrocarbon only selectivity was calculated in a similar fashion except the concentrations of CO₂ and alcohols were removed from the denominator. The olefin selectivity, R_n , was calculated as the molar ratio of olefins to paraffins for a given carbon number as shown in Equation 3:

$$R_n = \frac{C_{o,n}}{C_{p,n}} \quad \text{Eqn. 3}$$

where n is the carbon number, $C_{o,n}$ is the molar concentration in the effluent stream of olefin with carbon number n , and $C_{p,n}$ is the molar concentration in the effluent stream of paraffin with carbon number n . Based on the Anderson-Schulz-Flory (ASF) model [32, 33], the chain growth probability factor, α , was determined for each catalyst using the product distribution and Equation 4:

$$m_n = (1 - \alpha)\alpha^{n-1} \quad \text{Eqn. 4}$$

where m_n is the mole fraction of a hydrocarbon with chain length n .

2.4. Temperature Programmed Desorption and Reaction Experiments

The TPD and TPR_{xn} experiments were carried out in a Micromeritics 2910 AutoChem Chemisorption analyzer. The analyzer was equipped with a TCD and a Balzers Instruments ThermoStar GS300 quadrupole mass spectrometer (MS) for online analysis of the effluent

stream from the reactor. Approximately 100 mg of catalyst sample was loaded into a 15 mm I.D. quartz U-tube reactor and supported on a quartz wool plug. The mass of catalyst loaded was varied to achieve the same total number of CO adsorption sites (based on the CO uptake of the materials determined using CO pulse chemisorption). Prior to analysis, the Mo_2C and Mo_2N catalysts were pretreated as described earlier. After pretreatment, the temperature was increased by 10 °C and the catalyst sample was degassed in flowing He for 0.5 h. The catalysts were then cooled in He and were ready for analysis. It should be noted that all experiments carried out in the chemisorption analyzer were performed at atmospheric pressure. The experimental details for the various TPD and TPR_{rxn} experiments are discussed below.

For the H_2 -CO TPR_{rxn} experiments, the catalyst sample was exposed to a flowing mixture of H_2 and CO ($\text{H}_2/\text{CO} = 4$). The temperature was then linearly increased at a rate of 10 °C min⁻¹ to 450 °C. The effluent stream was monitored using the MS.

The CO TPD experiments were performed by dosing the catalyst sample at RT with 5 mL of a 5% CO/He mixture until saturation was achieved. Saturation was typically achieved within 4–8 doses. In flowing He, the temperature was then linearly increased at 30 °C min⁻¹ to 800 °C. The effluent stream was monitored using the MS and the TCD. The CO TPD spectra consisted of multiple peaks; therefore the TPD spectra had to be deconvolved. The deconvolution was performed using CasaXPS, a commercially available peak deconvolution software package that is typically used to analyze X-ray photoelectron spectra. The TPD spectra were deconvolved using a non-linear least squares method employing Gaussian distributions. The primary constraint imposed during fitting was that the relative intensities (i.e., relative peak areas) of the different peaks were held constant for each spectrum (i.e., the relative amounts of

the different CO adsorption sites on the catalyst surface should remain constant regardless of heating rate).

The CO adsorption energies were determined from the CO TPD spectra ($m/z = 28$) using the heating rate variation method [34, 35]. The rate of desorption of molecules on a catalyst surface, r_{des} , is described by the Polanyi-Wigner equation [34]:

$$r_{des} = -\frac{d\Theta}{dt} = v_n \exp\left(-\frac{\Delta E_{des}^{PW}}{RT}\right) \Theta^n \quad \text{Eqn. 5}$$

where t is time, Θ is the surface coverage, v_n is the frequency factor, T is temperature, R is the ideal gas constant, ΔE_{des}^{PW} is the activation energy of desorption, and n is the desorption rate order. Performing some basic calculus and assuming first order desorption ($n = 1$), Equation 5 can be written in the following form:

$$\ln \frac{T_{max}^2}{\beta} = \frac{\Delta E_{des}}{RT_{max}} + \ln \frac{\Delta E_{des}}{v_1 R} \quad \text{Eqn. 6}$$

where T_{max} is the temperature at which the maximum desorption rate occurs and β is the heating rate. By plotting $\ln(T_{max}^2 / \beta)$ vs. $1/T_{max}$ for a series of β values, ΔE_{des} was determined from the slope of the line. The linear regression was performed using commercially-available SPSS Statistics software. The β values used in this study ranged from 4 to 40 °C min⁻¹.

To probe CO dissociation and hydrogenation over Mo₂C and Mo₂N, an experimental sequence consisting of 4 steps (i.e., pretreatment, CO exposure, TPD, and H₂ TPR_{xn}) was performed, as shown in Fig. 1. Step 1 (pretreatment) was performed as described above in Section 2.1. The catalyst sample was then cooled down in Ar to a specified temperature. Step 2 (CO exposure) involved holding the catalyst at this temperature for 1 h while exposing it to a flowing mixture of 10% CO/Ar, so that CO can associatively and dissociatively adsorb to the

catalyst surface. For comparison, blank runs were also performed in which the catalyst sample was not exposed to CO (i.e., the sample was just held at the specified temperature for 1 h in flowing Ar). After Step 2, the catalyst was cooled to RT in Ar. Step 3 (TPD) involved increasing the temperature to 500 °C at a ramp rate of 20 °C min⁻¹ in flowing Ar. Based on the findings of St. Clair et al. [36], the maximum temperature of 500 °C was chosen to ensure desorption of all molecular CO and to minimize recombination of carbon and oxygen from dissociated CO. St. Clair reported recombination of C and O over Mo₂C catalysts at temperatures above 500 °C [36]. The final temperature was held for 10 min prior to cooling the sample back to RT. The goal of Step 3 was to desorb the associatively adsorbed CO, leaving only adsorbed carbon and oxygen from CO dissociation on the catalyst surface. To explore the impact of molecularly adsorbed CO, experiments were also performed in which Step 3 was bypassed. In this case, it is assumed that molecular CO and adsorbed carbon and oxygen remain on the catalyst surface. Lastly, in Step 4 (H₂ TPRxn), the sample was exposed to a mixture of 10% H₂/Ar and the temperature was linearly increased at 20 °C min⁻¹ to a final temperature of 500 °C. The goal was to hydrogenate the adsorbed carbon present from CO dissociation. The MS was used to monitor products in the effluent stream during all steps of the experiment.

Fig. 1. Experimental sequence used to investigate CO dissociation and hydrogenation over Mo₂C and Mo₂N.

3. Results and Discussion

3.1. Materials Characterization

X-ray diffraction patterns for the passivated carbide and nitride catalysts are shown in Fig. 2. Peaks attributable to the oxide precursors were not observed, suggesting that complete bulk carburization or nitridation of the starting materials was achieved. Except for the Mo_2C and W_2C catalysts, crystallites for all of the carbides and nitrides were fcc. For NbN, the small peaks at 2θ of $\sim 31^\circ$, $\sim 46^\circ$, and $\sim 62^\circ$ correspond to the hexagonal phase of NbN that can be formed under synthesis conditions similar to those used in this work [37]. The W_2C catalyst had an orthorhombic (distorted hexagonal close packed) structure while the crystalline structure of the Mo_2C catalyst was consistent with a mixture of $\alpha\text{-MoC}_{1-x}$ (fcc) and $\beta\text{-Mo}_2\text{C}$ (orthorhombic). This multi-phase Mo_2C material has been produced previously in our research group [14, 26, 27] and was found to have a surface area twice that of $\beta\text{-Mo}_2\text{C}$. It should be noted that modifying synthesis conditions to maximize the surface areas was not a focus of this research.

Fig. 2. X-ray diffraction patterns for the passivated (a) carbide and (b) nitride catalysts.

Results from surface area and CO chemisorption analysis are given in Table 1. The carbides and nitrides of Mo and W exhibited the highest CO uptakes and CO site densities. The VN and NbN catalysts exhibited CO site densities 4–5 times lower than those of the Mo and W carbides and nitrides. Differences have been reported previously, and may be due to carbon or

oxygen impurities on the catalyst surface or varying degrees of surface carburization/nitridation [38, 39]. The CO uptakes for VC and NbC were below the detection limit of the instrument ($\sim 1 \mu\text{mol g}^{-1}$), thus CO site densities could not be calculated.

Table 1. Surface areas, CO uptakes, and site densities for the pretreated carbide and nitride catalysts.

Catalyst	Surface Area ($\text{m}^2 \text{g}^{-1}$)	CO Uptake ^a ($\mu\text{mol g}^{-1}$)	CO Site Density ^b ($\text{molecules m}^{-2} \times 10^{18}$)
Mo ₂ C	106	268	1.52
Mo ₂ N	154	307	1.20
W ₂ C	36	74	1.24
W ₂ N	82	109	0.80
VC	9	<1	--
VN	28	8	0.27
NbC	10	<1	--
NbN	47	11	0.14

^aCO uptake calculated from CO pulse chemisorption performed at room temperature.

^bCO site density calculated from BET surface area and CO uptake for the pretreated catalysts.

3.2. Fischer-Tropsch Synthesis

Arrhenius plots of the gravimetric FTS product formation rates, excluding CO₂, for the carbide and nitride catalysts are shown in Fig. 3a. For the lower temperature range, only the Mo₂C and W₂C catalysts exhibited measureable product formation rates. On a gravimetric basis, the most active catalyst was Mo₂C. This result is not surprising as Mo₂C exhibited high CO uptakes, indicating that there is a high density of sites for CO to adsorb and potentially react. The Mo₂C catalyst was not tested at temperatures above 300 °C as it became very difficult to maintain control of the temperature due to the exothermic nature of the reaction. The VC and NbC catalysts were the least active catalysts tested; they did not exhibit measureable CO conversions under the conditions employed.

It should be noted that the VN catalyst exhibited behavior that differed from that for the other catalysts. In particular, the reaction rate for the VN catalyst did not increase with increasing temperature above 300 °C. This result could be due to a change in the catalyst's

structure, functional properties (e.g., deactivation, reaction pathway, or kinetics), or diffusion limitations. To assess the impact of diffusion effects for the VN catalyst as well as the other materials, the Weiss-Prater criterion, N_{W-P} , was evaluated [40]. Assuming either CO or H₂ as the limiting reactant, the N_{W-P} was determined to be less than 1×10^{-3} for all of the catalysts at 320 °C, which is much less than 0.3 indicating that the reaction is not diffusion limited under these conditions. The cause of the behavior observed for VN is unclear. We speculate that the catalyst deactivated, but additional investigation is needed to evaluate this possibility.

Fig. 3. Arrhenius plots of the product formation rates on a C₁ basis (excluding CO₂) for the carbide and nitride catalysts on (a) a gravimetric basis and (b) normalized by the CO uptakes.

To estimate the intrinsic activity of the catalysts, the product formation rates were normalized by the CO uptakes (Fig. 3b). On a CO normalized basis, the Mo₂C, W₂C, VN, and NbN catalysts exhibited similar product formation rates. Rates for the Mo₂N and W₂N catalysts were more than an order of magnitude lower. The activity trend for these materials is as follows: Mo₂C ~ W₂C ~ VN ~ NbN > Mo₂N, W₂N >> VC, NbC. Based on these results, there appears to be a significant difference in FTS activity for carbides and nitrides of the same parent metal. For example, the normalized rate for the Mo₂C catalyst was 0.36 s⁻¹ at 300 °C while the rate for Mo₂N was only 0.04 s⁻¹, even though these materials exhibited similar surface areas, CO uptakes, and CO site densities. Performance differences for carbides and nitrides of the same metal have

also been reported for acetone condensation [41] and n-butane hydrogenolysis, dehydrogenation, and isomerization [30]. For acetone conversion, the Mo₂N catalyst favored condensation producing mesityl oxide while the Mo₂C catalyst favored hydrogenation to isopropanol, followed by subsequent dehydration to propylene [41].

Using the normalized rates shown in Fig. 3b, the activity of the carbides and nitrides can be compared to typical Fischer-Tropsch catalysts containing, for example, Co. Based on a review by Ribeiro et al., the average CO hydrogenation turnover frequency for a series of supported Co catalysts was $0.017 \pm 0.014 \text{ s}^{-1}$ at 200 °C, 10 atm, and H₂/CO = 2 [42]. At 200 °C, the CO normalized rate observed for the Mo₂C catalyst ($0.004 \pm 0.002 \text{ s}^{-1}$) was ~4 times lower than the average value reported for supported Co catalysts. This result is consistent with the report by Shou et al., which indicated that while Mo₂C catalysts are capable of relatively high turnovers, a low apparent activity is typically observed due to an extremely low surface coverage of reaction intermediates [21].

Table 2. Fischer-Tropsch Synthesis apparent activation energies for the carbide and nitride catalysts.

Catalyst	E _{a,app} ^a (kJ mol ⁻¹)	
	Temperature Ranges	
	200–250 °C	270–320 °C
Mo ₂ C	107	98
Mo ₂ N	--	134
W ₂ C	66	76
W ₂ N	--	59
VN	--	85 ^b
NbN	--	91

^aE_{a,app} was calculated from product formation rates excluding CO₂.

^bE_{a,app} for VN was calculated from only the first three points (270 °C, 280 °C, and 290 °C).

The apparent activation energies ($E_{a,app}$) for the carbide and nitride catalysts are given in Table 2. For the temperature range 270–320 °C, the Mo₂N catalyst exhibited the highest $E_{a,app}$ of 134 kJ mol⁻¹, while the W₂C and W₂N catalysts exhibited the lowest values, 76 kJ mol⁻¹ and 59

kJ mol^{-1} , respectively. The Mo_2C catalyst exhibited an activation energy over this temperature range that was 36 kJ mol^{-1} lower than that for the Mo_2N catalyst, consistent with the observed differences in TOF. Activation energies for CO hydrogenation over the Mo_2C and Mo_2N catalysts reported in literature range from $60\text{--}170 \text{ kJ mol}^{-1}$ depending upon reaction conditions and the products [6, 9]. It should be noted that these reports employed H_2 to activate the catalysts. The $E_{a,app}$ values for the Mo_2C and Mo_2N catalysts examined in this study were within those reported ranges.

Table 3. Fischer-Tropsch Synthesis performance characteristics for the carbide and nitride catalysts at 25 bar and $\text{H}_2/\text{CO} = 2$.

Catalyst	T (°C)	CO Conv. (%)	TOF (s^{-1})	Product Selectivity on C_1 Basis (%)					R_n		α
				CH_4	$\text{C}_2\text{--C}_4$	C_{5+}	Alcohols	CO_2	C_2	C_3	
Mo_2C	200	0.7	0.004	27.7	31.2	9.7	17.2	14.2	0.23	1.02	0.45
	290	10.5	0.36	35.1	26.5	1.7	0.7	36.0	0.03	0.24	0.31
Mo_2N	290	2.1	0.014	31.9	20.7	1.6	0.7	45.1	0.16	1.03	0.33
W_2C	200	0.3	0.007	27.4	36.4	18.4	0.9	16.9	0.55	1.4	0.50
	290	2.9	0.35	41.5	33.4	3.6	3.3	18.2	0.06	0.50	0.35
W_2N	290	0.6	0.011	51.7	24.8	4.1	2.3	17.1	0.46	1.81	0.43
VN	290	1.7	0.20	58.5	29.0	2.1	2.0	8.4	0.18	1.30	0.35
NbN	290	2.4	0.22	65.7	23.0	1.3	2.1	7.9	0.06	0.74	0.31

The selectivities of the carbide and nitride catalysts are compared in Table 3. At 290°C , CO conversions for all of the catalysts were similar, allowing for an equitable comparison as the extent of conversion can affect selectivity [33]. The primary products were hydrocarbons and CO_2 . The hydrocarbon fraction was dominated by light products, $\text{C}_1\text{--C}_4$ ($>90\%$ on a C_1 basis), with selectivities to higher hydrocarbons (C_{5+}) between 2 and 5%. Only a small percentage of alcohols were produced; however, it should be noted that high temperatures are not favorable for alcohol formation. The product selectivities were affected significantly by temperature. At 200°C , the Mo_2C catalyst produced 68% hydrocarbons, 14% CO_2 , and 18% alcohols compared to

63% hydrocarbons, 36% CO₂, and 1% alcohols at 290 °C. Methanol and ethanol were the only alcohols produced, with ethanol being the more favored product at 290 °C. The VN and NbN catalysts exhibited the highest selectivities to hydrocarbons while the Mo₂C and Mo₂N catalysts exhibited the lowest selectivities to hydrocarbons at 290 °C. Based on the observed production of CO₂, all of the catalysts appeared to be active for water-gas shift (WGS). The trend in terms of CO₂ selectivity was as follows: Mo₂C ~ Mo₂N > W₂C ~ W₂N > VN ~ NbN.

The olefin selectivities, R_n , for all of the catalysts followed the same trend as a function of carbon number. The ratios were typically lowest for C₂ and highest for C₃. The W₂N catalyst exhibited the highest R_n while the Mo₂C catalyst exhibited the lowest R_n . It is not surprising that the Mo₂C catalyst favored saturated hydrocarbons as it has been reported to be active for a variety of hydrogenation reactions [43-45]. The chain growth probabilities, α , for each catalyst are listed in Table 3. At 290 °C, the highest α (0.43) was observed for W₂N and the lowest α (0.31) was observed for NbN and Mo₂C. The α values for the other catalysts were all within error of each other.

To directly compare the carbide and nitride catalysts to typical FTS catalysts, commercial Fe/SiO₂ and Co/Al₂O₃ catalysts were obtained and evaluated in the fixed bed FTS reactor. At 230 °C, 25 bar, H₂/CO = 2, and X_{CO} < 10%, the hydrocarbon selectivities on a C₁ basis to C₅₊ hydrocarbons were 37% and 41% for the Fe/SiO₂ and Co/Al₂O₃ catalysts, respectively. Under the same conditions, the C₅₊ hydrocarbon selectivity for the Mo₂C catalyst was ~10%. The ASF α values for these materials were 0.65, 0.66, and 0.43 for the Fe/SiO₂, Co/Al₂O₃, and Mo₂C catalysts, respectively. These results indicate that C-C coupling occurs much more readily over the Fe and Co based catalysts than over the Mo₂C catalyst. It should be noted that the Fe and Co based catalysts have been tuned to achieve high selectivity to C₅₊ products, as compared to the

unoptimized Mo₂C material. The C-C coupling is affected by a number of factors: reaction pathway (i.e., FTS mechanism), carbon mobility on the catalyst surface, and CO, H₂ and CH_x coverages under reaction conditions [46-48]. Overall, it appears that the selectivities of the carbides and nitrides lie in between those of Ni (which favors methane) and Fe (which favors long-chain hydrocarbons, but also produces CO₂ through WGS).

3.3. Temperature Programmed Desorption and Reaction Experiments

The TPD and TPR_{xn} experiments were performed to probe for differences that could explain differences in the FTS TOFs exhibited by carbides and nitrides of the same parent metal. The Mo₂C and Mo₂N catalysts were investigated for these experiments. The reactivities were first explored using a H₂-CO TPR_{xn}. The MS intensity ($m/z = 15$, CH₃ fragments) during the TPR_{xn} is shown in Fig. 4. The Mo₂C catalyst exhibited a light off temperature for CO hydrogenation of approximately 200 °C while the Mo₂N catalyst did not begin to produce CH₄ until 300–350 °C. This result is in accordance with the flow reactor experiments as the Mo₂N catalyst was not active over the lower temperature range (200–250 °C). The higher light off temperature is consistent with a higher activation barrier for CO hydrogenation over the Mo₂N catalyst compared to the Mo₂C catalyst, and a higher observed apparent activation energy (Table 2).

Fig. 4. Production of CH₃ fragments ($m/z = 15$) during H₂-CO TPRxn over the Mo₂C and Mo₂N catalysts.

The apparent activation energy is most significantly affected by the elementary step with the slowest forward rate, i.e. the rate-limiting step. The rate-limiting step for FTS is often reported to be either (i) adsorption and dissociation of CO or (ii) the hydrogenation of carbon species [33, 49, 50]. To investigate the first of these proposed rate-limiting steps, CO TPD experiments were performed (Fig. 5). Both the Mo₂C and Mo₂N catalysts exhibited similar CO TPD spectra; there was a broad desorption peak centered at ~100 °C. The similarity between these spectra suggested that the materials possessed similar molecular CO adsorption energies. However, a significant amount of CO₂ was also produced during TPD over the Mo₂C catalyst (Fig. S2), indicating that Mo₂C catalyzed the disproportionation of CO (Boudouard reaction). A negligible amount of CO₂ was observed over the Mo₂N catalyst during the TPD.

Fig. 5. CO TPD spectra for the (a) Mo_2C and (b) Mo_2N catalysts. For the blank, the catalyst surface was not exposed to CO. The heating rate was $30^\circ\text{C}/\text{min}$.

The molecular CO adsorption energies (i.e., the activation energy for desorption, ΔE_{des}) were experimentally determined for the Mo_2C catalyst using a heating rate variation method [34, 35]. To do so, the broad desorption peak was fit to 4 separate CO desorption peaks. The deconvoluted CO TPD spectra for the Mo_2C catalyst at the highest ($40^\circ\text{C min}^{-1}$) and lowest (4°C min^{-1}) heating rates are shown in Fig. 6. The temperature at which the maximum desorption rate occurs, T_{max} , was determined for each peak, and the CO desorption energies were calculated by plotting $\ln(T_{max}^2 / \beta)$ vs. $1/T_{max}$ (Fig. S3 and Table S2). The desorption energies were 91, 103, 126, and 148 kJ mol^{-1} for peaks 1-4, respectively. These values are similar to those reported by St. Clair (93 – 115 kJ mol^{-1}), determined via CO TPD from a Mo_2C single crystal, $\alpha\text{-Mo}_2\text{C}$ (0001) [36].

Fig. 6. Deconvoluted CO TPD spectra for the Mo₂C catalyst at heating rates of (a) 40 °C/min and (b) 4 °C/min.

CO dissociation and hydrogenation were investigated over the Mo₂C and Mo₂N catalysts using the four step experimental sequence shown in Fig. 1. A thorough description of the sequence is provided in Section 2.4, but briefly, this sequence was used to probe: (i) the effect of CO exposure temperature on the extent of CO dissociation and subsequent hydrogenation and (ii) the effect of molecularly vs. dissociatively adsorbed CO on FTS products. In particular, Step 3 allows us to selectively remove molecularly adsorbed CO, and thus interrogate its role in the FTS mechanism over these materials. Fig. 7 shows the MS intensity for CO ($m/z = 28$) during the Ar TPD step (Step 3) over the Mo₂C and Mo₂N catalysts as a function of the CO exposure temperature during Step 2. As the CO exposure temperature increased over the Mo₂C catalyst, the intensity of the CO desorption peak decreased and the peak shifted to higher temperatures. A similar shift, albeit to a lesser extent, was also observed for the Mo₂N catalyst, for which CO exposure temperatures of 240 °C and higher were used due to its lack of activity at lower temperatures. The shift in intensity and temperature may have been due to CO no longer occupying the adsorption sites with lower binding energies; the temperature for CO exposure was above the temperature at which CO desorbs from these sites. A similar shift in intensity and temperature was also observed for CO₂ produced during the TPD experiments (Fig. S4). At the highest temperatures for CO exposure (320 °C and 340 °C), there are CO desorption peaks present at temperatures above 350 °C. These peaks may be due to the recombination of adsorbed carbon and oxygen produced during CO dissociation [36].

Fig. 7. CO TPD spectra for the (a) Mo_2C and (b) Mo_2N catalysts as a function of CO exposure temperature. A blank spectrum is shown in which the catalyst was not exposed to CO.

The Ar TPD step (Step 3) is designed to remove molecularly adsorbed CO from the catalyst surface, leaving behind adsorbed carbon (from either direct CO dissociation (without H_2 assistance) or disproportionation) for subsequent hydrogenation during the H_2 TPRxn step (Step 4). Fig. 8 shows the MS intensity for $m/z = 15$ (CH_3 fragments) during the H_2 TPRxn step for the Mo_2C and Mo_2N catalysts as a function of CO exposure temperature. For a CO exposure temperature of 240 °C, a significant amount of CH_4 was produced over the Mo_2C surface compared to the blank (no CO exposure). The primary CH_4 desorption peaks were centered at ~450 °C. As the CO exposure temperature increased, the intensity of the CH_4 desorption peaks increased. This result suggests that higher exposure temperatures resulted in a higher concentration of adsorbed carbon.

Fig. 8. Methane (CH_3 fragment, $m/z = 15$) production during H_2 TPRxn spectra for the (a) Mo_2C and (b) Mo_2N catalysts as a function of CO exposure temperature. A blank is also shown in which the catalyst was not exposed to CO.

For the Mo_2N catalyst, the spectra for the sample exposed to CO at 240 °C and the blank were similar, suggesting that CO dissociation did not occur at this temperature. However, as the temperature for CO exposure was increased, three CH_4 desorption peaks at ~140 °C, ~180 °C, and ~220 °C were observed during TPRxn, and designated as α , β , and γ , respectively. Similar to the Mo_2C catalyst, the intensity of the CH_4 desorption peaks increased as the CO exposure temperature was increased. Additionally, the peaks shifted towards lower temperatures with increasing CO exposure temperatures. The ratio of intensity of the α to the β peak also increased with increasing CO exposure temperature. This shift with temperature and the change in relative peak intensities are consistent with the carbon surface coverage increasing with increasing CO exposure temperature. Increasing coverage results in weaker binding, thus the desorption peaks would shift to lower temperatures, as was observed. Moreover, at higher exposure temperatures, the less reactive sites would be capable of CO dissociation. Therefore, the least reactive sites (lowest desorption temperatures – α peak) would be occupied last, thus causing an increase in the intensity ratio for the α peak compared to the β peak.

Interestingly, for both the Mo₂C and Mo₂N catalysts, negligible amounts of H₂O were produced during the H₂ TPR_{rxn} (Fig. S5), suggesting that oxygen adsorbed on the surface from CO dissociation either remained tightly bound to the surface, diffused into the subsurface, or was removed via reaction with adsorbed carbon or CO to produce CO or CO₂, respectively. St. Clair et al. reported that adsorbed oxygen diffused into the bulk of α -Mo₂C (0001) during an O₂ TPD instead of burning off as CO [36]. The production of CO₂ during the H₂ TPR_{rxn} over the Mo₂C and Mo₂N catalysts is also shown in Fig. S5. A negligible amount of CO₂ was produced over Mo₂C; however, Mo₂N exhibited a peak at ~250 °C and the peak intensity and temperature decreased with increasing CO exposure temperature. These results, combined with the observed CO₂ production over the Mo₂C catalyst during the TPD step (Fig. S4), suggest that adsorbed oxygen is preferentially removed via reduction by CO to produce CO₂, in accordance with the high WGS activities for these materials.

In addition to CO dissociation and hydrogenation, the experimental sequence shown in Fig. 1 allowed for the investigation of the effect of molecularly vs. dissociatively adsorbed CO on the production of hydrocarbons. The TPD step (Step 3) removed molecularly adsorbed CO. By skipping this step, molecularly adsorbed CO would be expected to remain on the catalyst surface and its impact on hydrocarbon production during the H₂ TPR_{rxn} step (Step 4) can be investigated. Fig. 9 shows the MS intensity for $m/z = 15$ and $m/z = 29$ during the H₂ TPR_{rxn} step over the Mo₂C catalyst for which the Ar TPD step was either performed or not performed. The $m/z = 29$ corresponds to C₂H₅ fragments, which almost all C₂₊ hydrocarbons produce. Two CO exposure temperatures were tested: 240 °C and RT. For CO exposure at 240 °C, an increase in hydrocarbon production was observed over the Mo₂C catalyst in the temperature range of 100–200 °C when the TPD step was not performed (i.e., molecularly adsorbed CO remained on

the surface). This result was amplified for CO exposure at RT. These findings indicate that molecularly adsorbed CO plays a key role in hydrocarbon production. Moreover, the effect of molecularly adsorbed CO on C-C coupling (C_{2+} hydrocarbon production) was explored. As shown in Fig. 9c-d, the presence of molecularly adsorbed CO resulted in a significant increase in the production of C_{2+} hydrocarbons ($m/z = 29$), indicating that CO_{ads} plays a key role in C-C coupling.

Fig. 9. H_2 TPRxn spectra for the Mo_2C catalyst, for which the Ar TPD step was either performed or not performed. Production of CH_3 fragments ($m/z = 15$) for CO exposure temperatures of (a) 240 °C and (b) RT. Production of C_2H_5 fragments ($m/z = 29$) for CO exposure temperatures of (c) 240 °C and (d) RT.

3.4. Mechanism Interpretations

The interactions of CO and H₂ with the Mo₂C and Mo₂N surfaces were investigated to explain differences observed in the FTS rates as well as shed light on the FTS mechanism. Based on results from the TPD and TPR_{CO} experiments, the Mo₂C and Mo₂N catalysts adsorb molecular CO with similar binding energies (90–150 kJ mol⁻¹). However, at 240 °C, CO dissociation occurred readily over the Mo₂C surface while temperatures at or above 280 °C were required to dissociate CO over the Mo₂N surface (Fig. 8). This result is consistent with the FTS (Fig. 3) and H₂-CO TPR_{CO} results (Fig. 4), as the Mo₂N catalyst did not yield measurable FTS activity below 270 °C. One could conclude that CO dissociation is a key step during FTS over the Mo₂N catalyst. The Mo₂C and Mo₂N surfaces were capable of direct CO dissociation without the assistance of H₂, given the absence of H₂ during the experimental sequence.

From the H₂ TPR_{CO} experiments (Fig. 8), we learned that as the CO exposure temperature was increased, the intensity of the CH₄ desorption peaks increased for both the Mo₂C and Mo₂N catalysts. These CH₄ desorption peaks were centered at ~450 and ~150 °C for the Mo₂C and Mo₂N catalysts, respectively. This difference in desorption temperature indicated that the carbon was bound much more strongly to the Mo₂C surface than the Mo₂N surface. The high CH₄ desorption temperature observed for the Mo₂C catalyst is consistent with density functional theory calculations, in which the binding energy of carbon was reported to be very high, between -630 and -725 kJ mol⁻¹, depending upon the adsorption site [51]. Moreover, the high temperature CH₄ desorption peaks for the Mo₂C catalyst occurred over a similar temperature range as those for the material that was not exposed to CO; the CH₄ desorption peaks from the material that was not exposed to CO are due to the hydrogenation of carbidic carbon (i.e., carbon that is part of the Mo₂C structure). Similar results have been reported by Miyao et al., in which they observed the reduction of surface carbidic carbon for Mo₂C at ~490

°C [52]. This result suggests that C_{ads} , produced from dissociation of CO, prefers to reside in sites that are similar to those normally occupied by carbidic carbon in the Mo_2C lattice.

We propose that the activation barrier for CO dissociation is higher for the Mo_2N catalyst than the Mo_2C catalyst, and that this difference explains the observed difference in FTS rates. This higher activation barrier is consistent with the higher light off temperature (Fig. 4). Moreover, based on the Bronsted-Evans-Polanyi relationship, the activation energy for dissociative adsorption of molecules depends linearly on the reaction energy [53-57]. More specifically, the activation energy for CO dissociation is directly related to the dissociative CO adsorption energy. Accordingly, if the activation energy of CO dissociation decreases, then C and O will be bound more strongly to the catalyst surface. Our findings are consistent with this relationship as the Mo_2C catalyst had a lower CO dissociation activation energy than the Mo_2N catalyst, and carbon was bound more strongly to Mo_2C than to Mo_2N . Regarding the FTS activities, Bligaard et al. reported that the dissociative CO adsorption energy is a good descriptor for the CO hydrogenation activities of transition metal catalysts (Re, Fe, Ru, Co, Rh, Ni, Ir, Pd, and Pt) [57]. Consequently, materials with different CO dissociation activation energies (Mo_2C vs. Mo_2N) would be expected to exhibit different activities for CO hydrogenation.

Since the Mo_2C and Mo_2N catalysts were active for direct CO dissociation, one might assume that FTS occurred via the carbide mechanism (Fig. 10). However, for the Mo_2C catalyst, the desorption of CH_4 produced from hydrogenation of adsorbed carbon occurred primarily at temperatures above 350 °C. This temperature is higher than the temperatures employed during the FTS experiments, suggesting that adsorbed carbon from CO dissociation might remain bound to the Mo_2C surface under reaction conditions. On the other hand, the CH_4 desorption peaks for the Mo_2N catalyst were between 100 and 250 °C, within the typical temperature range for the

FTS experiments. Additionally, FTS activity was not observed for the Mo_2N catalyst until CO dissociation was favorable. Therefore, it is probable that FTS occurred via the carbide mechanism for the Mo_2N catalyst.

Carbide Mechanism

Oxygenate (enol) Mechanism

CO Insertion Mechanism

Fig. 10. Schematic showing the 3 primary FTS mechanisms: the carbide mechanism, the oxygenate mechanism, and the CO insertion mechanism. Adapted from [33, 58].

By exploring the effect of molecularly adsorbed CO vs. dissociatively adsorbed CO on reactivity, the mechanism for the Mo_2C catalyst was elucidated. As shown in Fig. 10, CO dissociation is required for the carbide mechanism, whereas the oxygenate and CO insertion mechanisms involve molecular CO adsorption. Fig. 9 shows that the presence of molecularly adsorbed CO on the Mo_2C surface resulted in an increase in hydrocarbon production as well as C-C coupling (production of C_{2+} hydrocarbons). These findings implicate an oxygenate species as the key reactive intermediate. In addition, since hydrogen was not pre-adsorbed to the surface prior to the H_2 TPRxn experiments, these results suggest that the dominant pathway over the Mo_2C catalyst was the oxygenate mechanism. Kojima et al. [4] speculated that the mechanism

for CO hydrogenation over Mo_2C involved the formation of a CH_xO intermediate, and Medford et al. [22] reported, based on computational results, that coupling of HCO species was more favorable than coupling of CH_x species over Mo_2C . Results reported in our paper are consistent with these findings. Furthermore, alcohols are expected to be side-products from the oxygenate mechanism. Similar to the Fe-based catalysts which have also been reported to follow the oxygenate mechanism [58], the Mo_2C catalyst produced alcohols during FTS. Finally, the TPD and TPRxn results reported in this paper suggest that the Mo_2C catalyst possessed at least two different types of catalytic sites: (i) CO dissociation sites and (ii) molecular CO adsorption sites that facilitate C-C coupling reactions. It may be possible to improve C-C coupling over the Mo_2C catalyst by enhancing its ability for associative CO adsorption (e.g., increasing the number of sites for molecular CO adsorption).

4. Conclusions

The catalytic properties of a series of high surface area early transition metal carbides and nitrides (Mo_2C , Mo_2N , W_2C , W_2N , VC, VN, NbC, and NbN) were evaluated for FTS under industrially-relevant conditions. The activity trend based on TOFs was $\text{Mo}_2\text{C} \sim \text{W}_2\text{C} \sim \text{VN} \sim \text{NbN} > \text{Mo}_2\text{N} \sim \text{W}_2\text{N} \gg \text{VC} \sim \text{NbC}$. The Mo_2C catalyst exhibited a TOF that was an order of magnitude higher than that for the Mo_2N catalyst; this difference was attributed to a significantly higher activation barrier for direct CO dissociation for the Mo_2N catalyst. While both materials were capable of direct CO dissociation, only the Mo_2N catalyst appeared to follow the carbide mechanism. Based on results from TPD and TPRxn experiments, the pathway for C-C coupling over the Mo_2C surface included an oxygenate intermediate.

Based on the observed product selectivities, demonstrated WGS activity, and the dominant reaction mechanism for C-C coupling, potential applications for the carbides and

nitrides include (i) conversion of biomass-derived syngas into light olefins, and (ii) coupling oxygenate species derived from biomass sources. Due to the availability of multiple types of catalytic sites and the ability to vary reactivity based on metal/non-metal atom, it may be possible to tune the properties of these materials to affect reactions of interest. Future work will be focused in this area.

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Appendix A. Supplementary Material

Supplementary data associated with this article, including Figs. S1–S5 and Tables S1 and S2, can be found in the online version.

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