Assessing C₃-C₄ Alcohol Synthesis Pathways over a MgAl Oxide Supported K/MoS₂ Catalyst via ¹³C₂-Ethanol and ¹³C₂-Ethylene Co-Feeds

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Abstract

Mechanisms of C₃-C₄ alcohol synthesis from syngas are elucidated over a Mg/Al mixed metal oxide (MMO) supported K/MoS₂ catalyst via ¹³C₂-ethanol and ¹³C₂-ethylene co-feeds. K/bulk-MoS₂ is used as a control catalyst to provide insight into the role of K/MoS₂ and K/MoS₂-MMO sites on higher alcohol formation pathways. Analysis of the products via ¹³C-NMR show preferential enrichment of terminal carbons in C₃-C₄ alcohols with both co-feeds, suggesting that CO insertion is the primary higher alcohol synthesis pathway, and that olefin carbonylation proceeds through the same pathway as alcohol formation. The observation of ¹³C₄-1-butanol species during the CO hydrogenation reactions with ¹³C₂-ethanol co-feeds provides conclusive evidence of ethanol self-coupling to 1-butanol as a secondary pathway. Additionally, acetate species are shown to be formed via an acyl precursor reacting with an alkoxy anion. Hydrogenation of an acetyl species (CH₃CO*) to an ethoxy intermediate (C₂H₅O*) is shown to be largely irreversible under the reaction conditions employed, as no preferential enrichment is observed for the acetyl group in acetate species. Propionate species are shown to be formed via esterification of propionate with the corresponding alcohol, while isobutyl alcohol formation observed over both the K/bulk-MoS₂ and the MMO supported catalysts occurs via methanol coupling with 1-propanol or 1-propanol derived species.

Keywords: Syngas, Higher alcohols, Molybdenum Sulfide, CO insertion, Ethanol coupling

1. Introduction

A promising route to meet the need for petroleum-free pathways for the production of lower olefins, the building blocks of the chemical industry, is the use of the versatile chemical feedstock, syngas, for the production of higher alcohols that can later be converted into olefins. This synthesis route has been investigated with different families of catalysts including noble metal Rh-based catalysts [1-6], alkali modified methanol synthesis catalysts over Cu based catalysts [7-11], modified Fisher Tropsch catalysts over Co and Fe based catalysts modified with Ir [12-15], and alkali promoted Mo-based catalysts [16-19]. Potassium promoted MoS₂ based catalysts are a particularly promising family of catalysts [20] due to their resistance to sulfur poisoning, less severe coke deposition, and high ethanol selectivity.

Early studies over unsupported alkali/MoS₂ and alkali/Co/MoS₂ with a ¹³C-methanol co-feed by Santiesteban et al. revealed that only preferential enrichment of the terminal carbon of ethanol occurred, suggesting that CO inserted into a methyl intermediate to form an acyl precursor that was hydrogenated to produce ethanol [21]. However, recent studies hypothesized that ethanol self-coupling reactions to 1-butanol may also be important over related catalysts [22-24]. Christensen et al. observed that the production of 1-butanol was more strongly enhanced than 1-propanol formation with increasing ethanol co-feed over a carbon supported K/Co-MoS₂ catalyst, suggesting that self-coupling of ethanol or ethanol-derived species leads to 1-butanol [23]. This is further supported by enhancement of 1-butanol production with an acetaldehyde co-feed over a K/Co-MoS₂ catalyst [25].

The use of supports to enhance the reactivity of K/MoS₂ catalysts has been widely investigated, exploring a variety of oxide and carbon supports [26-34]. However, limited understanding of reaction pathways over supported K/MoS₂ catalysts is available due to the complexity of the catalyst and reaction mechanism(s). Previous work in our group showed that Mo-support interactions directly affect the higher alcohol product distribution [35-38], with hydrotalcite-derived mixed MgAl oxide (MMO) supports containing small K/MoS₂

domains (predominantly double MoS₂ layers) yielding high C₂₊OH selectivity. Changes in product distribution over the MMO supported K/MoS₂ catalyst via ethanol and ethylene co-feeds provided insight into reaction pathways.[38] CO insertion was hypothesized to be the primary pathway to higher alcohols over the MMO supported catalyst. Similar C₃₊OH production rates over the MMO supported catalyst with ethanol and ethylene co-feed experiments indicated that alcohol formation with ethanol co-feed likely proceeded via the same acyl intermediate as olefin carbonylation. The MMO support was thought to influence secondary pathways involving methanol plus 1-propanol coupling to form isobutyl alcohol and catalyze ethanol self-coupling to 1-butanol.

In this work, we track the fate of ¹³C by ¹³C-NMR and GC-MS analysis in CO hydrogenation reactions with ¹³C₂-ethylene and ¹³C₂-ethanol co-feeds over the MMO supported catalyst to elucidate the higher alcohol reaction pathway(s). K/bulk-MoS₂ was used as a control catalyst subject to ¹³C₂-ethylene co-feed, with an emphasis on understanding the role of K/MoS₂ and K/MoS₂-MMO sites on higher alcohol formation pathways. The K/bulk-MoS₂ catalyst was not subjected to reactions with ¹³C₂-ethanol, as the ethanol co-feed was found to be largely unreactive previously [38]. This study provides an unprecedented level of insight into the reaction pathways to higher alcohols from syngas over MMO supported K/MoS₂ catalysts.

2. Experimental Procedure

The MMO support was prepared in a similar manner as described in previous work [35-37]. Magnesium nitrate hexahydrate (Alfa Aesar, 98-102%), and aluminium nitrate nonahydrate (Alfa Aesar, 98-102%) solutions (Mg:Al molar ratio of 7:3 and 0.6 M in metal ions) were coprecipitated with a 1.2 M NaOH solution (EMD, 97.0%) and a 0.15 M Na₂CO₃ solution (Aldrich, 99.5+%) at 65 °C and a pH of 9.5. Subsequently, the solution

was stirred for 48 h, washed and filtered with 2 L of deionized water, dried at 105 °C and calcined at 450 °C for 2 h under air flow.

Bulk MoS₂ was prepared with similar methods as described in the literature [39]. Ammonium sulfide ((NH₄)₂S) (Alfa Aesar, 20-24% aq.) was combined with ammonium molybdate tetrahydrate (AMT) (Sigma Aldrich, ACS Reagent) and stirred for 1 h at 65 °C in an oil bath. 25 mL of a 25 wt.% acetic acid solution was then added to the mixture to precipitate the thiomolybdate. Next, the precipitated solution was washed and filtered with deionized water. The material was then subsequently loaded into a quartz tube to decompose the thiomolybdate to the MoS₂ phase by heating to 450 °C for 2 h at 5 °C min⁻¹ under 40 mL min⁻¹ of flowing N₂. The resulting bulk MoS₂ was then passivated with 1% O₂ in He (Matheson Trigas, UHP) flow at 40 mL min⁻¹ for 8 h at room temperature.

MMO supported K/MoS₂ catalysts were prepared with an approximate Mo loading of 5 wt.%, K loading of 3 wt.%, and a molar ratio of Mo:K of 1 (referred to as MoKMMO). K was added to the synthesized bulk MoS₂ with a molar ratio of Mo:K of 1, with this sample referred to as K/bulk-MoS₂. Both supported and unsupported precatalysts were physically ground for 15 min with K₂CO₃ (Aldrich, 99%, stored in an oven at 105 °C) [40].

The prepared K/bulk-MoS₂ and MoKMMO catalysts were then pelletized, crushed, and sieved through a 20-40 mesh. The precatalysts were then loaded into a 6.35 mm steel tube reactor (1 g for MoKMMO and 0.15 g for K/bulk-MoS₂) and pretreated, in situ, with 10% H₂S/H₂ (Matheson Tri-Gas, UHP) to reduce the surface oxidized K/bulk-MoS₂ catalyst and precatalyst oxide phase of the MoKMMO catalyst to the MoS₂ phase at 450 °C for 2 h at a heating rate of 5 °C/min and a flow rate of 20 mL/min. The CO hydrogenation reactions with syngas (45% H₂, 45% CO, 10% N₂, and 50 ppm H₂S) were carried out at 310 °C and 1500 psig after in situ sulfidation.

The syngas flowrate was adjusted between 10-20 mL/min to reach pseudo steady state at 8% conversion after ~3 days of reaction. Then the ethanol co-feeds, unlabeled

ethanol (Sigma Aldrich, 99.5%) or 10% $^{13}\text{C}_2$ -ethanol (Sigma Aldrich, 99 atom% ^{13}C), balanced with ethanol (Sigma Aldrich, 99.5%), was introduced into the reactor using a 500D Isco Pump. Similarly, ethylene co-feeds, unlabeled ethylene (Matheson, 99.95%), or 10% $^{13}\text{C}_2$ -ethylene (Cambridge Isotope, 99%), balanced with ethylene (Matheson, 99.95%) was introduced into the reactor using a 100DX Isco pump. Ethanol and ethylene co-feed experiments containing natural abundance (~ 1.1 atom%) ^{13}C were conducted as control experiments. Ethanol co-feeds were heated to 200 °C to convert the liquid to the vapor phase and pressurized to 1500 psig before introduction into the reactor at 1 and 2 $\mu\text{L}/\text{min}$, making a 0-6 mol% composition with the syngas feed. The ethylene co-feed was pressurized to 1500 psig and introduced into the reactor at 3 and 4 $\mu\text{L}/\text{min}$, making a 0-9 mol% composition with the syngas feed.

The ethanol and ethylene co-feeds were fed into the reactor at the first flowrate set point until the reaction reached pseudo steady state. Once pseudo steady state was reached, the liquid reaction products were collected for 18 hrs using a liquid nitrogen trap placed downstream from the backpressure regulator and subsequently transferred to NMR tubes for ^{13}C -NMR analysis. The flowrate was then increased to the second set point (2 $\mu\text{L}/\text{min}$ for ethanol co-feed, 4 $\mu\text{L}/\text{min}$ for ethylene co-feed). After the reaction reached pseudo steady state a third time, the same procedure as discussed above was used to collect liquid products. Additionally, gas-tight NMR tubes were used to collect a gas aliquot for subsequent ^{13}C -NMR and GC-MS analyses. It is important to note that similar conversions and product distributions were observed before and after liquid product collection, as can be observed by the error bars in Fig. S1-S3 in the Supplementary Information (SI). This suggests that the catalyst was stable during liquid product collection. Finally, the co-feed was shut off until the product selectivity returned to its original state. Similar product distributions as obtained initially were observed after returning to the original state (Fig. S4), suggesting that the co-feeds did not cause any

significant change in the catalysts. It is important to note that ^{13}C co-feed experiments led similar product distributions to those obtained with unlabeled co-feed experiments, as previously reported [38].

The main products were quantified using single point calibration curves with an Agilent 7890 gas chromatograph (GC) (carbon dioxide, methane, ethane, ethylene, propane/propylene, $\text{C}_1\text{-C}_6$ linear alcohols). Isobutyl alcohol, as well as various aldehyde, acetate, and propionate species were also quantified as “other oxygenates” in Fig. S1-S2, S4. The productivity of reacting CO and the distribution of products were calculated in terms of moles C per g of Mo per hour from pseudo-steady-state data. These units were chosen to enable a direct comparison of reaction products.

The carbon distributions shown in terms of productivity in units of moles of C per gram of Mo per hour quantified from the GC data for the MoKMMO catalyst for 10% $^{13}\text{C}_2$ -ethanol co-feeds (Fig. S4a) and for 10% $^{13}\text{C}_2$ -ethylene (Fig. S4b) co-feeds are within 20% of closure (Table S1). The K/bulk-MoS₂ catalyst showed deviations within 10% of closure for 10% $^{13}\text{C}_2$ -ethylene co-feed (Table S1, Fig. S4c). Deviations in the carbon balance are likely attributed to the non-real-time determination of the inlet co-feed, as explained in SI, and deviations of ~5% of the internal standard (N_2) during reaction.

All catalysts were passivated at the completion of the reaction, in situ, with 1% O_2 in He for 8 h at room temperature at 20 mL/min. Catalysts were placed in a vial under nitrogen and stored in a desiccator. Ex situ characterization of the reaction-aged catalysts was performed via nitrogen physisorption and X-ray diffraction (XRD). A Micromeritics Tristar II was used for collecting nitrogen physisorption isotherms at -196 °C after the reaction-aged catalysts were heated to 200 °C under vacuum for 10 h prior to the analysis. A Philips X-pert diffractometer was used using Cu-K α radiation to collect XRD patterns of reaction-aged catalysts.

^{13}C NMR liquid samples were prepared by adding reaction products (300 μL) into CDCl_3 (600 μL) with THF (50 μL) as the internal standard. ^{13}C NMR spectra were recorded at room temperature on a Bruker AVIII-400 spectrometer using broad band proton decoupling. All chemical shifts are reported in parts per million (ppm) with reference to the center CDCl_3 solvent peak at 77.0 ppm. Quantitative measurements were made by suppressing the Nuclear Overhauser Effect using an inverse gated decoupling pulse sequence (zgig) and utilizing a 90° pulse angle with a sufficiently long pulse delay of 200 sec to ensure complete recovery, as determined from an inverse recovery T_1 experiment. GC-MS liquid samples were prepared by adding reaction products and THF (internal standard) in the ratio of 10:1 into acetone (solvent). GC-MS analysis was conducted on a Shimadzu GCMS-QP2010 S. The MS absolute intensity for all m/z of EtOH, 1-PrOH, and 1-ButOH products was normalized by the highest THF absolute intensity at $m/z=42.5$ to compare unlabeled and labeled co-feed experiments.

^{13}C NMR gas samples were prepared by pressurizing gas-tight NMR tubes to 80 psig after pulling vacuum on the tubes. ^{13}C NMR spectra were recorded at room temperature on a Bruker AVIII-400 spectrometer using broad band proton decoupling. Measurements were made by suppressing the Nuclear Overhauser Effect using an inverse gated decoupling pulse sequence (zgig) and utilizing a 30° pulse angle with a pulse delay of 6 sec. GC-MS gas samples were prepared by pressurizing gas-tight NMR tubes to 70 psig after pulling vacuum on the tubes. An Agilent 6890 GC coupled with a Micromass AutoSpec mass spectrometer were used for GC-MS analysis. The mass spectrometer was set to a mass resolution of 3000. The GC column used was an Agilent DB-5. The column was held at 30°C . Splitless injections were made, and the mass spectrometer was scanned from 10-110 Da at 0.5 sec/decade.

3. Results and Discussion

The XRD patterns of the reaction-aged catalysts are shown in Fig. S5. The diffraction peaks present in the reaction-aged K/bulk- MoS_2 catalysts can be indexed to the hexagonal MoS_2

phase (JCPDS: 00-037-1492). While the K/bulk-MoS₂ catalyst showed the [002] MoS₂ plane at 14° (indicative of MoS₂ stacking) [41], the [002] MoS₂ plane was negligible in the reaction-aged MoKMMO catalysts. This indicates a low degree of stacking associated with the predominant double MoS₂ layer formation over this catalyst [38]. The reaction-aged MoKMMO catalysts do show relatively broad peaks for the MoS₂ [100] (33°) and [110] (58°) and peaks characteristic of MgO at 44° and 64°.

Table S2 shows the BET surface areas calculated from N₂ physisorption data (P/P⁰ of 0.06-0.2) for the reaction-aged catalysts studied. The BET surface areas for the reaction-aged MoKMMO catalysts vary between 48 m²g⁻¹-63 m²g⁻¹ for co-feed experiments, similar to the reaction-aged catalysts without exposure to a co-feed [38]. As observed in previous work, the reaction-aged K/bulk-MoS₂ catalysts did not exhibit measurable porosity [38]. There is no measurable difference in the textural properties in the reaction-aged catalysts after co-feed exposure compared to those with only syngas hydrogenation exposure.

3.1 ¹³C₂-ethanol co-feed

The major product distribution quantified from the GC data for 10% ¹³C₂-ethanol (¹³C₂-EtOH) co-feed for the MoKMMO catalyst is shown in Fig. S1a. The ¹³C₂-EtOH co-feeds strongly perturbed the product distribution toward 1-propanol and 1-butanol over the MoKMMO catalyst, similar to what has been previously observed with unlabeled co-feed experiments [38]. It was previously hypothesized that CO insertion is likely the predominant pathway to higher alcohols (Fig. 1), as the chain growth probability decreased with increasing carbon chain length. It was also hypothesized that 1-propanol formation likely occurs through CO insertion into an ethyl species (C₂H₅^{*}) (derived from co-fed ethanol) to form a propionyl species (C₂H₅CO^{*}) that can be hydrogenated to form 1-propanol. Similarly, 1-butanol was hypothesized to be formed via hydrogenation of butanoyl species (C₃H₇CO^{*}) after CO insertion into a propyl intermediate.

Fig. 2 shows the ¹³C carbon enrichment of major products for the ¹³C₂-EtOH co-feed. A carbon was determined to be enriched as a result of the ¹³C₂-EtOH co-feed (open boxes) if the

enrichment factor was greater than that of the unlabeled ethanol co-feed (solid boxes). An example of ^{13}C carbon enrichment of 1-propanol over the MoKMMO catalyst for $^{13}\text{C}_2\text{-EtOH}$ can be observed in Fig S6. All the carbons in 1-propanol include a center peak attributed to unlabeled 1-propanol, and a doublet attributed to J coupling with the adjacent labeled carbon. Note that the C_1 in 1-propanol is not enriched (Fig. 2) and the doublet observed for this carbon (C_1) is attributed to the significantly enriched adjacent C_2 carbon. For ^{13}C -NMR analysis, the methanol peak area was normalized to one, as a means to account for experimental error between unlabeled and labeled experiments, since methanol productivity is not influenced by ethanol or ethylene co-feeds. The addition of the center peak and doublet areas normalized by the area of THF represents the ^{13}C carbon enrichment in Fig. 2. It is important to note that only singlets (corresponding to the center peak in labeled co-feed experiments) were observed for unlabeled co-feed experiments attributed to the natural ^{13}C abundance.

As expected, both carbons in ethanol were significantly enriched (also observed with GC-MS in Fig. S7) when 10% $^{13}\text{C}_2\text{-EtOH}$ was co-fed, as only ~56-67% of the ethanol is converted to higher chain products (Table S1). It is evident in Fig. 2 that preferential enrichment of the terminal carbons of the $\text{C}_3\text{-C}_4$ alcohols occurred. This is further supported by MS analysis, where $^{13}\text{C}_2\text{-1-PrOH}$ and $^{13}\text{C}_2\text{-1-ButOH}$ were observed (SI). The MS spectrum of 1-PrOH for $^{13}\text{C}_2\text{-EtOH}$ co-feed shows no ^{13}C enrichment of the C_1 carbon ($[\text{}^{13}\text{CH}_3\text{OH}]^+$ fragment with $m/z=32$) when compared to the unlabeled ethanol co-feed, further suggesting that the terminal carbon is not enriched (Fig. S8). The terminal carbons in 1-butanol are preferentially enriched, suggesting that 1-butanol formation primarily occurs through CO insertion into a propyl intermediate (derived from a propoxy intermediate in the route to 1-propanol, as shown in Fig. 1). These results elucidate that the findings by Santiesteban et al. [21], suggesting that CO insertion is the primary pathway for higher alcohol synthesis over unsupported $\text{K}_2\text{CO}_3/\text{Co}/\text{MoS}_2$, extend to supported catalysts (i.e. MoKMMO). Specifically, 1-propanol and 1-butanol formation

over the MoKMMO catalyst primarily proceeds through CO insertion into an alkyl intermediate to form an acyl precursor that can be hydrogenated to produce the corresponding alcohol (Fig. 1).

Even though the C_1 and C_2 ^{13}C carbon enrichment is subtle with increasing $^{13}\text{C}_2\text{-EtOH}$ co-feed over the MoKMMO catalyst compared to the unlabeled ethanol co-feeds (Fig. 2), the peaks in the NMR spectrum provide compelling evidence that $^{13}\text{C}_4\text{-1-butanol}$ species, indicative of ethanol self-coupling, are present in experiments with the $^{13}\text{C}_2\text{-EtOH}$ co-feed. A doublet is observed for the C_1 in 1-butanol for the $^{13}\text{C}_2\text{-EtOH}$ co-feeds (Fig. 3) in addition to the center peak attributed to unlabeled 1-butanol, indicating that the C_2 in 1-butanol is labeled. This is different from the 1-butanol ^{13}C -NMR spectrum with the 10% $^{13}\text{C}_2\text{-ethylene}$ ($^{13}\text{C}_2\text{-ethylene}$) co-feed (discussed below in section 3.2), where no doublet could be observed for the C_1 in 1-butanol (in addition to the center peak attributed to unlabeled 1-butanol), indicating that the C_2 is not enriched. Therefore, the doublet observed for the C_2 for 1-butanol for $^{13}\text{C}_2\text{-ethylene}$ co-feed experiments is attributed to J coupling with the significantly enriched C_3 in 1-butanol. The doublet observed for the C_2 in 1-butanol for the $^{13}\text{C}_2\text{-EtOH}$ co-feed suggests that the adjacent C_1 or C_3 in 1-butanol is enriched. The MS spectrum of 1-butanol for the $^{13}\text{C}_2\text{-EtOH}$ co-feed, shown in Fig. S9, provides evidence that the C_1 in 1-butanol is enriched, as enrichment of the $[\text{}^{13}\text{CH}_3\text{OH}]^+$ fragment with $m/z=32$ was observed compared to the unlabeled ethanol co-feed (not observed with $^{13}\text{C}_2\text{-ethylene}$ co-feed). The doublet observed for C_3 and C_4 and the ^{13}C enrichment in Fig. 2 provide evidence that both C_3 and C_4 are labeled and preferentially enriched, as explained above.

In addition, Fig. S10 shows that the ratio of the doublet to the center peak increases for both C_1 and C_2 in 1-butanol for increasing $^{13}\text{C}_2\text{-EtOH}$ co-feeds, indicated by an increase in the ratio of the coupling between $^{13}\text{C}_1$ and $^{13}\text{C}_2$. The combination of these results elucidate the presence of $^{13}\text{C}_4\text{-1-butanol}$ molecules with the $^{13}\text{C}_2\text{-EtOH}$ co-feed, suggesting that ethanol or ethanol-derived species self-coupling to 1-butanol occurs, particularly with increasing $^{13}\text{C}_2\text{-EtOH}$ co-feed. However, the preferential enrichment of the terminal carbons in 1-butanol indicates that ethanol

or ethanol derived species self-coupling to 1-butanol proceeds to a smaller extent as a secondary pathway compared to CO insertion over the MoKMMO catalyst. The work of Christensen et al. on K/CoMoS₂ and Santos et al. on K/MoS₂ catalysts previously suggested that higher alcohol formation proceeded not only through CO insertion, but also via aldol condensation of ethanol to 1-butanol with ethanol and nitrogen (syngas-free) co-feed experiments [23, 24]. The caveat of their syngas-free ethanol reaction is that it may be more (or less) likely to facilitate the ethanol self-coupling reaction due to the presence of a nitrogen atmosphere, with the reaction potentially occurring differently in a syngas atmosphere [22]. This observation highlights the importance of this work as the first study to conclusively show evidence for ethanol self-coupling to form ¹³C₄-1-butanol species in a syngas atmosphere over a K/MoS₂ based catalyst.

The distribution of other oxygenates quantified from the GC data for the ¹³C₂-EtOH co-feed for the MoKMMO catalyst is shown in Fig. S3a. The MoKMMO catalyst shows a variety of important products, as observed before with unlabeled co-feed experiments [38]. Ethyl acetate and ethyl propionate formation increases with increasing ¹³C₂-EtOH co-feeds, suggesting that ethanol is a precursor to these species [38]. Similarly, propyl propionate and propyl acetate increase with increasing ¹³C₂-EtOH co-feeds, likely a result of increasing 1-propanol formation, as 1-propanol is likely the precursor of these species.

Fig. 4 shows the ¹³C carbon enrichment of the minor products for the ¹³C₂-EtOH co-feed. It can be observed that the ethoxy group is preferentially enriched for ethyl acetate, suggesting that the ethoxy species (C₂H₅O*) derived from ethanol reacts with an acetyl species (CH₃CO*) (not enriched at 3% ¹³C₂-EtOH). Similarly, the terminal carbons in the propoxy group (C₃H₇O) of propyl acetate are preferentially enriched, indicating that a propoxy intermediate (formed in the route to 1-propanol) reacts with an acetyl species to form propyl acetate. This is in agreement with the study by Santiesteban et al., where they observed that the methyl group of methyl acetate was preferentially enriched with a ¹³C-MeOH co-feed, suggesting that methanol is a

building block for methyl acetate, formed via an acetyl intermediate reacting with a methoxy anion [21]. With increasing $^{13}\text{C}_2\text{-EtOH}$ co-feed (6.1% ^{13}C), the methyl carbon (CH_3) in the acetyl group (CH_3CO) of ethyl acetate becomes slightly enriched relative to the ^{13}C carbon enrichment of the propoxy group. No significant enrichment in the methyl carbon in the acetyl group of propyl acetate can be observed, as the increase in formation of ethyl acetate is significantly higher (~40%) than that of propyl acetate with increasing $^{13}\text{C}_2\text{-ethanol}$ co-feed. Since the enrichment of the acetyl group is only apparent in ethyl acetate with abundant (6.1%) $^{13}\text{C}_2\text{-EtOH}$ in the syngas feed, it can be concluded that hydrogenation of an acetyl species (CH_3CO^*) to the ethoxy intermediate ($\text{C}_2\text{H}_5\text{O}^*$) is largely irreversible under the conditions employed (Fig. 1).

It was previously hypothesized that ethyl propionate is formed via esterification of propionate (produced in the route to 1-propanol) with the co-fed ethanol [38]. Fig. 4 shows that both ethyl groups of ethyl propionate are preferentially enriched. Similarly, the terminal carbons in the propionate species and the propyl group are enriched in propyl propionate, suggesting that propyl propionate is formed via esterification of propionate with 1-propanol. These results elucidate that propionate species are formed via esterification of propionate with the corresponding alcohol. Additionally, it was hypothesized that the increase in 2-methyl-1-propanol formation observed over the MoKMMO catalyst with increasing ethanol co-feed was associated with the increase of 1-propanol derived species that coupled with methanol [38]. Even though it is not conclusive which of the methyl groups of 2-methyl-1-propanol is enriched, it can be concluded that only one of the methyl groups is labeled, as only a doublet is observed for the C_2 carbon in isobutyl alcohol (in addition to the center peak attributed to unlabeled isobutyl alcohol). Therefore, the preferential enrichment of terminal carbons of 2-methyl-1-propanol over the MoKMMO catalyst with $^{13}\text{C}_2\text{-EtOH}$ indicates that 1-propanol is coupled with methanol to form isobutyl alcohol.

3.2 $^{13}\text{C}_2\text{-ethylene}$ co-feed

The major product distribution quantified from the GC data for the $^{13}\text{C}_2$ -ethylene co-feed for the MoKMMO catalyst is shown in Fig. S1b. Similar to the $^{13}\text{C}_2$ -EtOH co-feeds, the $^{13}\text{C}_2$ -ethylene co-feeds shifted the product distribution toward C_3 - C_4 alcohols from C_2 - C_3 alcohols over the MoKMMO catalyst, as previously observed with unlabeled co-feed experiments [38]. It was hypothesized that alcohol formation from ethanol co-feed proceeds through the same intermediate as olefin carbonylation, as similar C_3 +OH formation rates were observed for $^{13}\text{C}_2$ -ethanol and $^{13}\text{C}_2$ -ethylene co-feed experiments when the major products were normalized by mol C of co-feed (Fig. S2) [38]. This hypothesis was supported by the work of Santiesteban et al. on a $\text{K}_2\text{CO}_3/\text{Co}/\text{MoS}_2$ catalyst, where they observed 1-propanol containing ^{13}C in two alternative positions ($^{13}\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3^{13}\text{CH}_2\text{CH}_2\text{OH}$, but not $^{13}\text{CH}_3^{13}\text{CH}_2\text{CH}_2\text{OH}$) with a $^{13}\text{CH}_3\text{OH}$ co-feed suggesting that CO insertion could occur on symmetric ethylene species [21]. Similar to the $^{13}\text{C}_2$ -EtOH experiments, it is evident in Fig. 5a that preferential enrichment of the terminal carbons of the C_3 - C_4 alcohols occurred over the MoKMMO catalyst with $^{13}\text{C}_2$ -ethylene co-feed experiments. This is further supported by MS analysis, where $^{13}\text{C}_2$ -1-PrOH and $^{13}\text{C}_2$ -1-ButOH were observed (SI). Fig. S11 shows peaks for $[^{13}\text{C}_2\text{-M}]^{+\bullet}$ with $m/z=62$ for doubly label 1-PrOH, and its corresponding $[^{13}\text{C}_2\text{-M-H}]^+$ with $m/z=61$. Even though no $[^{13}\text{C}_2\text{-M}]^{+\bullet}$ with $m/z=76$ was present for 1-butanol (Fig. S12), the peak at $m/z=58$ attributed to $[^{13}\text{C}_2\text{-M-H}_2\text{O}]^+$ indicates the presence of doubly labeled 1-butanol. Note that this peak is only present in the $^{13}\text{C}_2$ -ethylene co-feed experiment (not in the unlabeled ethylene co-feed). It can therefore be concluded that alcohol formation from ethanol proceeds via the same acyl intermediate as olefin carbonylation over the MoKMMO catalyst. It is important to note that the C_1 in 1-propanol and C_2 in 1-butanol are not enriched (Fig. 5a) and the doublets observed for these carbons are attributed to J coupling with the significantly enriched C_2 carbon in 1-propanol and C_3 in 1-butanol, respectively.

It has been previously observed that an ethylene co-feed significantly enhances the 1-propanol formation over the K/bulk-MoS₂ catalyst, unlike an ethanol co-feed, which was largely

unreactive [38]. However, the $^{13}\text{C}_2$ -ethylene co-feed over the K/bulk-MoS₂ catalyst does not influence the product distribution to C₃₊OH as significantly as over the MoKMMO catalyst (Fig. S1b, and Fig. S1c), supported by significantly lower $^{13}\text{C}_2$ -ethylene conversion (50-58%) over the K/bulk-MoS₂ catalyst compared to 100% $^{13}\text{C}_2$ -ethylene conversion over the MoKMMO catalyst, as shown in Table S1. Similar to the MoKMMO catalyst, preferential enrichment of the terminal carbons of the C₃-C₄ alcohols over the K/bulk-MoS₂ catalyst was observed with $^{13}\text{C}_2$ -ethylene co-feed experiments (Fig. 5b), also supported with GC-MS analysis (Fig. S13-S14). As discussed above, the doublet observed for the C₁ in 1-propanol and C₂ in 1-butanol is attributed to J coupling with the significantly enriched C₂ in 1-propanol and C₃ in 1-butanol, respectively. Relatively lower ^{13}C enrichment of the terminal carbons in 1-butanol was observed over the K/bulk-MoS₂ catalyst compared to that of the MoKMMO catalyst, consistent with the hypothesis that ethylene has the propensity to more favorably adsorb on smaller K/MoS₂ domains over the MoKMMO catalyst compared to large, multilayer K/MoS₂ domains over the K/bulk-MoS₂ catalyst [38]. Therefore, these observations provide support that the intimate contact between the K/MoS₂ domains and MMO has a synergistic effect in higher alcohol formation.

The distribution of other oxygenates quantified from the GC data for $^{13}\text{C}_2$ -ethylene co-feed over the MoKMMO catalyst is shown in Fig. S3b. As previously observed, propyl acetate and propyl propionate formation increases with increasing ethylene co-feeds over the MoKMMO catalyst, suggesting that 1-propanol is a precursor to these species [38]. Similar to the $^{13}\text{C}_2$ -EtOH co-feed over the MoKMMO catalyst, only the propoxy group in propyl acetate is preferentially enriched with $^{13}\text{C}_2$ -ethylene (Fig. 6a), providing further evidence that acetate species formation proceeds through the reaction of an alkoxy species and acetyl species (CH₃CO*). The propyl group and the terminal carbons in the propionate group are preferentially enriched in propyl propionate with $^{13}\text{C}_2$ -ethylene, similar to $^{13}\text{C}_2$ -EtOH. The terminal carbons of propanal can be observed to be enriched with $^{13}\text{C}_2$ -ethylene over the MoKMMO catalyst (Fig. 6a), as relatively more propanal is formed with ethylene co-feeds than ethanol co-feeds [38].

More apparent than with $^{13}\text{C}_2\text{-EtOH}$, the terminal carbons of 2-methyl-1-propanol were preferentially enriched with $^{13}\text{C}_2\text{-ethylene}$, indicating that the increased propanal formation, likely via ethylene hydroformylation, can lead to coupling with methanol to form isobutyl alcohol.

Although the productivity to other oxygenates is significantly smaller for the K/bulk-MoS₂ catalyst compared to the MoKMMO catalyst with $^{13}\text{C}_2\text{-ethylene}$ co-feeds (Fig. S3b-c), similar ^{13}C carbon enrichments in propanal, propyl acetate and propyl propionate were observed for both catalysts (Fig. 6a and 6b). It is important to note that the K/bulk-MoS₂ catalyst does catalyze 1-propanol plus methanol coupling to isobutyl alcohol,¹ as the terminal carbons of isobutyl alcohol were labeled with $^{13}\text{C}_2\text{-ethylene}$, similar to those over the MoKMMO catalyst. This suggests that the K/bulk-MoS₂ catalyst does contain the acid-base pairs necessary to catalyze isobutyl alcohol formation.

3.3 Gas sample analysis for $^{13}\text{C}_2\text{-EtOH}$ and $^{13}\text{C}_2\text{-ethylene}$ co-feeds

As previously observed, the co-fed $^{13}\text{C}_2\text{-ethylene}$ more strongly enhanced the formation of ethane compared to the $^{13}\text{C}_2\text{-ethanol}$ co-feed over the MoKMMO catalyst (Fig. S1a-b) [35]. Consistent with the reaction productivity results, the ^{13}C -NMR spectrum for the gas sample for the $^{13}\text{C}_2\text{-ethylene}$ co-feed over the MoKMMO catalyst showed a higher intensity singlet for C₂H₆ than the gas sample for $^{13}\text{C}_2\text{-EtOH}$ co-feed (Fig. 7). Similarly, a singlet is observed for C₂H₆ over the K/bulk-MoS₂ catalyst with $^{13}\text{C}_2\text{-ethylene}$ co-feed. Even though it can be observed via ^{13}C -NMR that ethane is enriched over the MoKMMO and K/bulk-MoS₂ catalysts with $^{13}\text{C}_2\text{-EtOH}$ and $^{13}\text{C}_2\text{-ethylene}$ co-feed experiments, it cannot be determined whether singly and/or doubly labeled ethane are present. GC-MS was used to investigate this issue further. It was found that doubly labeled ethane is likely present in reactions using both $^{13}\text{C}_2\text{-EtOH}$ and $^{13}\text{C}_2\text{-ethylene}$ co-feeds (Fig. S15-S17), but it cannot be ruled out that singly labeled ethane is also present due to fragment analysis complexity (refer to SI for further discussion).

¹Fig. S14c of Catal. Sci. Technol. 2016, 6, 1957-1966 has incorrect product labels. Refer to Fig. S3c for accurate product distribution.

CO and CO₂ singlets were observed in the ¹³C-NMR spectra of the MoKMMO catalyst with ¹³C₂-EtOH co-feed, while no peaks were observed for the unlabeled co-feed experiments over these catalysts under identical reaction and ¹³C-NMR conditions, indicating the presence of ¹³CO and ¹³CO₂. Additionally, ¹³CH₄ was observed with GC-MS analysis (not observed via ¹³C-NMR) over the MoKMMO catalyst with ¹³C₂-EtOH (Fig. S15). As discussed above, with increasing ¹³C₂-EtOH co-feed (6.1% ¹³C), the methyl carbon (CH₃) in the acetyl group (CH₃CO) of ethyl acetate becomes slightly enriched, suggesting that the dehydrogenation of the ethoxy intermediate (C₂H₅O*) to an acetyl species (CH₃CO*) is reversible to a small extent. Therefore, it is likely that the step involving CO insertion to the acetyl species (CH₃CO*), shown in Fig. 1, is also reversible, leading to the formation of ¹³CO and ¹³CH₄, with ¹³CH₄ formed from an enriched methyl precursor (¹³CH₃*). ¹³CO₂ is hypothesized to be formed over the MoKMMO catalyst through the water-gas shift (WGS) reaction, as K/MoS₂-based catalysts have a high WGS activity, which makes ¹³CO₂ an inevitable product [42-44]. With a ¹³C₂-ethylene co-feed the ¹³CO and ¹³CO₂ singlet decreases in intensity over the MoKMMO catalyst compared to that of the ¹³C₂-EtOH co-feed. This observation indicates that the formation of ¹³CO and ¹³CH₄ from ¹³C₂-ethylene is expected to occur to a lesser extent than with the ¹³C₂-EtOH co-feed, as the deoxygenation of the ethoxy species (C₂H₅O*) to form ethyl species (C₂H₅*) is likely largely irreversible in a reducing syngas atmosphere. Consistently, negligible ¹³CH₄ is observed with GC-MS analysis over the MoKMMO catalyst with ¹³C₂-ethylene co-feed (Fig. S16).

Less intense CO and CO₂ singlets were observed in the ¹³C-NMR spectrum of the K/bulk-MoS₂ catalyst when compared with that of the MoKMMO catalyst for ¹³C₂-ethylene co-feeds, indicating that the formation of ¹³CO and ¹³CO₂ with ¹³C₂-ethylene co-feeds is catalyst dependent, and; therefore, is unlikely to occur in the gas phase. It is thought that ethylene has the propensity to more favorably adsorb on smaller K/MoS₂ domains over the MoKMMO catalyst as compared to large, multilayer K/MoS₂ domains present in the K/bulk-MoS₂ catalyst, supporting the lower ¹³CO and ¹³CO₂ formation over the K/bulk-MoS₂ catalyst [38]. Additionally,

$^{13}\text{CH}_4$ is observed over the K/bulk-MoS₂ catalyst with a $^{13}\text{C}_2$ -ethylene co-feed (Fig. S17), further supporting that ^{13}CO and $^{13}\text{CH}_4$ formation likely occurs via an enriched acetyl precursor ($^{13}\text{CH}_3\text{CO}^*$).

Furthermore, it is important to note that the carbonyl groups of the acetate and propionate species were not enriched with $^{13}\text{C}_2$ -EtOH nor $^{13}\text{C}_2$ -ethylene co-feed over the MoKMMO and K/bulk-MoS₂ catalysts, thus providing evidence that the carbonyl carbon for these species originated from syngas CO. Similarly, CO insertion of ^{13}CO originating from $^{13}\text{C}_2$ -EtOH and $^{13}\text{C}_2$ -ethylene likely occurs on a minor scale, as the C₁ carbon from 1-PrOH and 1-ButOH shows little to no enrichment with both ^{13}C -NMR and GC-MS analysis.

4. Conclusions

Syngas conversion to higher alcohols was studied over the known MoKMMO and K/bulk-MoS₂ catalysts using 10% $^{13}\text{C}_2$ -ethanol and 10% $^{13}\text{C}_2$ -ethylene co-feeds, as a means to elucidate the reaction pathways to higher alcohols. Analysis of the ^{13}C carbon enrichment via ^{13}C -NMR clearly showed that (i) preferential enrichment of terminal carbons in C₃-C₄ alcohols over the MoKMMO catalyst occurred, and (ii) $^{13}\text{C}_4$ -1-butanol is observed during reaction over the MoKMMO catalyst with a $^{13}\text{C}_2$ -ethanol co-feed (not present with $^{13}\text{C}_2$ -ethylene co-feed) providing conclusive evidence for ethanol self-coupling to 1-butanol. It is concluded that higher alcohol formation over K/MoS₂ based catalysts primarily occurs through CO insertion, and the MMO support facilitates ethanol self-coupling to 1-butanol to only a small extent as a secondary pathway. Acetate species are formed via an acyl precursor reacting with an alkoxy anion, and propionate species are formed via esterification of propionate with the corresponding alcohol. $^{13}\text{C}_2$ -ethanol co-feeds additionally showed that the hydrogenation of acetyl species (CH_3CO^*) to ethoxy species is largely irreversible. It is also concluded that isobutyl alcohol formation observed over both the K/bulk-MoS₂ and the MoKMMO catalysts occurs via methanol coupling with 1-propanol or 1-propanol derived species. Formation of ^{13}CO and $^{13}\text{CH}_4$ over the MoKMMO and K/bulk-MoS₂ catalysts with $^{13}\text{C}_2$ -ethylene co-feeds and over the MoKMMO catalyst with

$^{13}\text{C}_2$ -ethanol co-feed provides evidence that ^{13}CO and $^{13}\text{CH}_4$ formation likely occurs via an enriched acetyl precursor ($^{13}\text{CH}_3\text{CO}^*$) derived from either a $^{13}\text{C}_2$ -ethylene or $^{13}\text{C}_2$ -ethanol.

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Fig. 1. Proposed CO insertion reaction mechanism over unsupported and MMO supported K/bulk-MoS₂ catalysts. ¹³C species are labeled in green.

Fig. 2. ¹³C carbon enrichment of C₁-C₄ alcohols over the MoKMMO catalyst for EtOH (solid boxes) and ¹³C₂-EtOH (open boxes). Doublets are labeled in blue.

a. MoKMMO $^{13}\text{C}_2$ -EtOH

— 6.1% ($10\% \text{ }^{13}\text{C}$)

b. MoKMMO $^{13}\text{C}_2$ -Ethylene

— 9.4% ($10\% \text{ }^{13}\text{C}$)

Fig. 3. ^{13}C -NMR spectra for 1-ButOH over the MoKMMO catalyst for 6.1% $^{13}\text{C}_2$ -EtOH (a) and 7.1% $^{13}\text{C}_2$ -ethylene (b) co-feed experiments. Arrows denote the peaks assigned to 1-ButOH. Intensity scale is consistent across all graphs. Note: the other peaks present in the C_3 and C_4 graphs do not correspond to 1-butanol.

Fig. 4. ^{13}C carbon enrichment of C_{2+} oxygenates over the MoKMMO catalyst for EtOH (solid boxes) and $^{13}\text{C}_2$ -EtOH (open boxes) co-feed experiments. Doublets are labeled in blue. Note that the methyl groups in isobutyl alcohol in ^{13}C -NMR are indistinguishable. The carbons denoted with an * have overlapping peaks for the open and solid boxes, and the total peak area was attributed to both carbons. Therefore, the ^{13}C carbon enrichment may be an overestimate, but does not significantly affect the results.

Fig. 5. ^{13}C carbon enrichment of C₁-C₄ alcohols over the MoKMMO (a) and K/bulk-MoS₂ (b) catalysts for ethylene (solid boxes), and $^{13}\text{C}_2$ -ethylene (open boxes) co-feed experiments. Doublets are labeled in blue.

Fig. 6. ^{13}C carbon enrichment of C_{2+} oxygenates over the MoKMMO (a) and K/bulk-MoS₂ (b) catalysts for ethylene (solid boxes) and $^{13}\text{C}_2$ -ethylene (open boxes) co-feed experiments. Doublets are labeled in blue. Note that the methyl groups in isobutyl alcohol in ^{13}C -NMR are indistinguishable. In plot (a) the carbons denoted with an * have overlapping peaks for the solid boxes. In plot (b) the carbons denoted with an * have overlapping peaks for the open and solid

boxes. For carbons denoted with an *, the total peak area was attributed to both carbons.

Therefore, the ^{13}C carbon enrichment may be an overestimate, but does not significantly affect the results.

Fig. 7. ^{13}C -NMR spectra for gas samples pressurized to 80 psig in gas tight NMR tubes at 6.1% $^{13}\text{C}_2\text{-EtOH}$ co-feed for the MoKMMO catalyst (a) and 9.4% $^{13}\text{C}_2\text{-ethylene}$ co-feed for the MoKMMO (b) and K/bulk-MoS₂ catalyst (c). Note: no peaks were observed for the unlabeled co-feed experiments over these catalysts under identical reaction and ^{13}C -NMR spectroscopy conditions.