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Enhanced Alcohol Production over Binary Mo/Co Carbide Catalysts in Syngas Conversion

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Abstract

Recently metal carbide catalysts have attracted attention as alternatives to pure metals for the conversion of syngas to higher oxygenates, a process which could enable the sustainable production of fuels, polymers, and chemicals. Although Mo and Co carbides have both shown promise for higher oxygenate production, they have not achieved the requisite activity and selectivity for practical implementation. In this work we synthesize and characterize a binary Mo and Co carbide catalyst that exhibits improved activity and oxygenate selectivity relative to either pure metal carbide. We apply a combination of advanced electron microscopy and X-ray diffraction to show that the binary Mo/Co carbide catalyst forms uniformly mixed amorphous nanoparticles. Through in situ X-ray absorption spectroscopy studies, we determine that the structure of the mixed metal carbide catalyst under reaction conditions consists of both carbidic and bimetallic components. By testing the catalytic properties of a series of Mo/Co carbide

catalysts prepared by different synthesis methods, we find that the Mo and Co sites must be in close contact to achieve improved syngas conversion to higher alcohols. Through in situ DRIFTS measurements, both Mo and Co atoms at the surface of the catalyst are identified as adsorption sites for reactive species.

1. Introduction

Non-renewable resources like coal, natural gas, and petroleum are widely used in the production of many common materials, including fuels, chemicals, and polymers.^{1–3} However, as these non-renewable carbon sources are rapidly depleted and the environmental impacts of their use become increasingly severe, it has become necessary to develop sustainable methods of producing fuels and high value chemicals. One promising strategy is the catalytic conversion of synthesis gas (syngas, $CO + H_2$) to higher oxygenates, which can be directly used as fuel additives or further refined to more valuable products.^{4–6} Because syngas can be produced from non-renewable carbon sources, as well as from biomass and CO_2 , the conversion of syngas to value-added products is well-suited to facilitate the transition to the utilization of sustainable resources.^{7,8}

The most significant challenge in the catalytic production of valuable chemicals from syngas is achieving high selectivity towards higher oxygenates. This stems from the two possible forms of CO adsorption on a catalyst surface. On one hand, CO can undergo dissociative adsorption on the catalyst surface, in which the carbon-oxygen bond is broken. Subsequent hydrogenation of the adsorbed carbon and coupling of alkyl species result in the formation of hydrocarbon products, as is characteristic of Fischer-Tropsch catalysts. On the other hand, CO can associatively adsorb on the catalyst surface and be hydrogenated to form methanol. Most

catalysts nearly exclusively support only one form of CO adsorption, and consequently exhibit high selectivity towards either hydrocarbons or methanol.⁹ However, the generally accepted mechanism for higher oxygenate formation involves a CO insertion step, in which a CO molecule inserts into an alkyl fragment, yielding an oxygenate with multiple carbon atoms.^{4,7} This requires a dual-function catalyst surface that supports both dissociative and non-dissociative CO adsorption. Because of the bifunctional surface site requirement, the development of a high performance catalyst for higher oxygenate synthesis necessitates the selection of multiple active materials, optimization of active site structure, and tuning of surface electronic properties in order to direct reaction pathways towards the desired products.

The best performing catalysts that have been developed are promoted rhodium materials, owing to the moderate intrinsic selectivity of Rh towards higher oxygenates.^{10–12} However, because Rh is extremely scarce and very expensive,¹³ the practical implementation of higher alcohol synthesis requires the development of less expensive catalytically active materials. To this end, metal carbides have emerged as a promising alternative to pure metal catalysts.¹⁴ Metal carbides have many similar properties to metals, including close-packed structure and electrical conductivity,^{15,16} making them good alternatives to metal catalysts traditionally used in syngas conversion. Moreover, the surface electronic properties of a metal carbide differ from those of the corresponding metal due to hybridization between the metal d and carbon 2p orbitals;¹⁷ thus, an inexpensive metal that shows poor performance for higher oxygenate synthesis can potentially be transformed into a highly selective metal carbide catalyst.

Previous studies have shown that both molybdenum and cobalt carbides exhibit intrinsic selectivity towards higher oxygenate synthesis from syngas.^{18–22} Pei et al.²³ and Singh et al.²⁴ demonstrated that Co/Co₂C catalysts possess relatively high selectivity towards methanol and

higher alcohols compared to pure Co, which is a known Fischer-Tropsch catalyst.²⁵ Both studies agreed that the catalyst surface supported different types of CO adsorption sites, thus enabling CO insertion and higher oxygenate formation. Christensen et al. compared the syngas conversion properties of Mo, W, and Nb carbides and concluded that molybdenum carbide showed the highest activity and selectivity towards alcohols.²⁶ The performance of Mo carbide catalysts has also been improved by the addition of alkali and transition metals. In particular, several studies^{27–31} have demonstrated that over Mo-based catalysts, including metallic Mo, Mo₂C, and MoS₂, the alcohol yield could be improved by adding Co. Despite the evidence for enhanced higher alcohol production from mixed Mo and Co carbide catalysts, there are still many questions regarding the structure of the catalyst under reaction conditions. Different catalyst phases have been observed in the Co-promoted Mo-based catalysts described in literature, including Mo₂C, Co₂C, Co₃Mo₃C, and metallic Mo and Co. In addition, active sites and the nature of the Mo/Co interaction that gives rise to improved catalyst performance have not been determined. Xiang et al.²⁸ suggested several possible roles of Co in promoting Mo₂C, including the formation of Co₃Mo₃C, the formation of Co₂C, or the electronic modification of Mo surface sites. On the other hand, Yin et al.²⁹ demonstrated enhanced alcohol production over Co-modified Mo₂C catalysts, but observed no Mo/Co interactions through spectroscopy or diffraction that could explain the improved catalytic behavior. Furthermore, Al-Megren et al.³⁰ and Christensen et al.³¹ utilized Co-modified Mo-based catalysts, but focused their studies on the effects of support and feed gas composition, and did not discuss Mo/Co interactions. Finally, in all these studies, K or Rb were utilized as promoters, which resulted in improved catalyst performance but convoluted the Mo/Co interactions with the effects of the alkali metal promoter.

In this work we seek to better understand how the structure and active sites of a binary Mo/Co carbide catalyst result in enhanced syngas conversion to higher alcohols. Measurements of the Mo/Co carbide catalytic reactivity are consistent with results in the literature that mixed Mo/Co carbide catalysts possess enhanced activity and higher oxygenate selectivity compared to either pure metal carbide. Interestingly, the pure Mo carbide catalyst forms the α -MoC_{1-x} phase, which shares similar catalytic properties to the more commonly studied β -Mo₂C phase. Using ex situ and in situ spectroscopic, scattering, and microscopic characterization methods, we demonstrate that the binary metal carbide catalysts form uniformly mixed, amorphous nanoparticles. Furthermore, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements of CO adsorbed on the catalysts reveal the presence of both Mo and Co binding sites on the surface of the mixed Mo/Co carbide. Finally, we compare the performance of mixed Mo/Co carbide catalysts prepared by different synthesis methods to determine the necessary conditions required to achieve improvements in activity and oxygenate selectivity. We show that improved catalyst performance only occurs when the Mo and Co carbide are in close contact, and as a result, we conclude that the mixture of Mo and Co active sites on the Mo/Co carbide surface are favorable for oxygenate formation.

2. Experimental Methods

2.1 Catalyst Synthesis

Silica gel (Davisil grade 643, Sigma-Aldrich) was used as the support material for all catalysts. To remove the effects of impurities in the silica support,³² the catalysts were prepared on silica gel that had been modified with the following pretreatments. To remove alkali and transition metal impurities from the support, the silica was washed in 2 M nitric acid at 80 °C for 2 h. The powder was rinsed with Milli-Q water until a neutral pH was obtained and subsequently

dried in air at 120 °C for 24 h.* Finally, the SiO₂ powder was calcined in air at 750 °C for 4 h to ensure that the subsequent high temperature annealing steps during catalyst synthesis and activation would not induce structural changes in the support.

Mo and Co were added to the catalyst by incipient wetness impregnation (IWI) of ammonium heptamolybdate tetrahydrate (AHT, (NH₄)₆Mo₇O₂₄·4H₂O, Sigma-Aldrich) and cobalt(II) nitrate hexahydrate (CNH, Co(NO₃)₂·6H₂O, Sigma-Aldrich). Catalysts were prepared both by co-impregnation, in which the AHT and CNH were mixed in the impregnation solution, and by sequential impregnation, in which the addition of AHT and CNH occurred in series. For all Mo impregnation processes, hexamethylenetetramine (HMT, (CH₂)₆N₄, Sigma-Aldrich) was also added to the impregnation solution as a carbon source to carburize the Mo with a 9:1 molar ratio of HMT to AHT, as reported elsewhere.^{33,34} The total weight loading of metal was fixed at 10% for all catalysts and the ratio of Mo:Co was controlled by varying the amounts of each metal precursor used in the synthesis. Prior to IWI, the SiO₂ powder was held under vacuum for 2 h to evacuate the pores. Appropriate masses of AHT and HMT were dissolved in 35% NH₄OH/H₂O (v/v). Similarly an appropriate mass of CNH was dissolved in milliQ water. The Mo and Co precursor solutions were mixed and quickly added dropwise to the SiO₂ under constant stirring. The powder was dried in air for 24 h, then calcined in N₂ at 700 °C for 2 h. The catalysts resulting from this procedure are denoted "as-prepared".

To differentiate the catalysts the following nomenclature will be used. Catalysts prepared by co-impregnation of the Mo and Co, in which the two precursors were simultaneously

^{*} In the absence of impurities the Co_2C phase formed in the 100Co catalyst was found to be unstable and decomposed to metallic Co under reaction conditions. Measurements of syngas conversion reactivity for the other Mo/Co carbide catalysts prepared by co-impregnation revealed no effect of impurities on catalytic performance (Figure S1). To ensure formation of the Co_2C phase, the 100Co catalyst studied in this work was prepared on unwashed SiO₂, whereas all other catalysts were prepared on the washed SiO₂. The effect of impurities on the formation and stability of Co_2C is the focus of current studies.

introduced to the powder, are termed "XMo/YCo" to denote that the 10 wt% metal consists of X atomic percent Mo and Y atomic percent Co. For example, 50Mo/50Co refers to a 10 wt% metal catalyst with a 50:50 atomic ratio of Mo:Co. Catalysts prepared by sequential impregnation are termed "50Mo/50Co seq imp" and "50Co/50Mo seq imp", with the metal impregnation occurring in the order listed. Finally, a physical mixture of the pure Mo and Co carbide catalysts was also tested. This mixture is denoted "100Mo + 100Co phys mix", and the masses of the powders used to create the physical mixture were chosen to yield a 50:50 atomic ratio of Mo:Co.

2.2 Syngas Conversion Testing

Catalytic performance was measured in an Altamira Benchcat 4000 HP packed bed reactor. In a typical experiment, 40 mg of catalyst powder was diluted with 60 mg silica gel and loaded into a 1/4 in. outer diameter stainless steel tube with a chemically inert coating (Silcolloy). The powder was packed between two plugs of quartz wool and supported by a bed of glass beads. The first catalyst pretreatment was a reduction step, in which the catalysts were exposed to 50 sccm H₂ (Airgas, 5.0 purity) at 450 °C for 2 h. The sample was then cooled to 250 °C and the reactor pressure was increased to 20 bar. In order to convert Co to Co₂C, the catalysts then underwent an additional carburization pretreatment, in which the samples were exposed to 50 sccm CO (Airgas, 5.0 purity) for 12 h at 250 °C and 20 bar.³⁵ In order to remove metal carbonyls, the CO was first passed through alumina pellets at 300 °C and a room temperature bed of carbon black (Vulcan XC-72). Following these pretreatment steps, the syngas conversion reactivity of the catalyst was measured at 250 °C, 20 bar with a feed of 10 sccm H₂ and 5 sccm CO for 24 h. The temperature, pressure, and gas flow rates were identical across all catalysts and chosen to ensure a low CO conversion so the intrinsic reactivity of the catalyst could be studied. Reaction products were analyzed by an Agilent 7890B gas chromatograph-mass spectrometer

and quantified by a flame-ionization detector. The percentage of CO conversion was calculated by dividing the total carbon content in all products by the CO concentration in the feed. Using the CO flow rate and catalyst mass, a normalized reaction rate was determined from the percent CO conversion. Carbon-weighted selectivities were calculated by dividing the total number of CO molecules converted to a given product by the total number of CO molecules converted to all products.

2.3 Catalyst Reduction and Ex Situ Characterization

Temperature-programmed reduction (TPR) experiments were performed in an Altamira Hybrid Chemisorption-Reactor system. 50 mg of catalyst powder was loaded into a quartz Ushaped tube and held in place by two quartz plugs. A thermocouple was loaded into the quartz tube and placed next to the catalyst bed to monitor the temperature. Catalysts were heated to 300 °C in 25 sccm He to remove excess water. After cooling to 40 °C, the TPR experiment was performed in 10% H₂/90% Ar with a ramp rate of 10 °C/min. The effluent gas was analyzed by a thermal conductivity detector (TCD) to monitor the catalyst reduction.

X-ray diffraction (XRD) was performed on a Bruker D8 Venture diffractometer using a Mo K α source (17.45 keV, λ = 0.7107 Å). Powders were loaded into 0.034 inch OD polyimide capillary for measurement. Diffraction patterns were collected by a 2D Photon 100 detector.

Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 F20 X-TWIN TEM system operated at 200 kV. Samples were prepared by sonicating 1 mg of powder in 1 mL ethanol for 5 minutes, then drop-casting on lacey carbon/copper TEM grids (Ted-Pella). Aberration corrected Scanning-TEM (STEM) imaging and energy dispersive X-ray spectroscopy (STEM-EDS) elemental mapping was performed at 200 kV using a JEOL NEOARM microscope equipped with dual SDD detectors. To minimize carbon contamination, powders were heated to

100 °C in N_2 for 12 hours prior to imaging. Particle compositions were calculated from the Co-K and Mo-L peaks in the EDS spectra integrated over each nanoparticle.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI VersaProbe III spectrometer with Al K α radiation (1486.6 eV). Pass energies of 224.0 and 55.0 eV were used for survey and high-resolutions scans, respectively. Samples were prepared by pressing powders into carbon tape, affixed to a Si wafer. Dual electron and ion neutralization were used during measurement to mitigate charging effects and a spot size of 200 µm was used. All binding energies were normalized to the position of the Si 2p peak at 103.5 eV.

2.4 In Situ Catalyst Characterization

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed in a Praying Mantis DRIFTS system (Harrick). Samples were loaded into a high temperature and pressure reaction cell with ZnSe windows. Gas flow rates were controlled using EL-Flow series mass flow controllers (Bronkhorst). CO was passed through a bed of alumina pellets at 300 °C to decompose iron and nickel carbonyl impurities. Prior to measurement, catalysts were reduced at 380 °C (ramp rate of 10 °C/min) in 20 sccm H₂ at 1 atm for 1 hr. After cooling to room temperature, background spectra were measured in 20 sccm N₂ at 1 atm. The feed gas was then switched to 50 sccm CO and the reaction cell was pressurized to 10 bar with pressure monitored using a pressure transducer (Setra). After exposure of the catalyst to 10 bar CO for 15 minutes to allow the surface to saturate, the feed gas was switched to 10 sccm N₂ and the pressure was reduced to 1 atm to purge excess gas phase CO. IR spectra were collected throughout the sample treatment process using a Bruker Vertex 70 spectrometer with a liquid nitrogen-cooled mercurycadmium-telluride (MCT) detector. Each spectrum was measured by averaging 200 scans over

the range 600 - 4400 cm⁻¹. The spectra presented in this work were measured after the pressure had reached 1 atm and most of the gas phase CO had been purged from the cell.

X-ray absorption spectroscopy (XAS) was performed on beamline 4-1 at the Stanford Synchrotron Radiation Lightsource. Samples were packed in a 1 mm OD quartz glass tube with wall thickness 20 µm between two plugs of quartz wool. The capillary was loaded into a custombuilt high temperature and pressure reactor described previously.³⁶ Gas flow rates were controlled using mass flow controllers (Brooks) and metal carbonyls were removed from the CO using a Nanochem Metal-X purifier (Matheson). Pressure was controlled with a back-pressure regulator (Brooks). Temperature was controlled with a Eurotherm PID controller and monitored with a K-type thermocouple in the catalyst bed. During syngas exposure, the effluent gas was analyzed by a mass-spectrometer (Hiden QGA) to ensure the reaction was taking place.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed at the Mo K-edge (20000 eV) and Co K-edge (7709 eV). Incident photon energy was set by step-scanning the Si (220) (crystal orientation φ = 0) double-crystal monochromator. XAS data was collected in transmission mode using ionization chambers (Ar used at Mo edge, N₂ used at Co edge) with the sample bed oriented at 45° relative to the beam. Spectra of the Mo and Co foils were simultaneously measured for energy calibration. Four replicates of each EXAFS spectrum were collected and merged to ensure a high signal-to-noise ratio.

A full in situ XAS experiment consisted of the same catalyst pretreatment and reaction condition exposures that were performed in the catalytic performance tests. First, EXAFS measurements were performed with the catalyst at room temperature and under 10 sccm He flow (as-prepared state). Catalysts were then reduced in 10 sccm H₂ at 450 °C with a ramp rate of 10

°C/min. XANES scans were collected every 7 min during the TPR process to monitor the state of the catalyst, and the reduction was judged to be complete when sequential XANES scans were identical. Following reduction, the temperature was reduced to 250 °C in H₂ and EXAFS measurements were taken (reduced state). The reactor was then pressurized to 20 bar in He, and once operating pressure had been reached, the feed gas was switched to 10 sccm CO at 250 °C to carburize the catalyst. XANES measurements were collected every 7 minutes during this carburization pretreatment step until the catalyst fully carburized as determined by consecutive XANES scans being identical (~180 min at Mo edge, ~70 min at Co edge). The structure of the catalyst was then measured by EXAFS (carburized state). Finally, the feed gas was switched to syngas reaction conditions, 10 sccm H₂ + 5 sccm CO at 250 °C and 20 bar, and XANES scans were collected to monitor the evolution of the catalyst structure during reaction. Spectra were collected for at least 90 minutes at each edge energy to provide enough time for structural changes during reaction to occur. EXAFS spectra were then taken under reaction conditions to determine the final structure of the catalyst (reaction state). The 50Mo/50Co catalyst was taken through the full experiment, with spectra collected at both the Mo and Co K-edges. Measurements were performed on 100Mo and 100Co catalysts through the carburization step. The 75Mo/25Co and 25Mo/75Co catalysts were studied up to the reduced state at both the Mo and Co K-edges.

The XAS data was processed using the Athena software of the Demeter package.³⁷ The replicate XAS spectra were aligned, merged, energy calibrated, and normalized. Linear combination fitting was attempted using MoO₃, MoO₂, Mo₂C, and bcc Mo foil as standards for the Mo XANES, and using CoO, Co(NO₃)₂, Co₃O₄, Co₂C and fcc Co foil as standards for the Co XANES.

Modeling of the EXAFS data was performed in the Artemis software of the Demeter package.³⁷ Models were built from absorber-backscatter scattering paths simulated from bulk material crystallographic data using FEFF6. S_0^2 was determined by modeling the Mo and Co foil EXAFS and found to be 0.94 and 0.77 for Mo and Co, respectively. Models of the catalyst EXAFS were optimized in R-space using k^1 , k^2 , and k^3 weightings, with all models obeying the Nyquist criterion.³⁸ Only the EXAFS spectra of the catalysts in the carburized and reaction states were modeled, because models of the catalyst structures under other conditions required more parameters than were available in the data. Fourier transformation was performed on EXAFS function (k = 3 - 11 Å⁻¹ for Mo; k = 3 - 10 Å⁻¹ for Co) and fitting was performed on an R-range of 1.3 – 3 Å for 100Mo and 50Mo/50Co at the Mo edge, 1 – 4 Å for 100Co, and 1 – 3 Å for 50Mo/50Co at the Co edge. Scattering paths generated from MoC, bcc Mo, and Co₇Mo₆ were used to model the Mo edge EXAFS, and paths generated from Co₂C and Co₇Mo₆ were used to model the Co edge EXAFS.

3 Results and Discussion





Figure 1: Steady state syngas conversion activity and selectivity of Mo/Co carbide catalysts. All reactions were carried out at 250 °C, 20 bar, 15 sccm total flow rate (2:1 H₂:CO). C_{2+} HC represents higher hydrocarbons and C_{2+} oxy represents higher oxygenates.

						% CO	Reaction Rate
Catalyst	CH ₄	$C_{2+}HC$	CO_2	MeOH	C ₂₊ oxy	Converted	(µmol CO/g*s)
100Mo	26 ± 3	40 ± 4	20 ± 6	10 ± 2	4 ± 1	1.1 ± 0.3	1.3 ± 0.3
75Mo/25Co	25 ± 3	29 ± 2	4 ± 1	27 ± 6	15 ± 2	2.6 ± 0.5	3.2 ± 0.7
50Mo/50Co	24 ± 2	30 ± 3	5 ± 2	25 ± 7	16 ± 2	2.5 ± 1.4	2.5 ± 0.3
25Mo/75Co	32 ± 5	34 ± 4	4 ± 1	17 ± 2	13 ± 4	1.9 ± 1.2	2.5 ± 0.6
100Co	44 ± 0.3	21 ± 0.3	11 ± 10	7 ± 4	16 ± 6	0.9 ± 0.03	0.7 ± 0.1
50Mo/50Co	26	28	3	25	18	1	3.7
seq imp	26	2.4					2.6
50Co/50Mo seg imp	36	34	4	15	11	3	3.6
100Mo + 100	45	30	9	12	3	0.6	0.3
Co phys mix							

 Table 1: Steady State Syngas Conversion Performance of Mo/Co Carbide Catalysts

Measurements performed at 250 °C, 20 bar syngas, 15 sccm total flow (H₂:CO = 2:1). C₂₊ HC represents higher hydrocarbons and C₂₊ oxy represents higher oxygenates. Uncertainties shown are standard deviations across three batches of sample.

Figure 1 and Table 1 show the syngas conversion activity and selectivity for Mo/Co carbide catalysts. While the pure metal carbides, 100Mo and 100Co, both show some selectivity towards methanol and higher oxygenates, consistent with results reported in literature,^{18,24,26} the binary Mo/Co carbide catalysts prepared by co-impregnation show several improvements in performance. First, the selectivities towards higher oxygenates (C_{2+} oxy) are significantly higher in the mixed Mo/Co carbide catalysts compared to the 100Mo catalyst and are comparable to the 100Co catalyst. The mixed carbide catalysts also show higher methanol selectivities than either pure metal carbide. This suggests a greater surface coverage of non-dissociated CO, which can be hydrogenated to methanol or undergo CO insertion to form C₂₊ oxygenates. Second, the binary Mo/Co carbide catalysts show slight decreases in hydrocarbon selectivity and significantly decreased CO₂ production. This is also consistent with a decrease in CO dissociation on the Mo/Co carbide surface, which leads to less surface coverage of oxygen, and

thus less CO₂ formation either through the Boudouard reaction or via water formation and subsequent water-gas shift. These changes in hydrocarbon and oxygenate selectivity are most significant when some Co is added to the Mo carbide, as seen in comparing the 100Mo and 75Mo/25Co catalysts. With decreasing Mo:Co ratio, the oxygenate selectivity decreases and the methane selectivity increases, trending towards the performance of the pure Co carbide catalyst. Third, the binary Mo/Co carbide catalysts have higher CO conversion rates compared to the pure metal carbides. The addition of Co to the Mo carbide initially causes a 2.5-fold increase in activity, as seen in the 75Mo/25Co catalyst, and the activity decreases as the Co content in the catalyst increases.

To understand the types of active sites in the binary metal carbide catalysts, the catalytic reactivity was compared between several Mo/Co carbide catalysts with a 1:1 atomic ratio of Mo:Co, prepared by different methods. Figure 1 and Table 1 show the catalytic performance of Mo/Co carbide catalysts prepared by sequential impregnation, both with the Mo deposited before the Co, and in the opposite order. The catalytic performance of a physical mixture of the pure Mo and Co carbide catalysts was also tested, with the amounts of each catalyst selected to yield a 1:1 atomic ratio of Mo:Co. The physical mixture of the 100Mo and 100Co catalysts shows no enhancement in catalytic performance, with activity and selectivity comparable to each individual metal carbide. In contrast, both catalysts prepared by sequential impregnation show similar increases in activity and oxygenate selectivity that were observed in the binary catalysts prepared by co-impregnation. The differences in selectivity between the two sequentially impregnated catalysts may result from particle size effects, as will be discussed in section 3.3. These results suggest that the two metal carbides must be in close contact in order to achieve the improved catalytic performance. Thus, it is suggested that the active sites for higher oxygenate

formation are present on the mixed Mo and Co carbide surface, with no gas phase intermediates that transport from one metal carbide to the other. Furthermore, the similarity in observed catalytic performance between the co-impregnated and sequentially impregnated catalysts suggests that these catalysts have similar morphologies under reaction conditions. This morphology will be characterized and discussed in the next sections.

3.2 Characterization of As-prepared and Reduced Catalysts



Figure 2: XRD patterns of Mo/Co carbide catalysts in (a) as-prepared, (b) post reduction, and (c) post carburization conditions. Standard diffraction patterns for MoC_{1-x} , fcc Co, and Co_2C are plotted for reference. The patterns have been offset vertically for clarity.

The formation of Mo and Co carbides was achieved in two steps. The first step occurred during incipient wetness impregnation of the Mo and Co. Hexamethylenetetramine was added to the impregnation solution as a carbon source and the catalyst was calcined to form the Mo carbide as has been reported in the literature.³³ The calcined catalysts are denoted "as-prepared". Following reduction of the catalyst, the second carburization step was performed to ensure formation of Co carbide. Conversion of metallic Co to Co carbide was achieved via a high pressure CO exposure.^{24,35} Attempts were made to carburize the Mo through this high pressure CO exposure rather than using hexamethylenetetramine, but no Mo carbide formation was observed. The state of the catalyst following the high pressure CO exposure will be denoted "carburized". This second carburization step was performed immediately prior to syngas

reaction, and thus was performed in the syngas conversion reactor. In order to characterize the phases present in the catalyst, the structure of the material in each stage of the catalyst lifetime was measured, as discussed in sections 3.2 - 3.4.

The crystalline phases present in the as-prepared catalysts were characterized by XRD (Figure 2a). The 100Mo catalyst shows diffraction peaks consistent with molybdenum carbide in the α -MoC_{1-x} phase (PDF No. 00-015-0457). This phase has a rock-salt structure and can potentially contain vacancies at the carbon sites.^{39,40} The slight shifts in diffraction peak positions in the 100Mo catalyst relative to the MoC_{1-x} standard may result from a difference in carbon vacancy content or strain in the MoC_{1-x} lattice due to the small nanoparticle size.⁴¹ As the Co content increases, the intensities of the MoC_{1-x} peaks decrease and new peaks attributed to fcc Co emerge (PDF No. 00-015-0806). In particular the reflection at $q \approx 3.1$ Å⁻¹ grows more intense and a peak at q ≈ 3.6 Å⁻¹ emerges, both of which are consistent with fcc Co. We note, however, that these peaks are broad and weak in intensity, indicating that the majority of Co species are either highly dispersed or not crystalline, and thus cannot be fully characterized by XRD. The presence of MoC_{1-x} without cobalt carbide in the as-prepared catalyst suggests that the Mo carbide phase is stable under high temperature N₂ conditions, as has been reported previously,³³ whereas the cobalt(II) nitrate decomposes under these synthesis conditions to form metallic Co and dispersed Co species. The 100Co catalyst in the as-prepared state shows peaks that can all be assigned to a Co₃O₄ phase (PDF No. 00-042-1467). This is unexpected for the decomposition of cobalt(II) nitrate in N_2 ,⁴² and it is possible that a small leak resulted in exposure of the sample to air during synthesis and oxidized the Co to Co₃O₄.⁴³ However, because the catalyst is reduced at 450 °C to fcc Co prior to carburization and reaction, the presence of Co₃O₄ in the as-prepared 100Co catalyst should not affect any of the characterization or catalytic reactivity results.

TPR experiments were performed to determine the effect of reduction pretreatment on the catalyst structure and oxidation state. Reduction profiles are shown in Figure S2. The peaks in the reduction profile can be ascribed to the reaction of H_2 with surface oxide species to form H_2O , but may also result from the decomposition of surface carbide species to form CH_4 . The profile for the 100Co catalyst shows two peaks, corresponding to the two step reduction of Co_3O_4 to CoO and then to Co. The 100Mo and Mo/Co carbide catalysts show reduction peaks centered at 380-450 °C.

The oxidation states of Co and Mo during the reduction process were studied by in situ TPR XANES. For the 75Mo/25Co, 50Mo/50Co, and 25Mo/75Co catalysts, the Co K-edge TPR XANES profiles show a reduction in the white line intensity and a decrease in edge energy consistent with reduction of the catalysts (Figure S3).^{44–46} The presence of isosbestic points in the Co XANES scans indicates a 1-to-1 transformation between the initial and final catalyst structures. The chemical structure of the catalyst was characterized by linear combination fitting of the Co XANES of the as-prepared and reduced catalysts to bulk standards (Figure S4, Table S1). The features in the XANES spectra of the as-prepared catalyst are similar to those of CoO, and in the reduced catalysts, the structures are similar to fcc metallic Co. We attribute the discrepancies between the measured XANES data and the fits to either the presence of Mo, which may affect the structure of the Co phases, and/or the phases in the catalysts being present as nanoparticles, which will exhibit weaker intensity oscillations in the XANES spectra compared to bulk standards.⁴⁷ The TPR XANES spectra for the 100Co catalyst shows a multistep reduction process (Figure S3d). Fitting the XANES spectra to Co_3O_4 , CoO, and fcc Co foil standards reveals the two-step reduction process of Co₃O₄ to CoO to Co (Figure S5), consistent with the reduction profile for this catalyst.

The Mo K-edge TPR XANES profiles for the catalysts are shown in Figure S6. A decrease in edge energy is observed for all catalysts during the TPR process, indicating a reduction in the oxidation state of Mo.⁴⁸ The lack of isosbestic points in the TPR XANES spectra indicates that the reduction occurs through a multi-step process, which is consistent with the presence of multiple reduction peaks observed in the TPR profiles. The Mo XANES spectra for the 75Mo/25Co, 50Mo/50Co, and 25Mo/75Co as-prepared catalysts show a pre-edge peak, which is characteristic of Mo⁶⁺ species.⁴⁹ However, once reduction is complete, the pre-edge peak is no longer present, and the XANES spectra of all catalysts have a relatively similar shape. This suggests that the structure of the Mo is qualitatively similar across all reduced catalysts. The results of these reduction studies are consistent with the removal of a passivating surface oxide encapsulating the catalyst nanoparticles. With the exception of the 100Co catalyst, the asprepared catalysts consist of MoC_{1-x} and metallic Co, which are passivated by a surface oxide layer upon exposure to air. To confirm the presence of MoC_{1-x} and fcc Co in the reduced catalysts, ex situ XRD measurements of the reduced samples were performed (Figure 2b). The diffraction peaks attributed to MoC_{1-x} are present in the reduced catalysts, demonstrating the stability of the Mo carbide phase during the reduction process. With increasing Co content, the reflection at $q \approx 3.1$ Å⁻¹ grows in intensity, consistent with the presence of fcc Co. Thus, we find that the reduction treatment at 450 °C is appropriate to remove the surface oxides, while leaving the underlying MoC_{1-x} and metallic Co intact.



Figure 3: In situ XANES spectra of reduced Mo/Co carbide catalysts at (a) Mo K-edge and (b) Co K-edge. Reduction was performed at 450 °C, 1 atm, 10 sccm H_2 , and measurements were performed at 250 °C, 1 atm, 10 sccm H_2 . Spectra are offset for clarity.

To characterize structural differences between the catalysts, the XANES spectra of the reduced catalysts were compared. The Mo and Co K-edge positions of the reduced catalysts are shown in Table S2 along with Mo and Co oxide and carbide standards for comparison. The Mo edge energies are very close to those of Mo metal and the Mo₂C standard. This is consistent with the presence of a Mo carbide, which is expected to have metal-like properties.¹⁵ The Co edge energies are also very similar to that of the Co foil, in agreement with the formation of metallic Co in the reduced catalyst. The reduced catalyst XANES spectra are plotted in Figure 3. The variations in the positions and intensity of the XANES features observed between the catalysts may result from the differences in bonding environments of a typical Mo or Co atom as the catalyst composition is changed. There is, however, a general trend that the oscillations in the XANES spectra for catalysts with intermediate Mo/Co compositions are broadened and weaker in intensity than those of the 100Mo or 100Co samples. The weakened intensity of the XANES oscillations can result from either a smaller nanoparticle size or a decrease in crystallinity of the

mixed metal carbide catalysts.⁵⁰ Each of these possibilities will be discussed further in the next section.

3.3 Ex Situ Characterization of Carburized Catalysts

Following reduction, the catalysts underwent a carburization step, before being exposed to syngas reaction conditions. The carburized catalysts were characterized in order to determine the structure and species present at the start of the syngas reaction. TEM images of the carburized catalysts are shown in Figure S7. In all catalysts, nanoparticles are formed and the average diameter of the nanoparticles increases with Co content (size range 3.4 - 8.5 nm diameter). TEM images of the sequentially impregnated catalysts show that depositing Co before Mo produces larger nanoparticles than the reverse order (Figure S8).

The variations in particle size across these catalysts may have an effect on reactivity. In particular, from a purely geometric perspective with all other factors unchanged, the total catalytic surface area per gram of material is expected to be inversely proportional to the nanoparticle diameter. To quantify the effects of nanoparticle size on catalyst reactivity, area-normalized activities were computed for each catalyst, assuming spherical nanoparticles with a homogeneous distribution of Mo and Co (Table S3). The trends in the area-normalized catalyst activities are very similar to those presented in Figure 1 and Table 1, with the mixed Mo/Co carbide catalysts showing a factor of 2-3 increase in activity compared to either pure metal carbide. Thus the primary factor driving the improved syngas conversion activity in the mixed metal carbides is likely the variation in Mo:Co ratio, rather than the total exposed catalytic surface area.

There may, however, be some effects of catalyst nanoparticle size on selectivity. For both the co-impregnation and sequential impregnation synthesis methods, the catalysts with larger

particle sizes showed greater selectivity towards hydrocarbons rather than oxygenates. Such trends in catalyst performance likely result from variations in ratios of different types of surface sites as a function of particle size and have been reported extensively in the literature.^{51–54} Thus, although the differences in catalyst composition undoubtedly impact selectivity, these results suggest that variations in nanoparticle size may also be driving the observed changes in product selectivity.



Figure 4: TEM images and STEM-EDS elemental maps of Mo/Co carbide catalysts postcarburization. Catalysts are (a) 75Mo/25Co, (b) 50Mo/50Co, (c) 25Mo/75Co, (d) 50Mo/50Co seq imp, and (e) 50Co/50Mo seq imp. Maps show Co (red), Mo (green), and overlay map along with Si (blue).

To characterize the distribution of Mo and Co atoms in the binary metal carbides, high

resolution STEM-EDS elemental mapping was performed on the carburized catalysts. In the

catalysts prepared by co-impregnation, the elemental maps reveal that the Mo and Co atoms are uniformly mixed within each nanoparticle (Figure 4a-c). This is expected because the impregnation solution contained a mixture of the metal precursors, and the results show that no significant phase separation between the species occurs during the reduction and carburization steps. However, somewhat surprisingly, the Mo and Co atoms in the catalysts prepared by sequential impregnation are also uniformly mixed (Figure 4d-e), suggesting that a mixed structure is more stable than one where the metals are phase segregated. This conclusion is in agreement with the reactivity results, which showed that the co-impregnated and sequentially impregnated catalysts have similar catalytic properties, implying that they have similar structures. The Co and Mo EDS signals from Figure 4 were integrated over each nanoparticle for all the catalysts and the resulting Mo fractions are shown in Figure 5. The average atomic fraction of Mo in each nanoparticle agrees well with the nominal value expected from the synthesis. We note some inhomogeneity in the Mo:Co ratio for each sample. Despite the variations in particle composition, the presence of both Mo and Co atoms in all the nanoparticles agrees well with the catalytic results showing that a close contact between Mo and Co is necessary to achieve improved performance. Finally, STEM-EDS mapping of carbon was also attempted to assess the spatial and elemental distribution of the metal carbides. Although efforts were made to clean the catalyst surface prior to measurement, the carbon maps for most of the catalysts were dominated by carbon contamination, making it impossible to distinguish carbon in the metal carbide from that of the contamination. A carbon map with sufficiently low background signal could only be performed for the 25Mo/75Co catalyst (Figure S9). In this sample the location of carbon coincides with that of Co and Mo, consistent with the formation of metal carbides.



Figure 5: Box-whisker plots of nanoparticle compositions. Compositions were quantified from STEM-EDS spectra integrated over each nanoparticle. From bottom to top, horizontal lines in each box-whisker plot indicate minimum, first quartile, median, third quartile, and maximum in particle composition. + sign indicates the mean particle composition. Expected Mo concentrations are shown as horizontal lines for 75Mo/25Co, 50Mo/50Co, and 25Mo/75Co compositions.

The phases present in the carburized catalysts were probed by XRD (Figure 2c). The 100Mo catalyst shows peaks consistent with MoC_{1-x}, as expected from the previous XRD measurements collected post-reduction. The structure of the 100Co catalyst is Co₂C (PDF No. 04-004-4639), indicating that the Co metal is carburized by the high temperature and high pressure CO treatment. XRD patterns of the binary Mo/Co carbide catalysts show some peaks that are attributable to both MoC_{1-x} and Co₂C. In particular, as the Co content increases, the peak at $q \approx 3 \text{ Å}^{-1}$ becomes more intense, aligning with the strongest peak in Co₂C. In the 25Mo/75Co catalyst, additional structure can be observed in the peak from 2.8-3.2 Å⁻¹, resulting from the three peaks in the Co₂C diffraction pattern in this range. The XRD patterns of the sequentially impregnated catalysts also show MoC_{1-x} features and an increased intensity of the $q \approx 3 \text{ Å}^{-1}$ reflection compared to pure MoC_{1-x} that can be attributed to Co₂C (Figure S10). However, in all of the binary metal carbide catalysts the diffraction peaks are very broad and low in intensity.

in the mixed metal carbides. Because the TEM images discussed above show that the nanoparticles are not only large enough to be detected by XRD (> 3 nm), but also increase in size with Co content, we attribute the weak, broad peaks to poor crystallinity and conclude that the structure of the binary metal carbide catalysts lack the long-range order that is present in the pure metal carbides. This conclusion is consistent with the XANES spectra of the reduced catalysts, which also showed a decrease in oscillation intensity in the mixed metal carbides as a result of the amorphous structure.

Finally, XPS measurements were performed on the carburized catalysts to characterize the Mo and Co oxidation states present at the surface. XPS survey scans of the catalysts show Mo and Co peaks from the nanoparticles, as well as Si from the SiO₂ support (Figure S11). The oxygen peaks arise primarily from the SiO₂ support, but may also have contributions from surface oxidation of the nanoparticles. Additionally, C peaks can be observed, but likely result from adventitious carbon as well as the carbon tape used to affix samples for the measurement. The atomic percentages of each element, along with the fraction of Mo relative to Mo+Co are shown in Table S4. The atomic fraction of Mo follows the expected decreasing trend as Co content increases. The minor discrepancies between the expected and nominal Mo concentrations likely result from the very low atomic percentages measured for Mo and Co, approaching the lower detection limit of the instrument. High resolution scans of the Mo 3d and Co 2p regions of the XPS spectrum are shown in Figure S12. For a single Mo oxidation state, the Mo 3d region is expected to have 2 peaks with a separation of 3.15 eV, resulting from the $3d_{5/2}$ and $3d_{3/2}$ spinorbit splitting. The Mo XPS spectra for the catalysts show multiple peaks, indicating a mixture of oxidation states (Figure S12a). The low oxidation state Mo can be assigned to Mo carbide,^{20,55} in which the Mo is expected to have metal-like characteristics. The higher oxidation state Mo likely

results from surface oxidation that occurred when transporting the sample from the reactor to the XPS spectrometer. The Co 2p region of the XPS spectrum also shows a mixture of oxidation states (Figure S12b). The Co⁰ peak is assigned to cobalt carbide, which has nearly identical binding energy to that of metallic Co.^{56,57} An additional Co²⁺ peak can be observed, which likely arises from air exposure resulting in surface oxidation to CoO when transferring samples to the XPS spectrometer. Together, the ex situ spectroscopic and structural characterization of the carburized samples reveals that the metal carbide catalysts form homogeneous, uniformly mixed nanoparticles, which have the expected Mo:Co ratios and an amorphous structure.

3.4 In Situ Characterization of Catalysts under Carburization and Reaction Conditions



Figure 6: In situ Mo K-edge XANES for (a) 100Mo and (b) 50Mo/50Co catalysts. Measurements are shown for the catalyst in as-prepared (25 °C, 1 atm, 10 sccm He), reduced (250 °C, 1 atm, 10 sccm H₂), carburized (250 °C, 20 bar, 10 sccm CO), and reaction (250 °C, 20 bar, 10 sccm H₂, 5 sccm CO) conditions. XANES spectra for bulk bcc Mo and Mo₂C standards are shown. (c) Magnitude (black) and imaginary component (blue) of the EXAFS Fourier transform are shown. Measured data are shown as points and fits are shown as solid lines. Catalyst spectra were fit in an R range of 1.3-3 Å. Spectra are offset for clarity. Corresponding *k*-space EXAFS and table of EXAFS fitting results are shown in Figure S14 and Table S5.

In situ XAS experiments were performed on the 100Mo, 100Co and 50Mo/50Co catalysts to confirm the presence of the carbide phases observed in ex situ measurements and determine if the structure is stable under reaction conditions. After reduction, the time evolution

of the Mo K-edge XANES for the 100Mo catalyst under carburization conditions show some slight changes, but similar overall structure, consistent with the presence of MoC_{1-x} in the carburized catalyst (Figure S13a). The in situ XANES spectra of the 100Mo catalyst in the asprepared, reduced, and carburized states are all similar, demonstrating the stability of MoC_{1-x} throughout these pretreatment conditions (Figure 6a). We note that the XANES spectra of the catalyst show different features from both the bcc Mo and Mo₂C standards. This is expected because the structure of the MoC_{1-x} phase present in the catalyst differs from the structures of these standards. To further understand the in situ structure of the carburized 100Mo catalyst, detailed modeling of the EXAFS spectrum was performed (Figures 6c, S14, Table S5). The model consists of a first shell Mo-C scattering path, and a second shell Mo-Mo scattering paths. In order to obtain a satisfactory fit, Mo-Mo scattering paths from both MoC and bcc Mo needed to be included in the EXAFS model. We note that the contributions of the Mo-Mo paths from MoC and bcc Mo are out of phase with one another (Figure S15), and as a result, the magnitude of the Mo-Mo scattering peak in the Fourier transform is low and the uncertainties on the Mo-Mo coordination numbers are large. However, the catalyst is expected to be primarily Mo carbide based on the MoC_{1-x} phase measured by XRD and the lack of change in the XANES spectra throughout the reduction and carburization processes. In addition, we note that the coordination numbers are slightly lower than would be expected for bulk MoC (6 for Mo-C and 12 for Mo-Mo). This is expected for the EXAFS model of the 3-4 nm nanoparticles observed by TEM, since the surface atoms are undercoordinated.⁵⁸ Because the XRD and XANES measurements indicate that the catalyst structure is primarily MoC_{1-x} , we suggest that the Mo-Mo scattering path from bcc Mo in the model of the catalyst EXAFS represents a distortion in the MoC_{1-x} structure rather than the presence of a metallic Mo phase. This assertion is consistent

with the catalyst XRD patterns, which show shifts in the 100Mo diffraction peak positions relative to the MoC_{1-x} standard pattern and no detectable metallic Mo phase. The distortion in the Mo-Mo bond length may arise from carbon vacancies in the MoC_{1-x} structure or from strain induced by the small nanoparticle sizes. Thus the EXAFS modeling of the 100Mo catalyst reveals a Mo carbide structure, but with some distortions from a perfectly crystalline MoC_{1-x} phase.



Figure 7: In situ Co K-edge XANES for (a) 100Co and (b) 50Mo/50Co catalysts. Measurements are shown for the catalyst in as-prepared (25 °C, 1 atm, 10 sccm He), reduced (250 °C, 1 atm, 10 sccm H₂), carburized (250 °C, 20 bar, 10 sccm CO), and reaction (250 °C, 20 bar, 10 sccm H₂, 5 sccm CO) conditions. XANES spectra for bulk fcc Co and Co₂C standards are shown. (c) Magnitude (black) and imaginary component (blue) of the EXAFS Fourier transform are shown. Measured data are shown as points and fits are shown as solid lines. Catalyst spectra were fit in an R range of 1-4 Å for 100Co and 1-3 Å for 50Mo/50Co. Spectra are offset for clarity. Corresponding *k*-space EXAFS and table of EXAFS fitting results are shown in Figure S16 and Table S6.

Following reduction, XANES evolution of the 100Co catalyst during carburization shows a 1-to-1 transformation from fcc Co to Co₂C, indicated by the presence of isosbestic points in the XANES spectra (Figures 7a, S16a). The EXAFS of the carburized 100Co catalyst can be fit well with a model consisting of the first three shells of bulk Co₂C (Figures 7c, S17, Table S6). When performing the fit, the coordination numbers were fixed at bulk values for Co₂C, which is reasonable for the relatively large nanoparticle sizes in the 100Co catalyst observed by TEM.

The formation of a Co_2C phase in the 100Co catalyst is consistent with ex situ XRD measurements of the carburized catalyst and prior studies of Co-based catalysts.

The 50Mo/50Co catalyst shows slight changes in both Mo and Co K-edge XANES spectra during carburization (Figures S13b, S16b). However, no changes in catalyst structure were observed from the carburized state throughout syngas reaction conditions (Figure 6, 7, S18). The lack of structural change in the catalyst during reaction was verified by ex situ XRD measurements, in which the patterns for the post-carburization and post-reaction ("spent") catalysts are identical (Figure S19). Because of this, the EXAFS spectra for the 50Mo/50Co catalyst after carburization and under steady state reaction conditions were modeled and fit simultaneously. The model for the Mo K-edge EXAFS of the 50Mo/50Co catalyst consisted of three paths: a Mo-C scattering path generated from bulk MoC, and Mo-Mo and Mo-Co scattering paths from the bimetallic Co₇Mo₆ (Figures 6b, S14, S20 Table S5). The coordination number of Mo-C is 2.9 ± 0.3 , which is 48% of the value expected for bulk MoC. This suggests that approximately half of the Mo atoms are in a carbide-like structure. The remaining Mo in the 50Mo/50Co catalyst is in a metallic structure, indicated by the presence of metallic Mo-Mo and Mo-Co scattering paths in the model and the relatively low Mo-C coordination number. The EXAFS fit yielded similar coordination numbers for the Mo-Mo and Mo-Co paths, showing that the average Mo atom is expected to have both Mo and Co neighbors. This result is consistent with the well-mixed nanoparticles observed by STEM-EDS elemental mapping.

The Co K-edge EXAFS model for the carburized and reaction condition 50Mo/50Co catalyst was achieved using four scattering paths: Co-C and Co-Co from Co₂C, and Co-Mo and Co-Co from Co₇Mo₆ (Figures 7c, S17, Table S6). As with the Mo EXAFS model, a satisfactory fit to the Co EXAFS data could only be achieved by including both carbidic and metallic

scattering paths in the model. Analysis of the components of the model reveals that the contributions from the carbidic and metallic scattering paths are not in phase and have different peak intensities (Figure S21). As a result, both carbide and metal contributions are needed to accurately model the catalyst structure during reaction. This result indicates that not all of the metallic Co in the reduced 50Mo/50Co catalyst is converted to a carbidic state during the high temperature and pressure CO treatment. The Co-C coordination number obtained from the fit to the data is 1.5 ± 1.7 . This value is 50% of the bulk first shell Co-C coordination value for Co₂C, indicating that about 50% of the Co is in a carbide-like state. In the second shell, the Co-Co coordination number (from Co_2C) is 5.1 ± 11.6, whereas the total Co-Co and Co-Mo coordination (from Co_7Mo_6) is 5.7 ± 10.9. These coordination numbers suggest that ~47% of the Co is carbidic, which is comparable to the result considering only the Co-C coordination number. Furthermore, the observation that roughly half the Co is carbidic and the remainder is metallic agrees well with the results from modeling the Mo K-edge EXAFS, which indicated that about half of the Mo is carbidic. Finally, the model of the Co EXAFS shows that the typical Co atom is expected to have both Co and Mo neighbors, consistent with the well-mixed nanoparticles observed by STEM-EDS.

It is important to note that the structures of the bulk Co₇Mo₆ and metal carbides used to construct the EXAFS models contain additional complexities which are not reflected in the models of the catalyst EXAFS. In particular, many shells of the bulk structures for these metals and metal carbides contain several different scattering paths of varying distances (Table S7). Attempts to include all the details of the varying path distances in the models of the 50Mo/50Co catalyst EXAFS did not yield satisfactory fits. Instead, the models needed to be simplified significantly to use only a few paths to represent an average nearest neighbor (metal-carbon) and

average second nearest neighbors (metal-metal). Discussions of the unsuccessful attempts to fit the Mo and Co EXAFS are included in the supporting information. This simplification of the EXAFS model is consistent with the amorphous catalyst structure indicated by the XRD and XANES measurements. The presence of amorphous nanoparticles is also reflected in the relatively value of σ^2 , (Tables S5, S6), which quantifies disorder in the catalyst structure and is relatively large due to the variation in bond lengths in the amorphous structure.⁵⁹

In summary, the EXAFS models of catalyst structure under reaction conditions reveal that the primary phases present in the 100Mo and 100Co catalysts are MoC_{1-x} and Co_2C , respectively. In the 50Mo/50Co catalyst, approximately half of the Mo and Co atoms have nearest neighbor C atoms, and thus are in a carbide-like structure, while the remaining Mo and Co atoms are metallic. Both the carbidic and metallic structures in the mixed catalyst do not have long-range order and instead are amorphous. The Co and Mo atoms in the nanoparticles are uniformly mixed based upon the detection of Mo-Co and Co-Mo scatterings paths and corroborated by the STEM-EDS mappings of the mixed particles.

3.5 Characterization of Surface Sites

The uniformly mixed nanoparticles detected by in situ EXAFS and ex situ STEM-EDS elemental maps suggest that Mo and Co are both present that the surface of the mixed catalysts. This result is also directly evident from measurements of the surface composition by ex situ XPS. However, it is not clear from these measurements whether both the Mo and Co atoms participate as adsorption sites for reactive species. To probe the active sites on the surface of the 100Mo, 50Mo/50Co, and 100Co catalysts, in situ CO DRIFTS measurements were performed. Due to temperature and pressure limitations of the DRIFTS system used for these measurements, catalyst reduction was performed at 380 °C (rather than 450 °C) and IR spectra were measured

after exposure of the catalyst to 10 bar CO (rather than 20 bar) at room temperature. Because these treatment conditions differ from those used for reaction and XAS characterization, the catalyst morphology in the DRIFTS measurements may not represent the actual structure during reaction.



Figure 8: In situ DRIFTS measurements of CO bound to (a) 100Mo, (b) 50Mo/50Co, and (c) 100Co catalysts. Spectra were measured at 1 atm, 26 °C in 10 sccm N_2 after exposure of the catalyst to 10 bar CO at 26 °C. (d) comparison between the DRIFTS spectra of each catalyst. Vertical lines indicate the positions of the CO vibration peaks in the 50Mo/50Co catalyst.

CO DRIFTS spectra for the 100Mo, 50Mo/50Co, and 100Co catalysts are shown in Figure 8a-c. In all spectra, the rovibrational spectrum of gaseous CO is present and decreases in intensity over time as CO is purged from the DRIFTS cell. In the 100Mo catalyst, CO vibration peaks are observed at 2023 cm⁻¹ and 1983 cm⁻¹, which can be assigned to CO bound to Mo¹⁺ and Mo⁰ sites, respectively.^{60,61} These Mo oxidation states are consistent with those observed by XPS (Figure S12) and are indicative of MoC_{1-x}.²⁰ Multiple CO vibration peaks are observed in the

DRIFTS spectrum of the 100Co catalyst, indicating the presence of many different adsorption sites. Peaks in the ranges of 2000 – 2050 cm⁻¹, 1850 – 1950 cm⁻¹, and 1750 – 1850 cm⁻¹, have been assigned to CO bound to Co⁰ in 1-fold (on-top), 2-fold (bridge), and 3-fold (hollow) configurations, respectively.^{62–64} The peak at ~2077 cm⁻¹, is assigned to CO adsorbed on Co₂C,⁶⁴ and demonstrates the presence of carbidic Co sites at the surface of the 100Co catalyst. Previous studies of CO adsorption on a carburized Co surface have shown that the CO vibration frequency increases relative to CO on metallic Co, resulting from an electron withdrawing effect of C, which decreases back-bonding of Co to the π^* antibonding orbitals of the CO molecule.⁶⁴ The presence of a significant amount of metallic Co, which was not observed in the XRD or EXAFS characterization of this catalyst during reaction, may result from the limitations in the DRIFTS system to reproduce the reduction and carburization conditions used in the other experiments.

The DRIFTS spectrum of the 50Mo/50Co catalyst shows three CO vibration features. The adsorption sites for each of these peaks are assigned by comparison to the 100Mo and 100Co spectra (Figure 8d). The CO vibrations at 2059 cm⁻¹, and 1937 cm⁻¹, both align with regions of high CO absorption intensity for the 100Co catalyst and where no CO adsorption peaks are observed in the 100Mo catalyst, indicating that these both result from CO bound to Co sites. On the other hand the peak at 1986 cm⁻¹ agrees very well with the highest intensity peak observed in CO bound to the 100Mo catalyst, indicating CO bound to Mo sites. Finally, we observe that the intensities of the CO adsorption peaks in the 50Mo/50Co catalyst decrease in time, as CO desorbs from the surface (Figure 8c). The desorption of CO demonstrates that both the Mo and Co sites on this catalyst can bind CO strongly enough for reactions to occur on the surface, but do not bind so strongly that the surface is poisoned by unreactive CO and C species. Consequently, we conclude that both Mo and Co atoms at the surface of the catalyst actively

participate as adsorption sites for CO and reaction intermediates. In particular, the synergy between Mo and Co is not purely an electronic interaction between the atoms, but instead requires a mixture of Mo and Co sites at the surface of the catalyst.

The participation of both Co and Mo as CO adsorption and activation sites is consistent with previous studies on the syngas reactivity of pure Co and Mo catalysts. Co is a well-known CO dissociation catalyst,⁶⁵ and metallic Mo has shown selectivity for syngas conversion to methanol,⁶⁶ indicating non-dissociative CO adsorption. Thus the interfaces between the Mo and Co atoms would create the appropriate bifunctional surface sites for higher oxygenate formation.⁶⁷ This assignment of active sites is consistent with the comparison of the catalytic reactivity between the 50Mo/50Co catalysts prepared by co-impregnation, sequential impregnation, and the physical mixture, which demonstrated that the Mo and Co must be in close contact to achieve improved catalyst performance.

4. Conclusions

We have synthesized and tested the syngas conversion catalytic properties of binary Mo/Co carbide catalysts. Reactivity testing demonstrates that the mixed Mo/Co carbide catalysts show improved selectivity towards methanol and higher oxygenates and an enhanced rate of CO conversion relative to either pure metal carbide. Under reaction conditions, the pure Mo and Co carbide catalysts form MoC_{1-x} and Co_2C phases, respectively. Through a combination of ex situ and in situ characterization we show that the binary catalysts form homogeneous amorphous nanoparticles, in which the Mo and Co atoms are uniformly mixed. XAS studies of the 50Mo/50Co catalyst under reaction conditions reveal a ~50/50 mixture of carbide-like and metal-like structures. The comparison of the catalytic performances of Mo/Co carbide catalysts with respect to their preparation method and structural characterization show that close contact

between Mo and Co is necessary to yield improved oxygenate yield. DRIFTS measurements of CO adsorbed on the catalysts indicate that both Mo and Co sites on the catalyst surface play an important role as adsorption sites for reactive species and in facilitating oxygenate formation. Taken together, the characterization of the catalyst structure and identification of the CO adsorption sites demonstrate that improvements in higher oxygenate yield are not contingent on the formation of a particular mixed metal/carbide phase, but instead result from the presence of both Mo and Co reaction sites in close contact at the surface of the catalyst. The metal carbides studied here show promise as alternatives to pure metal syngas conversion catalysts. The strategy of utilizing multi-component metal carbide systems employed in this work can be used in the design of catalysts to achieve the heterogeneity of CO adsorption sites required for higher oxygenate synthesis.

Associated Content

Supporting Information

Catalytic reactivity testing of washed and unwashed catalysts; Spectroscopic catalyst characterization by XPS and structural characterization by XRD, TEM, and STEM-EDS; In situ XAS studies including XANES profiles of catalyst reduction, carburization, and reaction, and details of in situ EXAFS fits.

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Notes

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Highlights

- Binary Mo/Co carbide catalysts show improved activity and oxygenate selectivity in syngas conversion reactions compared to pure metal carbides
- Catalysts form uniformly mixed, amorphous nanoparticles with carbidic and bimetallic species
- Enhanced higher oxygenate formation results from the presence of Mo and Co reaction sites in close contact at the surface of the catalyst

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

