Tuning of Higher Alcohol Selectivity and Productivity in CO Hydrogenation Reactions over K/MoS₂ Domains Supported on Mesoporous Activated Carbon and Mixed MgAl Oxide

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Abstract

Higher alcohol synthesis from syngas is studied over K/MoS₂ domains supported on mesoporous carbon (C), mixed MgAl oxide (MMO), or mixtures thereof. While the carbon support offers high ethanol productivity, the MMO support yields enhanced C₃+OH selectivity. MoKMMO-C, whereby Mo is initially contained on MMO then ground with carbon, behaves similarly to the parent MoKMMO catalyst, as Mo on MMO has limited mobility during reaction. In contrast, on MoKC-MMO, significant Mo migrates from C to MMO during reaction, giving reactivity associated with Mo species on both supports (high C₃+OH selectivity and productivity). MoS₂ domain structures are correlated with the selectivity of the catalysts (C₃+OH selectivity ~ double MoS₂ layers, total hydrocarbon selectivity ~ single MoS₂ layers). This study advances the

understanding the support's effect on structure-reactivity relationships for this family of catalysts and introduces a new catalyst composition with desirable reactivity.

Keywords: Syngas, Higher alcohols, Molybdenum Sulfide, Potassium, Mixed Metal Oxide, Activated Carbon

Introduction

Even though U.S. oil production has boomed in recent years due to hydraulic fracturing, the need for petroleum-free routes to value-added chemicals will continue to intensify in the future when carbon building blocks become increasingly scarce. Lower olefins (C_2 - C_4), primarily produced today by steam cracking, are key building blocks in the chemical industry, with ethylene being the largest volume petrochemical produced worldwide at approximately 80 million metric tons per year.[1] Another

versatile petrochemical is propylene, with 40 million metric tons produced every year. The demand for olefins will continue to increase, with propylene demand expected to exceed production capacity, inevitably requiring the development of alternative routes to olefins.

Syngas is a versatile chemical feedstock that can be produced from coal, biomass, methane, and mixtures thereof, with commercial technologies. Syngas-based processes to olefins include long chain hydrocarbon cracking, methanol to olefin conversion (MTO), and higher alcohol (C_2 - C_4) dehydration. Two of these building blocks are currently commercially produced from syngas: methanol over Cu based catalysts[1] and long chain hydrocarbons over Fischer-Tropsch (FT) catalysts.[2] However, there is no commercially viable catalyst to produce higher alcohols from syngas.

Higher alcohol synthesis has been investigated with different families of heterogeneous catalysts including noble metal Rh based catalysts,[3-11] modified Cu based methanol synthesis catalysts,[12-16] and modified FT catalysts based on Co, Ru, and Fe. [5, 8, 17-19] A particularly promising non-noble metal family of catalysts, MoS_2 based catalysts modified with potassium,[20, 21] has been widely studied due to its resistance to sulfur poisoning, less severe coke deposition, and ability to form higher alcohols with a high selectivity to ethanol. However, MoS_2 based catalysts are less active than noble metal catalysts and require higher pressures to achieve reasonable productivities.

Supported MoS_2 catalysts have also been widely studied as means to improve higher alcohol selectivity and productivity using SiO_2 , TiO_2 , MgO , Al_2O_3 , CeO_2 , and a

variety of carbons as supports.[22-25] Further studies were performed with activated carbon[26-32] and multi-walled carbon nanotubes (MWCNT)[17-19, 33-36] as supports that enhanced productivity due to higher dispersion of MoS₂ domains. These studies showed that catalytic activity is enhanced by dispersing the MoS₂ over the support and that Mo-support interactions can affect the reactivity and product distribution of the catalyst by facilitating alcohol reaction pathways. Recently, Morrill et al.[37, 38] developed new potassium promoted MoS₂ catalysts supported on a mixed Mg/Al oxide (MMO) support, derived from a hydrotalcite, that strongly perturbed the product distribution towards higher alcohols. The intrinsically basic properties of the support were suggested to promote alcohol-forming reactions, unlike common acidic γ -alumina[39-42] known to promote alcohol dehydration and subsequent hydrocarbon formation. The studies indicated that MMO supports yielded high C₃₊OH selectivity influenced by Mo-MMO interactions, but generally also yielded low catalytic productivity. It has further been shown that the Mo:MMO ratio greatly affected the reaction selectivity, while catalyst preparation methods had little impact on this parameter.[38]

It was also observed that low Mo loading, resulting in enhanced higher alcohol selectivity, could be correlated with highly dispersed, smaller MoS₂ domains with few stacked layers. Chianelli et al. previously investigated the effect of the degree of MoS₂ stacking on selectivity for hydrodesulfurization (HDS) reactions.[43] The proposed “Rim-Edge model” described the catalyst as a stack of several disks, with the top and bottom disks associated with rim sites and the disks in between associated with edge sites. The results showed that hydrogenation reactions

occurred on rim-sites only, whereas HDS reactions occurred on both rim and edge sites. Based on this model, it is hypothesized that CO hydrogenation reactions over K/MoS₂ supported on MMO should primarily occur on rim sites.

Furthermore, Morrill et al. noted that carbon supports yielded high methanol and ethanol selectivities.[37] Previous work on mesoporous carbon, prepared at Oak Ridge National Laboratory (ORNL), yielded catalysts with greater alcohol productivity than similar catalysts supported on a commercial activated carbon.[32, 44, 45] In this work, we seek to evaluate the hypotheses that molybdenum supported on a mixed support comprised of MMO and mesoporous activated carbon may allow for elevated higher alcohol productivity (due to MoS₂ domains on the carbon support) and good higher alcohol selectivity (due to MoS₂ domains on the MMO support), with an emphasis on understanding the MoS₂ structure-reactivity relationships over the carbon/MMO composite supported catalysts. A particular focus is placed on determining the effect of the support on MoS₂ structure, as well as the mobility of Mo species on the two supports under reaction conditions.

Experimental Section

Mesoporous activated carbon was prepared via a published procedure developed at ORNL. Mesoporous carbon was synthesized by carbonization of nanostructured polymeric, obtained by self-assembly of block copolymer and phenolic resin under acidic conditions *via* soft-template method, under flowing N₂ at 850 °C for 2h. The mesoporous carbon was then activated with KOH and subsequently washed by dilute HCl to remove residual KOH. For KOH activation, a physical mixture of solid

KOH (16 g) and mesoporous carbon (4 g) was loaded to a quartz tube in a nickel crucible and heated under flowing N₂ to 900 °C and held for 2h. The resulting material was washed with deionized water and then mixed with a ~0.2 M HCl solution that was then heated up to 80 °C with stirring for 30 min. The activated mesoporous activated carbon was collected by filtration, washed with deionized water, and dried at 100 °C.[46] MMO was synthesized using the same method described in our previous studies[37, 38] by coprecipitation of magnesium nitrate hexahydrate (Alfa Aesar, 98-102%), and aluminum nitrate nonahydrate (Alfa Aesar, 98-102%) aqueous solutions with a Mg:Al molar ratio of 7:3 (0.6 M in metal ions) together with a 1.2 M NaOH (EMD, 97.0%) and 0.15 M Na₂CO₃ (Aldrich, 99.5+%) at 65 °C and a pH of 9.5. The resulting solution was stirred for 48 h, filtered, washed with deionized water, dried overnight at 105 °C, and then calcined at 450 °C for 2 h.

A set of four catalysts using a mixture of mesoporous activated carbon (C) and MMO supports were synthesized with an approximate Mo loading of 5 wt.%, K loading of 3 wt.%, and a molar ratio of Mo:K of 1. The parent catalysts in this study, which are derived from a single support, are referred to as MoKMMO and MoKC. The mixed supported catalysts in this study are referred as MoKC-MMO and MoKMMO-C, where the parent catalyst is first prepared and is ground with a bare secondary support in a mass ratio of MMO:C of 3.6 to yield the final precatalysts (Figure 1). Mo_{0.15}K_{0.09}C was used as the parent catalyst for MoKC-MMO, and Mo_{0.06}K_{0.04}MMO was used as the parent catalyst of MoKMMO-C, so that when ground with the secondary support the desired Mo and K loadings were achieved. The precatalysts were then pressed into pellets for catalyst testing in the fixed bed reactor. MoKMMO

was pelletized to ~3000 psig, whereas mixed supported catalysts (MoKMMO-C and MoKC-MMO) were pelletized to ~6000 psig to obtain self-supporting pellets. In Table S1 in the SI, it is shown that upon pelletization the MMO and MMO-C supports lose ~20% of their surface area, and ~10% of their pore volume. Therefore, there is no considerable decrease in porosity upon pelletization.

Mo was added to the supports via incipient wetness impregnation using ammonium molybdate tetrahydrate (AMT) (Sigma-Aldrich, ACS Reagent) dissolved in DMSO for the MMO support (the solution was stirred for 12 h until AMT was dissolved) and water for the carbon support. DMSO was used as the impregnation solvent for MMO instead of water to limit the recrystallization of the hydrotalcite phase, which can be induced by water, thereby “burying” the potassium promoter.[14, 47, 48] The resulting materials were dried in open atmosphere at 135 °C for 12 h for the MMO support and at 100 °C for 12 h for the carbon support, and then placed in a quartz tube, whereby the AMT was decomposed via heating to 200 °C for 6 h at 5 °C/min, followed by further heating to 450 °C for 2 h at 5 °C/min under 40 mL/min of flowing N₂. After the decomposition step, the parent oxide precatalysts were physically ground for 15 min with K₂CO₃ (Aldrich, 99%, stored in an oven at 105 °C).[49] For the mixed supported catalysts, the parent catalyst was ground for an additional 15 min with the secondary support to create the precatalysts with mixed supports.

The prepared precatalysts containing MMO were pelletized, crushed, and sieved through 20-40 mesh prior to loading in the reactor, while for MoKC, silicon carbide (Alfa Aesar, 46 grit SiC) was mixed with the powder catalyst (but not ground)

in a 5:1 SiC:catalyst mass ratio to minimize plugging and hot spots, as self-supporting pellets could not be made with the carbon-rich catalyst. It is important to note that SiC is inert under the reaction conditions, as verified with a blank, SiC-only, reaction. The precatalysts were then loaded into a 6.35 mm steel tube reactor (1 g for MoKMMO, 0.8 g for the mixed supported catalysts, and 0.4 g for MoKC) for catalytic evaluation.

The precatalyst bed was then pretreated with 10% H₂S/H₂ (Matheson Tri-Gas, UHP) at 450 °C at a heating rate of 5 °C/min and then held at 450 °C for 2 h with a flow rate of 20 mL/min to reduce the oxide precatalyst to the sulfide phase, in situ. After in situ sulfidation, the reactions with syngas, 45% H₂ (Airgas, UHP), 45% CO (Airgas, UHP, purified with 5A molecular sieve carbonyl trap), 10% N₂ (Airgas, UHP) as an internal standard, and 50 ppm H₂S (from 5000 ppm H₂S in He, Matheson Tri-Gas, UHP) were carried out at 310 °C and 1500 psig at flow rates 10-60 mL/min (700-6500 mL/g_{catalyst}/h) to reach 3-4 different steady-state, isothermal CO conversion levels for a total of ~12 days of time on stream. All the catalysts studied reached the first isothermal CO conversion after 3 days of reaction, as shown in Figure S1. For the 2-3 additional isothermal CO conversion levels studied in each run, reactions were carried out until the productivity and product selectivity were stabilized for ~3 days. H₂S was added to the syngas feed to prevent sulfur leaching and maintain steady-state sulfur levels on the surface of the catalyst to ensure catalyst stability. No major change in activity was observed during ~12 days of reaction, with less than 10% change in the CO conversion observed over this period. Please note that significant safety precautions are required to study toxic (CO, H₂S) and flammable (H₂, CO, H₂S) gases under high pressure and temperature.

The main reaction products were quantified with an Agilent 7890 gas chromatograph (methane, ethane, ethylene, carbon dioxide, propane/propylene, methanol, ethanol, 1-propanol, 1-butanol, isobutyl alcohol, acetaldehyde, methyl formate, methyl acetate, ethyl acetate, methyl propionate, and ethyl propionate) using single point calibration curves. CO conversion, product productivity and reaction selectivity were calculated from pseudo-steady-state data.

At the completion of the reactions, all catalysts were passivated in situ with 1% O₂ in He (Matheson Trigas, UHP) for 8 h at room temperature at 20 mL/min. Catalysts were then placed in a vial under argon and stored in a desiccator. The reaction-aged catalysts were characterized ex situ via elemental analysis, nitrogen physisorption, X-ray diffraction (XRD), Raman spectroscopy, X-ray absorption spectroscopy (XAS) including the near-edge and extended X-ray absorption fine structure (XANES and EXAFS), and scanning transmission electron microscopy (STEM). In addition, the carbon and MMO supports were characterized with nitrogen physisorption and the carbon support was subject to ammonia and carbon dioxide temperature programmed desorption (TPD) experiments.

Elemental analysis was performed at ALS Environmental; for carbon analysis, the samples were directly analyzed using Perkin Elmer 2400 II (combustion/ thermal conductivity), and for metal analysis the samples were first digested in a microwave (Anton Paar Multiwave 3000) with nitric, hydrochloric, hydrofluoric, and peroxide, and the analysis was performed with inductively coupled plasma optical emission spectroscopy (ICP-OES) using Perkin Elmer Optima 3000 DV. Nitrogen physisorption isotherms were collected at -196 °C using Micromeritics Tristar II after being heated

to 200 °C under vacuum for 10 h prior to the analysis. Ammonia and carbon dioxide experiments were conducted on an AutoChem II 2920 instrument from Micromeritics. Approximately 35 mg of the sample was placed in a quartz U-tube, which was mounted on the instrument. For Ammonia TPD experiments, the sample was pretreated under a helium atmosphere by heating to 500 °C at a heating rate of 10 °C/min. Ammonia gas (1984 ppm in He) was introduced into the tube for one hour after cooling the sample to 120 °C. The system was then purged with helium for one hour at 120 °C. The TPD profile was recorded until the temperature reached 800 °C in helium flow at a heating rate of 10 °C/min. A similar procedure was followed for carbon dioxide TPD experiments, the sample (~ 35 mg) was pretreated under a helium atmosphere by heating to 700°C at a heating rate of 10°C/min. CO₂ gas (99.99%) was introduced into the tube for one hour after cooling down the sample to 50°C. The system was then purged with helium for 30 min at 50°C. The TPD profile was recorded till 700°C in helium flow at a heating rate of 10°C/min. XRD was performed using a Philips X-pert diffractometer using Cu-K α radiation. A Witec confocal Raman microscope (Alpha 300R) was used to obtain Raman spectra for the reaction-aged catalysts with an Ar⁺ ion laser (λ =513.998 nm) with 1.5 mW excitation source intensity and 1800 grading with <0.9 cm⁻¹ pixel resolution. Bulk MoS₂, molybdenum (IV) sulfide, purum, powder (Aldrich) was used as a reference material. Samples for STEM imaging were prepared by dispersing the particles in methanol and dropping them on a lacy carbon coated Cu grid. Images were collected on an aberration-corrected JEOL 2200FS STEM operated at 200 kV at ORNL.

X-ray absorption spectroscopy (EXAFS and XANES) was performed at beamlines 12-BM of the Advanced Photon Source (APS), Argonne National Laboratory, and beamline X18B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The XAS data were obtained in transmission mode at the Mo K-edge (20 keV) with a spot size of 0.5 mm x 1.2 mm at APS and 0.5 mm x 5 mm at NSLS. The Mo K-edge spectra were measured at room temperature in air with Mo foil as an energy reference. The reaction-aged catalysts were ground with boron nitride (99%, Sigma-Aldrich) and loaded into a polyamide tube (0.16 in. I.D.) to obtain an attenuation length of approximately one. Two scans from 19800 to 21000 eV were collected for each sample. The XAS data were then processed with Athena software for background removal, edge-step normalization, and Fourier transform.

Results and Discussion

XRD patterns of the reaction-aged catalysts after passivation are shown in Figure 2. Small, relatively broad peaks for the MoS₂ [101] (33°) and, [110] (58°) planes were observed in all of the reaction-aged catalysts. The MoS₂ [002] plane at 14° was observed for MoKC, MoKC-MMO, and MoKMMO-C, but was absent in MoKMMO. The presence of the [002] plane in the carbon containing catalysts could be indicative of a higher degree of MoS₂ stacking compared to MoKMMO.[50] Diffraction lines characteristic of the MgO at 44° and 64° were apparent in all MMO containing catalysts. It is important to note that the carbon-containing catalysts exhibited a diffraction line at 26°, corresponding to MoO₂ domains. Additional peaks at 37°, 44°, 53° were also characteristic of MoO₂ domains in the MoKC catalyst. The

presence of MoO₂ domains in carbon-containing catalysts are most likely attributed to incomplete reduction during in situ sulfidation.

N₂ physisorption isotherms of the mixed supported reaction-aged catalysts shown in Figure S3 in Supporting Information (SI) depict a double hysteresis due to a bimodal pore-size distribution (~34 nm due to the macroporous MMO support and ~10 nm due to the mesoporous carbon support) calculated with the Barret-Joyner Halenda (BJH) model. The Brunauer-Emmett-Teller (BET) surface areas calculated from the nitrogen physisorption data of the mixed supported catalysts were substantially smaller than those from the carbon supported catalyst due to the presence of the relatively low surface area MMO support (Table 1). This observation is consistent with the work of Dalai et al., where they observed a significant decrease in porosity upon binder incorporation to the CoRhMoS₂, MWCNT-supported catalysts as a means of enhancing pelletization for industrial applications.[51]

Elemental analysis results shown in Table 1 confirm that the catalysts were prepared within 10% of the target Mo and K wt. % loadings. It has been previously observed that the Mo:MMO mass ratio greatly affected catalyst selectivity.[38] Therefore, maintaining the Mo:MMO mass ratio for the MMO supported catalysts allows for meaningful comparison of the catalytic performance across the family of catalysts. Similarly, a constant MMO:C mass ratio for the mixed supported catalysts was used to shed light into the Mo mobility between the two support phases in the mixed supported catalysts, as it is thought that Mo species are highly mobile during sulfidation and possibly the early stages of the catalytic reaction.[52] It should also be

noted that the mass ratio of Mo/S was similar among all the catalysts and minor deviations did not follow any specific trend for the catalysts studied.

The reactivity results for the family of carbon and MMO supported K/MoS₂ catalysts are shown in Figure 3. Linear alcohol and total hydrocarbon selectivity, as well as C₂₊ alcohol productivity (C₂₊OH) are plotted against CO conversion. Selectivities are quantified on a CO₂-free basis for a clear depiction of higher alcohol synthesis, since CO₂ selectivities over these catalysts are high, due to water-gas shift reactions facilitated over MoS₂ based catalysts (Table S2).[53-56] A second set of catalysts prepared from different batches of MMO and C supports were prepared and reacted to ensure the reactivity trends were consistent and reproducible. The second set of catalyst's reactivity trends are shown in Figure S4.

The total non-alcohol oxygenate (acetaldehyde, methyl formate, methyl acetate, ethyl acetate, methyl propionate, and ethyl propionate) selectivities for all the catalysts in this study were less than 3% (Table S2), indicating that primarily linear alcohols were the oxygenates formed over these catalysts. As previously observed, MoKC was primarily selective towards methanol and ethanol, whereas MoKMMO shifted the product distribution from C₁-C₂ to C₂-C₄ linear alcohols.[37] It is observed in this work that the MoKMMO catalyst had the highest C₃₊OH selectivity, as expected, whereas the MoKC catalyst had the lowest C₃₊OH selectivity but showed improved C₂₊OH productivity compared to MoKMMO. The enhanced C₂₊OH productivity over the MoKC catalyst may be associated with the acidic nature of the carbon support, as suggested from NH₃ TPD (Figure S5a), supported by the work of Liakakou et al. correlating increased CO conversion with increased acidity of a similar

catalyst (K-NiMo supported on acid pretreated activated carbon).[32] The $C_{3+}OH$ selectivity trend for the MoKC-MMO catalyst was between that of the MoKMMO and MoKC parent catalysts (Figure 3), suggesting that some of the Mo was able to move from the originally (Mo) impregnated carbon support to the MMO support during sulfidation and reaction, creating a catalyst that was more selective towards $C_{3+}OH$, characteristic of the Mo domains on the MMO support. Unlike what was observed in the work by Dalai et al. upon binder incorporation to a CoRhMoS₂/MWCNT catalyst, the addition of the intrinsically basic MMO support to MoKC resulted in increased $C_{3+}OH$ selectivity instead of a significant reduction of total alcohol selectivity.[51] It is particularly striking to note that the MoKC-MMO catalyst gave the highest alcohol productivity in this family of catalysts with more than a two-fold increase in $C_{2+}OH$ productivity compared to that of the related MoKMMO and MoKMMO-C catalysts. In contrast, the MoKMMO-C catalyst had selectivity and productivity trends similar to MoKMMO, suggesting that the strong Mo-MMO interactions that existed when Mo was originally impregnated on MMO limited the ability of Mo to migrate to the carbon support under reaction conditions. It is important to note that the MoKMMO-C catalyst had a slightly higher total hydrocarbon selectivity, resulting in slightly lower $C_{2+}OH$ selectivity when compared to the MoKMMO catalyst. The addition of the acidic carbon support to MoKMMO to create MoKMMO-C resulted in increased hydrocarbon formation by promoting dehydration/hydrogenation reactions [32, 57].

The Anderson-Schulz-Flory (ASF) distribution for linear alcohols and linear hydrocarbons is shown in Figure S6. Consistent with the selectivity trends, the catalysts where the Mo was initially contained on the MMO (MoKMMO and

MoKMMO-C) had higher linear alcohol chain growth probabilities ($\alpha=0.49$) followed by the MoKC-MMO and MoKC catalysts. The MoKMMO material had the lowest alpha value for linear hydrocarbons, whereas the carbon containing catalysts (MoKC, MoKMMO-C, and MoKC-MMO) had increased alpha values. The MoKMMO-C catalyst had the highest alpha value (0.41) for linear hydrocarbons, consistent with higher hydrocarbon formation due to the acidic nature of the carbon support, as discussed above. Approximate turnover frequencies (TOFs) for $C_{2+}OH$, Total hydrocarbons (HC), and based on CO conversions are provided in Figure S7 and Table S4. A lower bound (LB) TOF estimate is provided, assuming all Mo atoms are active sites. In addition, a middle estimate (ME) of the TOF is provided, assuming all edge sites are active. Consistent with the productivity trends, the catalysts where the Mo was initially contained on the MMO support (MoKMMO and MoKMMO-C) had lower ME TOFs based on 5 % CO conversion (5.0 and 5.7 hr^{-1} , respectively) compared to catalysts whereby Mo was initially contained on the carbon support (MoKC (11.1 hr^{-1}) and MoKC-MMO (13.7 hr^{-1})). These values are an order of magnitude lower than values obtained for rhodium catalysts at similar reaction conditions, as shown in Table S5, as expected.

Mo-support interactions not only seem to affect Mo mobility, but also may facilitate certain reaction pathways. Mg/Al mixed oxides (MMO) can facilitate Guerbet coupling reactions due to their acid-base pairs, where the Lewis acidic Al is thought to stabilize the aldehyde and ketone intermediates.[58] It can be observed in Figure 3 that in MMO containing catalysts, ethanol selectivity decreased with increasing conversion, while 1-butanol selectivities increased, suggesting that ethanol self-

coupling may be an important secondary reaction over these catalysts. Even though MoS₂ is acidic in nature and the presence of potassium increases the basicity of the catalyst (creating the possibility of having both acid and base sites), the carbon support lacks the base sites present in MMO (Figure S5b), and therefore, this trend was not observed over MoKC. Furthermore, isobutyl alcohol selectivity, an indicator of methanol + 1-propanol coupling reactions, was measurably lower over MoKC than MoKMMO, as shown in Table S2. Further experiments need to be conducted to investigate the importance of coupling pathways over these catalysts, which will be the subject of a subsequent investigation.

To gain a deeper understanding of these reactivity trends it was necessary to explore the structural properties of the catalysts and how these properties affected the productivities and selectivities. The modification of MoS₂ based catalysts with potassium is well known to shift the product distribution from hydrocarbons to alcohols by inhibiting hydrocarbon formation, as shown in Figure S8a.[59] Unpromoted MoC and MoMMO catalysts were compared to promoted MoKC and MoKMMO catalysts. MoC and MoMMO catalysts were mainly selective towards hydrocarbons and upon K promotion their selectivity shifted from hydrocarbons to higher alcohols. The MoC material was not active towards higher alcohols (C₂₊OH productivity was close to zero), whereas the MoMMO catalyst showed similar C₂₊OH productivity compared to MoKMMO, as the intrinsically basic MMO support facilitates higher alcohol formation. Therefore, modification with potassium over the MMO supported catalysts affects only the selectivity of the catalyst by inhibiting hydrocarbon formation, without increasing the rate of alcohol formation. Additionally,

potassium is thought to play a role in the active sites for production of alcohols.[21, 60-63] X-ray photoelectron spectroscopy (XPS) analysis shown in Table S6 demonstrates that there was a decrease in sulfur content between the MoMMO and MoKMMO catalysts, which may be attributed to sulfur vacancies created when potassium intercalates in the MoS₂ stacked layers, which may inhibit hydrocarbon formation. This hypothesis is supported by the work of Beltrami et. al., where they correlated the sulfur loss (anionic vacancies) observed over an unsupported Ni/MoS₂ catalyst to the promotion of higher alcohol formation.[64] It has also been observed in the literature that alkali metal intercalates between the layers of MoS₂, [65-69] which are held together by van der Waals forces, and this weak binding force allows the interlayer gap to increase to accept alkali metal ions.

Raman spectra shown in Figure 4 of the MoKMMO and MoKMMO-C materials depict two bands at 379.5 and 401.5 cm⁻¹, which correspond to $\nu(E_{2g}^1)$ and $\nu(A_{1g})$ MoS₂ vibrational modes, respectively. The MoKC-MMO catalyst showed similar bands shifted to higher frequencies, 380.6 cm⁻¹ for $\nu(E_{2g}^1)$ and 402.4 cm⁻¹ for $\nu(A_{1g})$ vibrational modes. Similar to the MoKMMO and MoKMMO-C materials, the bulk MoS₂ commercial standard had a band at 379.5 cm⁻¹ corresponding to $\nu(E_{2g}^1)$, but the $\nu(A_{1g})$ band was shifted to 405.1 cm⁻¹, suggesting that the interlayer distance between the MoS₂ stacked layers was smaller than the MMO and carbon supported MoS₂ catalysts.[70] This difference may be caused by a lesser degree of MoS₂ stacking in the supported catalysts compared to the bulk MoS₂ material, resulting in a less compact MoS₂ domain[71] and/or by K intercalation between the MoS₂ stacked layers.[67] Figure S8b shows that promoted catalysts had a longer induction period

compared to unpromoted catalysts, which may be attributed to potassium intercalating in the MoS_2 structure.[60] The shift to higher frequencies observed in the MoKC-MMO catalyst compared to the MoKMMO and MoKMMO-C catalysts can be attributed to the increased number of MoS_2 domains with 3+ layers, as observed from STEM (Figure 6a) and discussed below, that have smaller interlayer distance compared to MoS_2 domains with mainly double layers (larger interlayer distance) present in MoKMMO and MoKMMO-C.[71] In contrast to the above materials, the Raman spectra for the MoKC material showed no Mo-S vibration bands, as MoKC was mainly comprised of single layers with highly dispersed Mo, as observed by STEM imaging, and described below. Additionally, it should be noted that the lack of Mo-S vibration bands for the MoKC catalyst is likely not associated with spectral fluorescence because a higher Mo content supported on the carbon showed these bands clearly (data not shown).

High-angle annular dark field (HAADF) STEM imaging was used as the primary means to characterize the MoS_2 domain size and [002] layer stacking in the various materials. A total of 790 STEM images were analyzed to determine the fraction of MoS_2 stacked layers in each sample of this family of catalysts, taking into account over 240 MoS_2 domains for the each of the MoKC, MoKC-MMO, and MoKMMO-C catalysts and 150 MoS_2 domains for the MoKMMO catalyst (a similar MoKMMO catalyst was previously by STEM[38]) The number of MoS_2 [002] stacked layers was quantified as single, double, triple and 3+ layers, as exemplified in Figure 5, and the percentage of MoS_2 [002] layers as a function of number of layers for each catalyst is quantified in Figure 6a. It should be noted that domains with fewer MoS_2

stacked layers (1-3 layers) were generally shorter in length than the domains with 3+ layers, among all the catalysts studied.

Analogous to the MoKMMO sample and consistent with the work of Morrill et al.[38], the MoKMMO-C catalyst contained mainly double MoS₂ layers (Figure 6a), consistent with reactivity trends selective toward C₃₊ alcohols, as described above. Figure 6b shows that as the number of double layers increases, the C₃₊OH selectivity increases. Dorokhov et al. observed a similar trend over K/MoS₂ supported on γ -Al₂O₃-SiO₂, where the total alcohol yield increased with an increasing fraction of 2+ layers, with double layers being the dominant domain size.[68] MoKMMO and MoKMMO-C have the highest fraction of double layers with correspondingly higher C₃₊OH selectivity, followed by MoKC-MMO, and MoKC having the lowest C₃₊OH selectivity with lowest fraction of double layers. This trend suggests that K/MoS₂ interactions with MMO play an important role in the formation of higher alcohols, as strong support-Mo interactions limit the growth of the number of MoS₂ stacked layers, compared to carbon supported MoKC and MoKC-MMO catalysts that have a significant amount of 3+ layers due to weaker Mo-carbon interactions.

It can be further inferred that the MoKC catalyst had predominately single layers (without potassium intercalation, which is not possible for a single layer), which facilitate hydrocarbon formation. This is in agreement with the Rim-Edge model, where rim sites are responsible for hydrocarbon formation and single layers only possess rim sites.[43] Figure 6b further supports that single Mo rim sites correlate with production of hydrocarbons, as the selectivity for total hydrocarbons increased with an increase in the percentage of single layers present in the catalysts, as also

observed by Dorokhov et al.[68] The MMO-containing catalysts had a significantly lower fraction of single layers, supporting the low selectivity of these catalysts towards hydrocarbons.

A detailed analysis of domains comprised of 3+ layers and the MoO_2 domains, which were also present over the MoKC catalyst, was necessary to provide further insight into the single layer domain formation and their effect on hydrocarbon formation. Figure S12a shows that MoKC formed domains with 3+ layers in the proximity of MoO_2 domains, suggesting that MoO_2 domains supply Mo species for growth of nearby domains of 3+ MoS_2 layers. However, not all the MoO_2 domains were fully reduced to form MoS_2 stacked layers under the conditions used, as further supported by the peaks associated with crystalline MoO_2 domains observed in the XRD pattern of MoKC (Figure 2). Increasing the Mo and K loading to 15 and 9 wt.%, respectively, over a carbon support ($\text{Mo}_{0.15}\text{K}_{0.09}\text{C}$), resulted in the formation of predominantly domains with 3+ layers, as shown in Figure S15, suggesting that clustering of Mo species is necessary for the formation of highly stacked MoS_2 domains. Therefore, it is hypothesized that single layers over MoKC are formed due to the highly dispersed Mo species across the support (due to low Mo, K loading) that do not agglomerate to grow beyond the critical nucleus size necessary for growth of MoS_2 stacked layers, compared to $\text{Mo}_{0.15}\text{K}_{0.09}\text{C}$ with higher Mo and K loading. The XRD pattern of the higher loading $\text{Mo}_{0.15}\text{K}_{0.09}\text{C}$ material, shown in Figure S16, exhibited a MoO_2 diffraction line at 26° , also present in MoKC, further supporting that the presence of MoO_2 domains contribute to the formation of MoS_2 stacked layers and likely not single layers. In addition, the MoKC precatalyst in oxide form, without

undergoing in situ sulfidation, was selective towards methanol and ethanol (see Table S2) when it was used as the catalyst, supporting the notion that the MoO_2 domains do not strongly influence hydrocarbon formation under the conditions employed, and that single layer MoS_2 domains were likely responsible for hydrocarbon formation.

Additionally, it should be noted that the MoKC-MMO sample had a more even distribution of 2, 3, and 3+ MoS_2 stacked layers, supporting the observation that the selectivity trends for this catalyst were in between that of the MoKMMO and MoKC samples, as noted above, yielding a catalyst that was both active and selective to higher alcohols. This is consistent with our original hypothesis, whereby the MMO supported domains were suggested to provide sites that could yield good higher alcohol selectivity due to strong Mo-MMO interactions that limit the growth of stacked layers, and carbon supported domains would more effectively activate the hydrogen and carbon monoxide, yielding higher reaction rates due to weak Mo-C interactions that facilitate Mo dispersion across the supports. It should be noted that these correlating observations, however, do not necessarily prove causality, and it is unclear at this stage if reaction intermediates from carbon-supported domains migrate and further react on MMO supported domains. As mentioned above, the $\text{Mo}_{0.15}\text{K}_{0.09}\text{C}$ catalyst showed increased MoS_2 [002] stacking with an increase in loading compared to the MoKC material. This increase in stacking resulted in an increase in C_{2+}OH selectivity and productivity, as shown in Table S7. MMO supported catalysts showed an increase in stacking with increase in loading as well, similar to the C support. However, the catalyst with a lower Mo loading with fewer stacked layers was more selective towards C_{2+}OH and more productive towards C_{3+}OH . [38] It is hypothesized

that intimate contact between the K/MoS₂ domains and MMO has a synergistic effect in the formation of higher alcohols.

To further investigate the reactivity trends observed for the mixed supported catalysts, the MoKC-MMO and MoKMMO-C samples were subjected to different reaction times on-stream followed by STEM characterization to quantify changes of MoS₂ domain size as a function of reaction time. The MoKC-MMO catalyst underwent a significant change in the layer distribution as shown in Figure 7a. After ex situ sulfidation but without catalytic reaction, the catalyst possessed mainly double layers, but during the transient period at the initial stages of the catalytic reaction, the layer distribution shifted to 3 and 3+ layers, and the sample was comprised of mainly 3+ layers when the catalyst reached steady-state. It is important to note that the layer distribution of MoKC-MMO at steady-state was similar to that of the reaction-aged Mo_{0.15}K_{0.09}C shown in Figure S15, which suggests the majority of the Mo species formed large clusters (3+ layers) on the carbon when the reaction approached steady-state. This observation is consistent with the MoKC-MMO preparation, where the Mo_{0.15}K_{0.09}C oxide precatalyst was ground with the bare MMO, suggesting that MoKC-MMO will possess largely 3+ layers, similar to Mo_{0.15}K_{0.09}C, before the bulk of the Mo species redistribution across the supports occurs (if the Mo species were mobile during reaction). The drastic shift in layer distribution observed for the reaction-aged MoKC-MMO indicates that the Mo species were in fact highly mobile during the reaction and redistributed between the carbon and MMO supports, as there was an even distribution of 1, 2, 3, and 3+ layer domains in the catalyst after reaction. The Mo species were able to redistribute effectively because they

(relatively) weakly interacted with the parent carbon support compared to the MMO support. This Mo redistribution may allow vacancies or defects to be created on the MoS₂ domains, resulting in higher productivity, as discussed above. On the other hand, the MoKMMO-C catalyst did not undergo any significant change in the layer distribution as the reaction progressed, as shown in Figure 7b. This observation further supports the idea that when Mo was impregnated on the parent MMO support, the Mo species were more strongly bound to the MMO and were not significantly redistributed between the carbon and MMO supports during reaction, as with the MoKC-MMO counterpart. Additionally, Figure 7c shows that the significant change in productivity over MoKC-MMO during the first three days of reaction can be attributed to the growth of MoS₂ stacking. On the other hand, MoKMMO-C had no significant change in higher alcohol productivity (Figure 7d) over the first three days of reaction, from ex situ to steady-state, compared to MoKC-MMO, consistent with the lack of a change in layer distribution throughout the reaction.

It is also interesting to note that the layer distributions for both the MoKC-MMO and MoKMMO-C samples that were ex situ sulfided but not reacted with syngas were comparably similar (Figure 7a and 7b), indicating that the sulfidation process led to similar arrays of MoS₂ domains in the absence of syngas. However, specific Mo-support interactions affected the spontaneous growth of the Mo domains under syngas conversion conditions. In the case of MoKMMO-C, strong Mo-MMO interactions prevented significant redistribution of the array of MoS₂ stacked layers. In contrast, comparably weak Mo-C interactions in the MoKC-MMO catalyst facilitated significant redistribution of Mo and changed the array of MoS₂ stacked layers.

EXAFS spectroscopy was also used to shed light into the structure of the MoS₂ layers present over the family of carbon and MMO supported catalysts. The Fourier transform k^3 -weighted Mo K-edge EXAFS spectra show that the supported catalysts had lower Mo-Mo coordination numbers compared to bulk MoS₂, as the Mo-Mo peak intensity was far lower than the bulk MoS₂ counterpart, as also observed by Morrill et al.[38]. Lower Mo-Mo coordination numbers compared to the bulk MoS₂ may indicate monolayer defects created during the sulfidation and reaction. Among the catalysts studied, MoKC seemed to have the smallest Mo-Mo coordination number (Figure S17), as expected due to high dispersion of Mo species on the carbon support, which contained many single layer domains. The mixed supported catalysts (MoKC-MMO, MoKMMO-C) appeared to have Mo-Mo coordination numbers in between that of MoKMMO and MoKC, with MoKMMO having the highest Mo-Mo coordination number due strong Mo-MMO interactions that limited the dispersion of the Mo species on the support.

An assessment of the electronic structure of the MoS₂ domains was inferred from XANES spectroscopy, as shown in Figure 8.[72] Specifically, isosbestic points where the reaction-aged catalysts intersected bulk MoS₂ were an indication that the reaction-aged catalysts had chemical states similar to that of bulk MoS₂. Following the overlay of the XANES edges, it was unsurprising that the catalysts where Mo was originally impregnated on carbon (MoKC and MoKC-MMO in Figure 8a) were similar to each other just as those supported on MMO (MoKMMO and MoKMMO-C in Figure 8b) were similar as well. What is clear, however, is that the support interaction was quite subtle and that even though MoKC and MoKC-MMO had different isosbestic

points from MoKMMO and MoKMMO-C (at 20015 eV and 20005 eV, respectively), with both sets being slightly different from bulk MoS₂, all the catalysts studied had overall similar chemical signatures to that of the bulk MoS₂. In addition, the normalized first derivative, shown in the inset of Figure 8, offers further insight into the catalysts' chemical state. The adsorption edge energy of MoKC and MoKC-MMO shifted to higher values compared to that of MoKMMO and MoKMMO-C samples, suggesting a higher average Mo oxidation state for the catalysts where Mo was originally impregnated on carbon. The shift in adsorption energy of the MoKC and MoKC-MMO samples may be associated with the MoO₂ domains present after reaction, as seen in the XRD patterns in Figure 2 and STEM images (Figure S12). In addition, the spectra of the MoKC and MoKC-MMO catalysts, shown in Figure 8, differed from that of bulk MoS₂ in that they did not show the sharp feature at 20010 eV characteristic of bulk MoS₂, and there was an increase of intensity in the tail of the edge just before the white line at (20025 eV). These differences further suggest that both the MoKC and MoKC-MMO catalysts were not fully reduced from the oxide phase to the sulfide phase.[73, 74]

Conclusions

Two distinct supports, a layered MMO material and a mesoporous activated carbon, were combined to tune the higher alcohol selectivity and productivity of K/MoS₂ domains during syngas conversion. The reactivity and structural data compiled here are consistent with the hypothesis that Mo had the ability to migrate from the carbon support (where mobility was high) to the MMO support (where

mobility was lower), creating in the case of the MoKC-MMO material, a hybrid catalyst that was both productive and selective towards higher alcohols. In contrast, when the Mo was originally impregnated on the MMO support, Mo migration under reaction conditions was decreased, yielding a less active catalyst that behaved more like the parent MoKMMO material. The C₃₊OH selectivity over the family of catalysts was shown to correlate with the percentage of double [002] MoS₂ layers present in reaction-aged catalysts. Strong Mo-MMO interactions in MoKMMO and MoKMMO-C, which contained mainly double layers, were thought to limit the growth of MoS₂ stacked layers, resulting in the highest observed C₃₊OH selectivity over the catalysts studied. On the other hand, catalysts that contained many single [002] MoS₂ layers, without potassium intercalation, were shown to be more selective towards hydrocarbons, with MoKC having the highest total hydrocarbon selectivity. The structure-reactivity relationships (MoS₂ domain stacking vs. selectivity) explored in this work provide the basis for further investigations focused on understanding reaction pathways over these interesting catalysts.

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Figure 1. Catalyst schematic for (a) MoKC-*MMO* and (b) MoKMMO-*C* precatalysts with Mo oxide domains represented by spheres, mesoporous activated carbon represented by cylinders, and *MMO* represented by a rectangular box.

Figure 2. XRD patterns of *MMO* (gray) standard and reaction-aged MoKC (green), MoKMMO (blue), MoKC-*MMO* (magenta), MoKC-*MMO* (black) catalysts. (♦) MoS_2 (▲) MoO_2 (●) MoO_3 .

Table 1. BET surface area and composition for MMO and C supports and reaction-aged MoKC, MoKC-MMO, MoKMMO-C, MoKMMO catalysts.

Sample	BET Surface Area (m ² /g)	Mo wt. %	K wt. %	C wt. %	Mo/Mg mass ratio	Mo/S mass ratio
MMO	180	-	-	-	-	-
C	1989	-	-	-	-	-
MoKC	1263	5.3	2.3	74.1	-	1.60
MoKC-MMO	237	4.5	2.3	16.5	0.21	1.30
MoKMMO-C	266	5.6	2.4	15.6	0.24	1.97
MoKMMO	45	5.3	2.5	-	0.19	1.63

Figure 3. C₁-C₄ linear alcohols, total hydrocarbons (HC) and C₃+OH selectivity (CO₂-free), as well as C₂+OH productivity vs. CO conversion over MoKC, MoKC-MMO, MoKMMO, MoKMMO-C catalysts. Reaction conditions: 310 °C and 1500 psig. All reaction results are given after ~3 days of time on stream at steady state.

Figure 4. Raman spectra of bulk MoS_2 and reaction-aged MoKC, MoKMMO, MoKMMO-C, and MoKC-MMO catalysts.

Figure 5. Dark field STEM images of single layer (a), double layer (b), triple layer (c) and 3+ layer (d) examples of MoS_2 [002] stacking of the reaction-aged catalysts in this study.

Figure 6. (a) Layer distribution of MoS₂ stacked layers for the reaction-aged catalysts in this study (b) C₃+OH selectivity (CO₂-free) vs. % double layers (solid line) and total hydrocarbon selectivity (CO₂-free) vs. % single layers (circles) determined from Figure 6a.

Figure 7. Layer distribution of MoS₂ stacked layers with different reaction times on-stream: ex situ- 0 days, transient period (trans)- 0.5 days, steady state (ss)- 3 days, reaction-aged (R)- 10 days for MoKC-MMO (a) and MoKMMO-C (b). EtOH and C₃₊OH Productivity as a function of time for MoKC-MMO (c) and MoKMMO-C (d).

Figure 8. XANES Mo K-edge spectra of bulk MoS_2 , and reaction-aged (a) MoKC, MoKC-MMO, and (b) MoKMMO, MoKMMO-C catalysts; (inset) first derivative of the Mo K-edge spectra.

Graphical abstract