Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

Insight into Reaction Pathways in CO Hydrogenation Reactions over K/MoS_2 Supported Catalysts via Alcohol/Olefin Co-Feed Experiments

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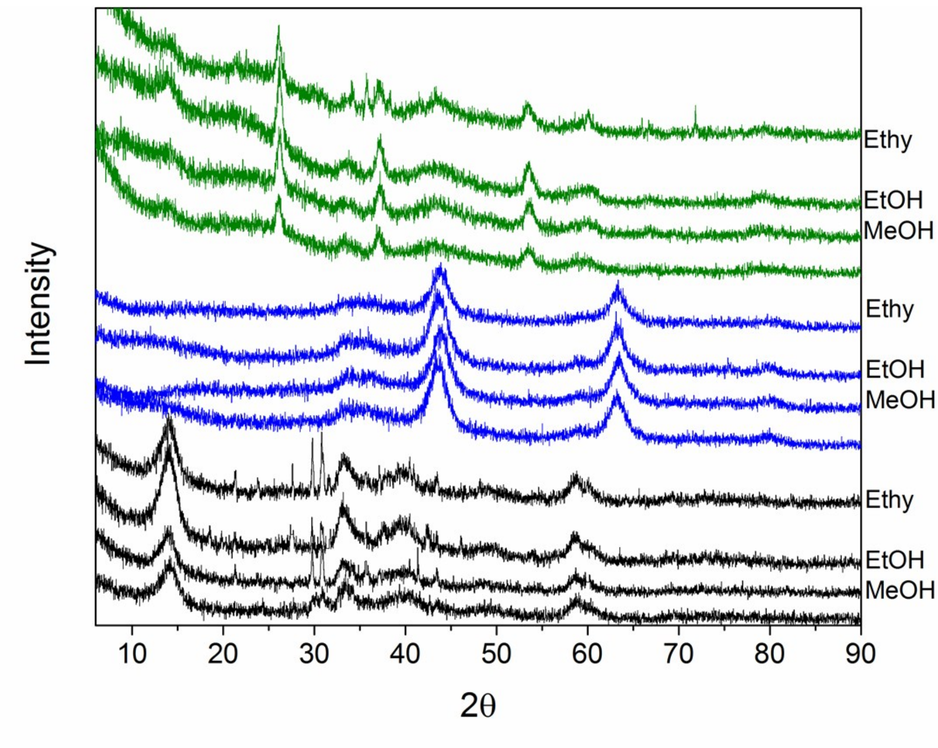

Fig. S1 XRD patterns of reaction-aged K/bulk MoS_2 (black), MoKMMO (blue), MoKC (olive) catalysts from methanol, ethanol, and ethylene co-feed experiments.

Table S1 Brunauer-Emett-Teller (BET) surface areas for reaction-aged MoKMMO and MoKC catalysts.

Catalyst	Co-feed	BET SA (m^2/g)
MoKC	-	1155
MoKC	MeOH	1378
MoKC	EtOH	1374
MoKC	Ethy	985
MoKMMO	-	62
MoKMMO	MeOH	52
MoKMMO	EtOH	52
MoKMMO	Ethy	56

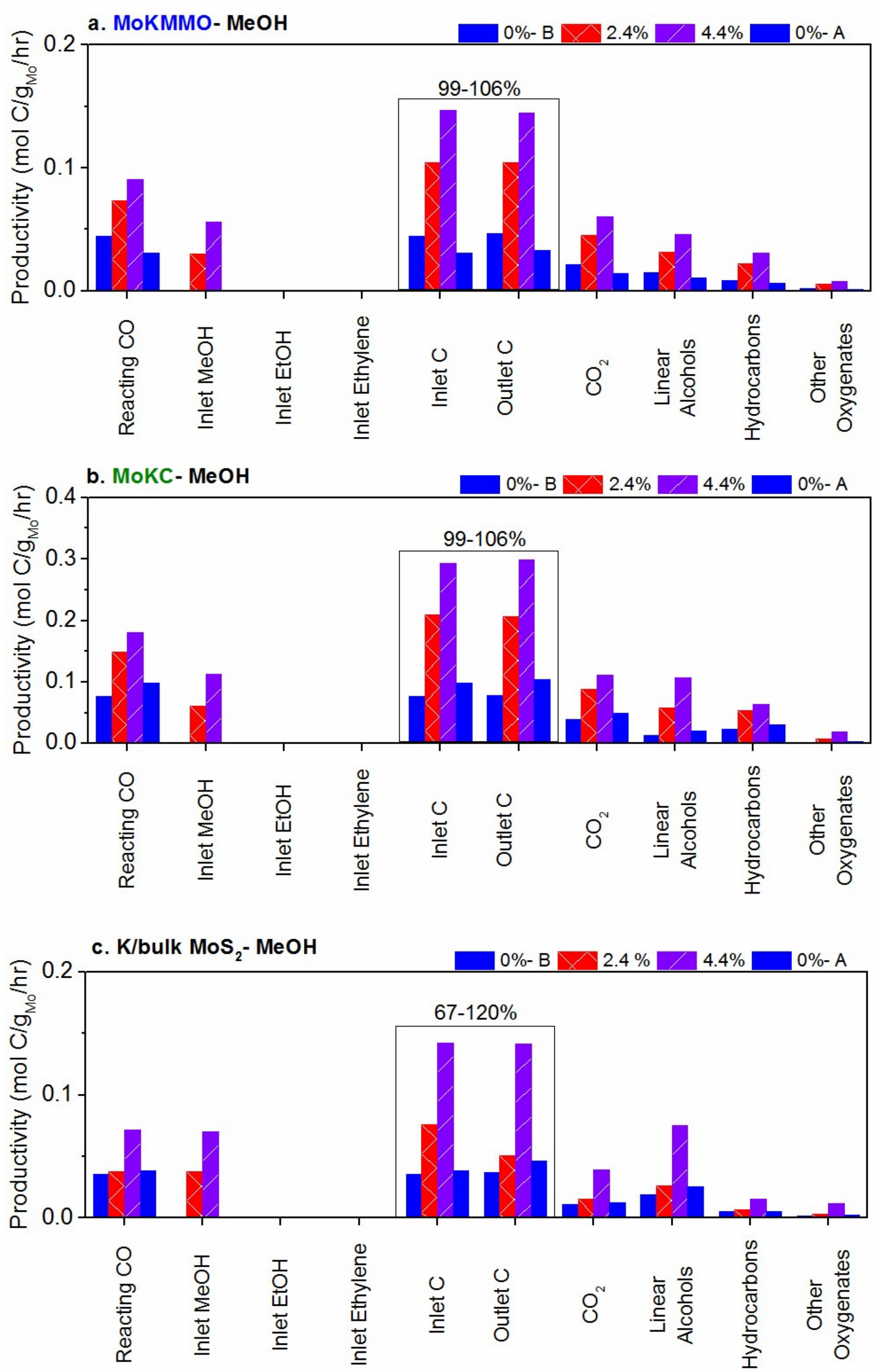

Fig. S2 Carbon balance for methanol co-feed experiments for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

Note: Linear Alcohols include C_1-C_6 linear alcohols, whereas hydrocarbons include methane, ethane, ethylene and propane/propylene. C_{4+}HC were not included in the carbon balance or product distributions as these products cannot be accurately quantified with the GC columns used for this study. Butane overlaps with methanol in the TCD column; therefore with methanol co-feed experiments, butane is embedded in the methanol peak. Pentane and Hexane are observed in the FID, but all hydrocarbons evolve in 0.4 min; making it difficult to accurately deconvolute these species.

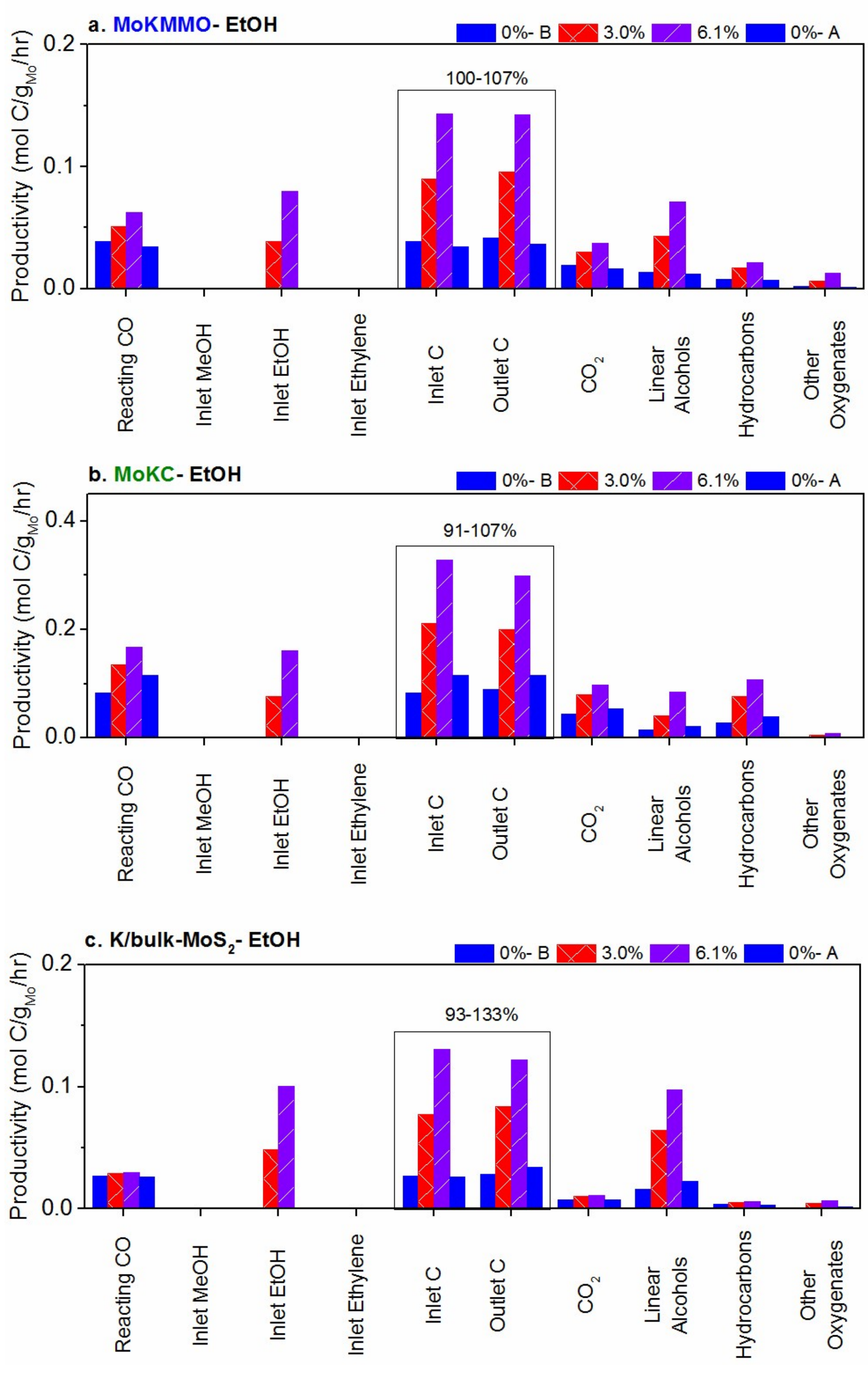

Fig. S3 Carbon balance for ethanol co-feed experiments for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

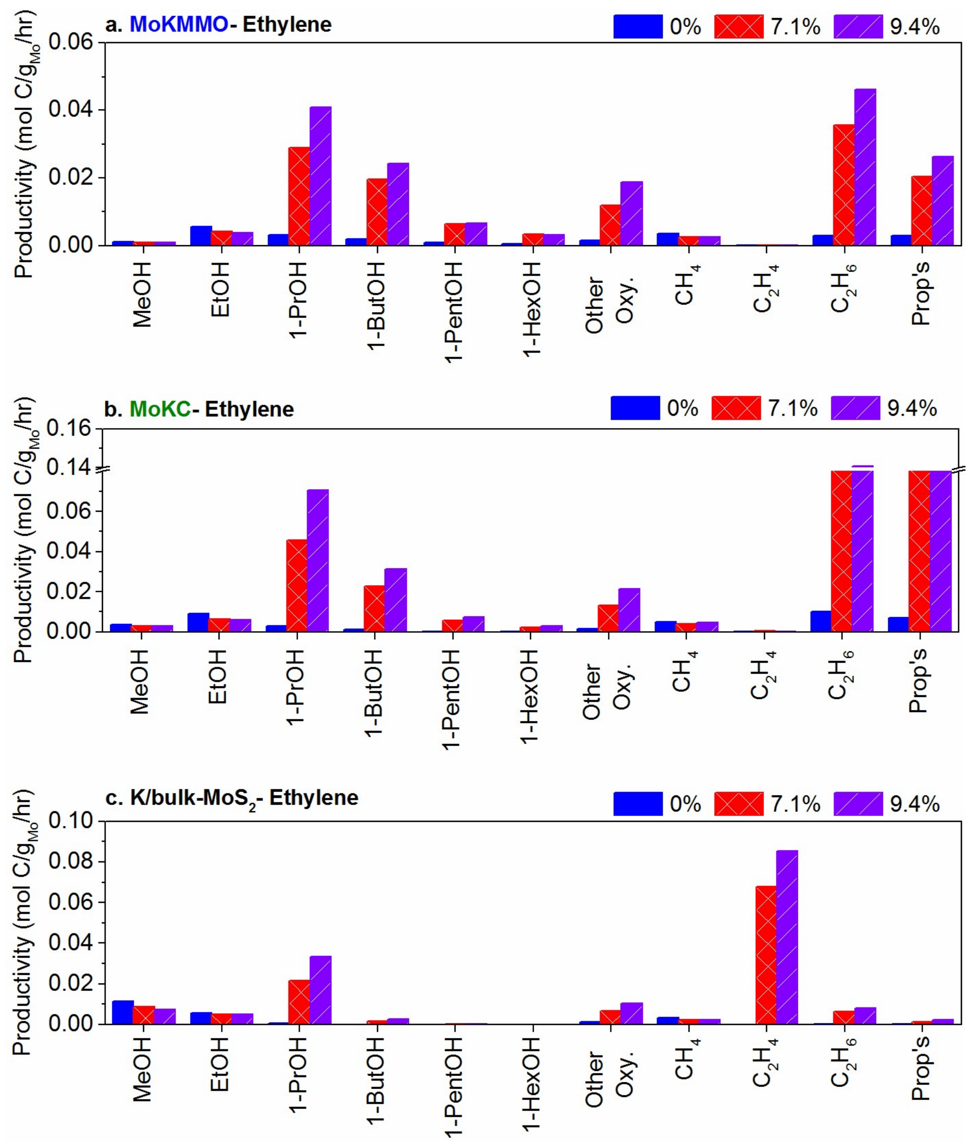

Fig. S4 Carbon balance for ethylene co-feed experiments for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

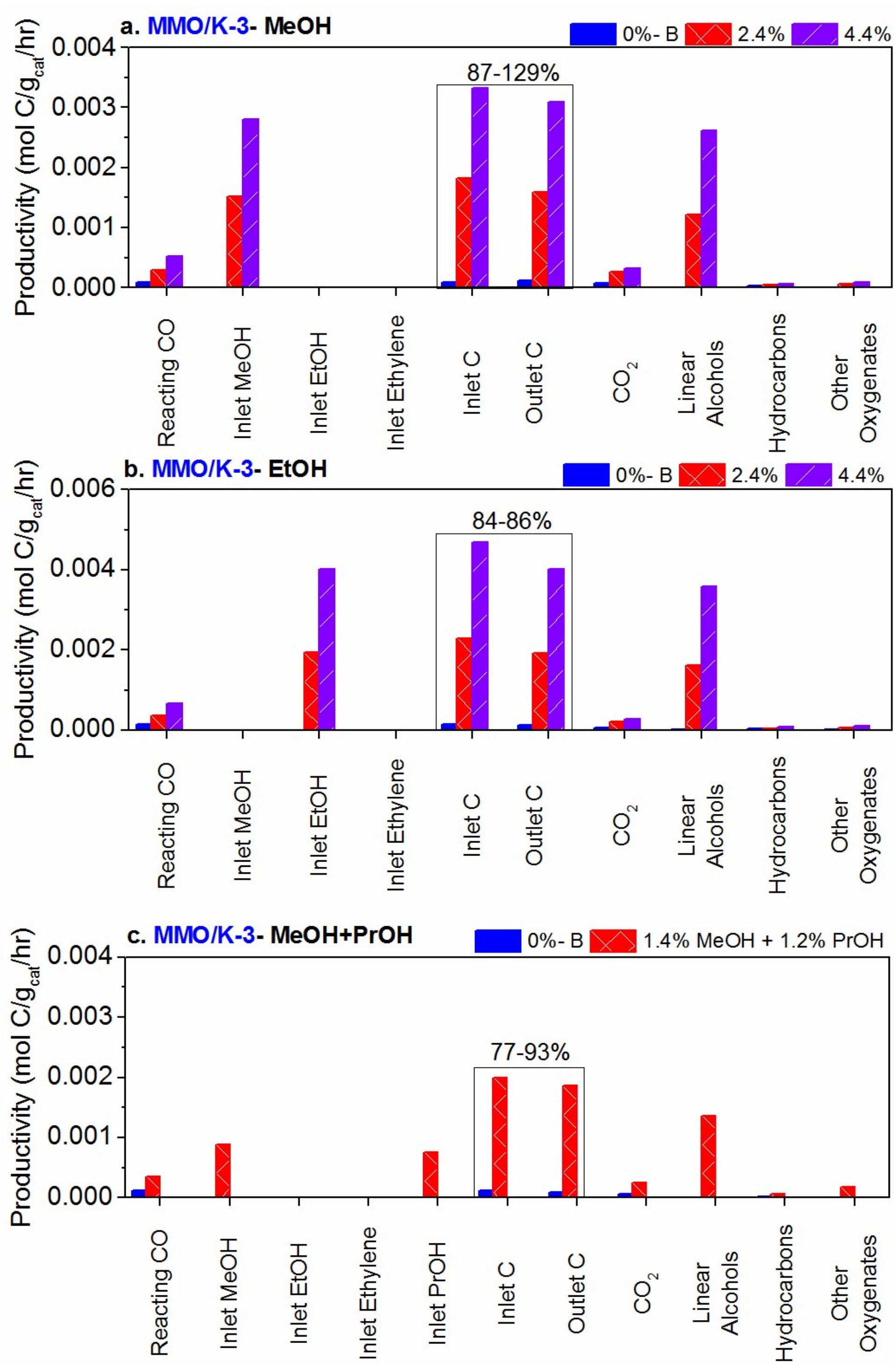

Fig. S5 Carbon balance for the Mo-free MMO/K catalyst for (a) methanol and (b) ethanol co-feed experiments.

Mo-free MMO/K was also subject to methanol co-feed experiments as a control experiment. The carbon balance shown in Figure S5 shows that CO conversion is largely unaffected by the introduction of methanol, ethanol and a mixture of methanol and 1-propanol; its minor increase may be associated with the water gas shift reaction to form CO_2.

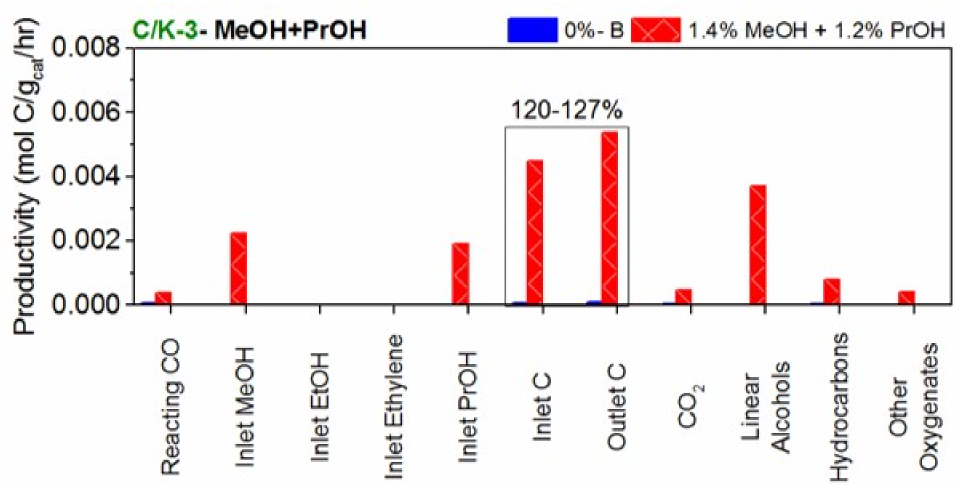

Fig. S6 Carbon Balance for the Mo-free C/K catalyst for mixture of methanol and 1-propanol. The carbon balance shows that CO conversion is largely unaffected; its minor increase may be associated with the water gas shift reaction to form CO_2 as explained for Fig. S5.

Table S2 Reactivity data for MoKMMO, MoKC and K/bulk-MoS_2 catalysts from methanol, ethanol, and ethylene co-feed experiments. Reaction conditions: 310 °C and 1500 psig.

Catalyst	Co-feed	Carbon Balance (%)	CO conv. (%)	Co-fed conv. (%)	Total OH Sel. (CO_2 Free) (%)	Total HC Sel. (CO_2 Free) (%)	EtOH/1-PrOH formation rate	1-ButOHl/1-PrOH formation rate
MoKMMO	0% -MeOH	104	8.2		59.1	33.8	1.8	0.7
MoKMMO	2.4%- MeOH	100	12.7	83.1	49.1	41.1	2.7	0.6
MoKMMO	4.4%- MeOH	99	15.2	67.4	41.8	46.2	2.8	0.5
MoKMMO	0%- MeOH	106	5.3		57.7	35.8	2.1	0.7
MoKC	0% -MeOH	101	8.4		33.7	62.6	2.9	0.4
MoKC	2.4%- MeOH	99	16.0	73.6	40.8	52.8	3.4	0.4
MoKC	4.4%- MeOH	102	19.0	47.8	37.3	49.1	3.9	0.3
MoKC	0%- MeOH	106	10.0		39.1	57.0	2.8	0.5
K/bulk-MoS_2	0% -MeOH	105	7.2		72.4	20.4	10.9	0.1
K/bulk-MoS_2	2.4%- MeOH	67	7.2	91.2	69.9	21.5	12.1	0.1
K/bulk-MoS_2	4.4%- MeOH	100	13.0	49.2	59.2	22.9	9.2	0.1
K/bulk-MoS_2	0%- MeOH	120	7.4		76.7	15.2	11.8	0.1
MoKMMO	0% -EtOH	107	8.5		58.8	33.4	1.8	0.7
MoKMMO	3%- EtOH	107	10.3	64.5	55.8	32.1	1.7	0.6
MoKMMO	6.1%- EtOH	100	12.4	60.5	53.5	29.4	2.1	0.6
MoKMMO	0%- EtOH	106	7.0		58.2	34.4	1.9	0.7
MoKC	0% -EtOH	107	7.4		33.4	63.8	3.4	0.4
MoKC	3%- EtOH	94	11.3	80.3	24.0	72.3	2.7	0.4
MoKC	6.1%- EtOH	91	14.0	72.5	25.8	69.2	2.8	0.4
MoKC	0%- EtOH	101	9.7		33.3	63.5	2.8	0.4
K/bulk-MoS_2	0% -EtOH	104	6.9		76.4	18.1	11.9	0.1
K/bulk-MoS_2	3%- EtOH	108	7.3	5.3	66.1	18.5	17.9	0.5
K/bulk-MoS_2	6.1%- EtOH	93	7.7	23.0	61.1	19.0	18.4	0.6
K/bulk-MoS_2	0%- EtOH	133	6.5		82.9	11.7	13.2	0.1
MoKMMO	0%- Ethy	104	8.3		54.2	38.6	1.8	0.7
MoKMMO	7.1%-Ethy	99	15.2	100.0	47.1	43.6	0.1	0.7
MoKMMO	9.4%-Ethy	98	18.1	100.0	45.8	43.0	0.1	0.6
MoKMMO	0%-Ethy	106	8.5		52.9	40.2	1.8	0.7
MoKC	0%- Ethy	105	8.2		42.3	53.9	3.1	0.4
MoKC	7.1%-Ethy	94	18.4	99.9	28.6	66.7	0.1	0.5
MoKC	9.4%-Ethy	96	19.6	100.0	30.6	63.9	0.1	0.4
MoKC	0%-Ethy	107	8.9		45.9	49.7	2.9	0.5
K/bulk-MoS_2	0%- Ethy	103	6.9		79.0	15.9	12.3	0.1
K/bulk-MoS_2	7.1%-Ethy	102	8.7	25.4	69.5	18.1	0.2	0.1
K/bulk-MoS_2	9.4%-Ethy	101	9.8	30.6	67.6	17.8	0.2	0.1
K/bulk-MoS_2	0%-Ethy	99	7.4		79.4	14.9	12.2	0.1

Total alcohol and hydrocarbon selectivity (CO_2 free) does not include unreacted co-feed carbon to better depict the selectivity of total alcohols and hydrocarbons with co-feed experiments. However, it is important to note that, for instance in methanol co-feed experiments, methanol productivity is assumed to be the same as in the original state (at 0% co-feed) with increasing co-fed methanol. Similar assumptions were made for ethanol productivity with ethanol co-feed experiments, and ethylene productivity with ethylene co-feed experiments.

Total alcohol selectivity for K/bulk-MoS_2 is higher for all co-feed experiments compared to their supported counterparts. This is associated with the small increase in CO conversion with increasing co-feed compared to the supported counterparts, which results in higher total alcohol selectivity. Hydrocarbons are formed by secondary reactions; therefore, the selectivity towards total hydrocarbons increases with increasing CO conversion

Table S3 Reactivity data for MoKMMO, MoKC and K/bulk-MoS_2 catalysts from methanol, ethanol, and ethylene co-feed experiments. Reaction conditions: 310 °C and 1500 psig.

Catalyst	Co-feed	Carbon Balance (%)	CO conv. (%)
MMO/K-3	0% -MeOH	129	0.3
MMO/K-3	2.4%- MeOH	87	1.1
MMO/K-3	4.4%- MeOH	93	1.8
MMO/K-3	0% -EtOH	85	0.5
MMO/K-3	3%- EtOH	84	1.3
MMO/K-3	6.1%- EtOH	86	2.4
MMO/K-3	0% -MeOH + PrOH	77	0.4
MMO/K-3	1.4%- MeOH + 1.2 % PrOH	93	1.3
MMO/K-3	0% -MeOH + PrOH	127	0.1
MMO/K-3	1.4%- MeOH + 1.2 % PrOH	120	0.5

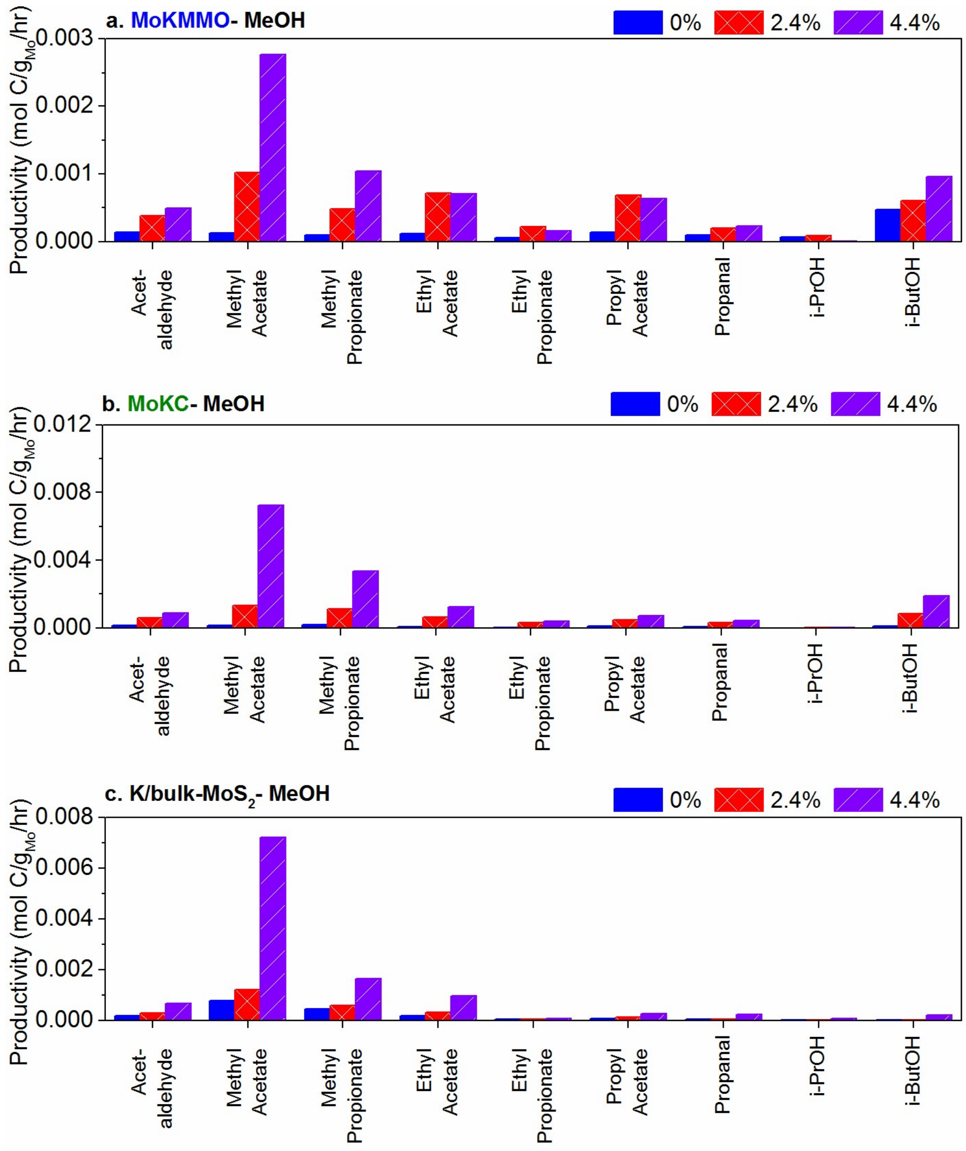

Fig. S7 Minor products for methanol co-feed experiments for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

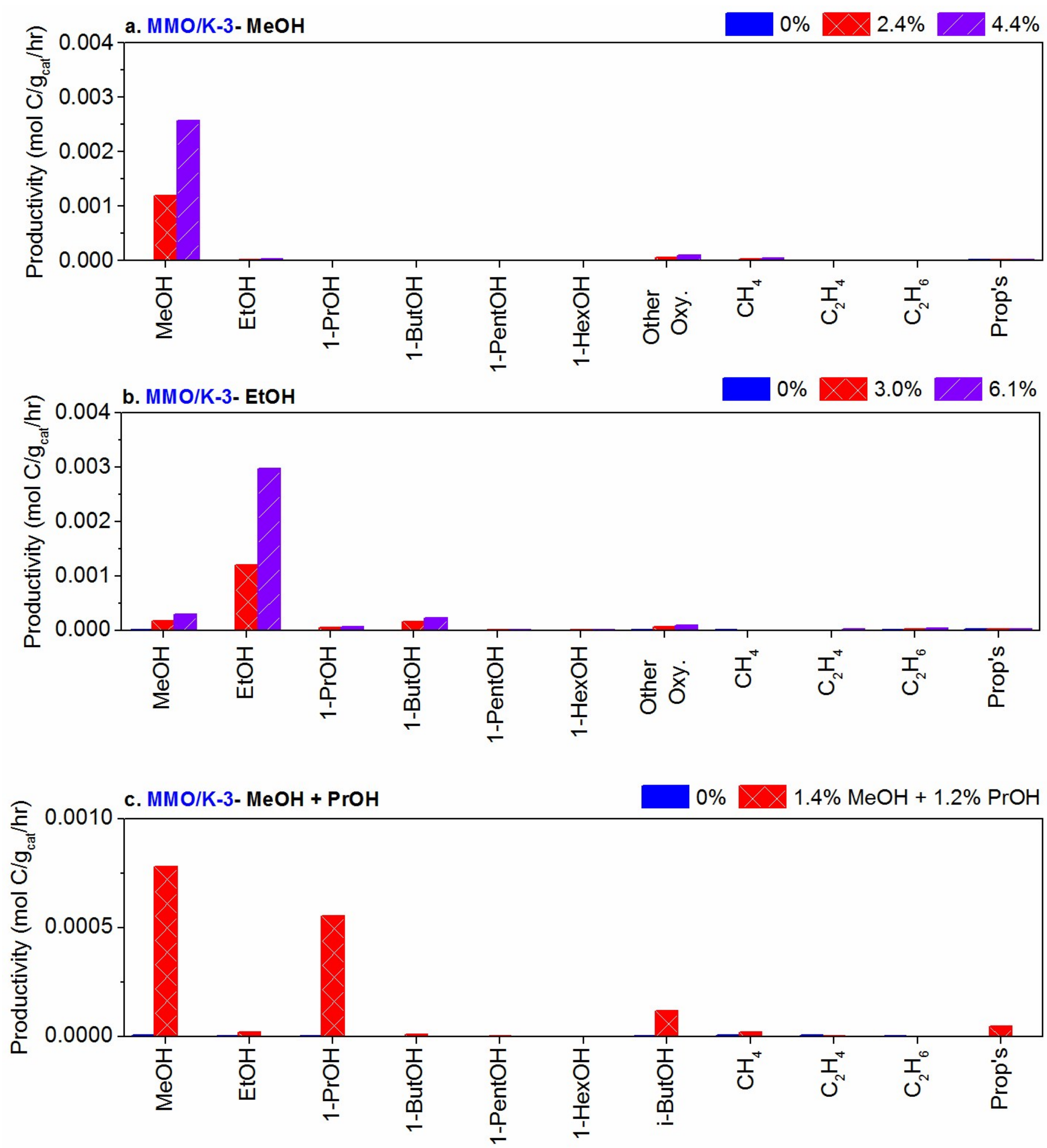

Fig. S8 Major products for the Mo-free MMO/K material for (a) methanol (b) ethanol, and (c) methanol + ethanol co-feed experiments.

Note: The MeOH (a), and EtOH (b) co-feed experiments in Fig. S8 were run in succession over the same MMO/K-3 catalyst; therefore the small increase in MeOH formation with increasing ethanol co-feed is a result of leftover methanol in the co-feed line when running the ethanol co-feed. For all other experiments in this study, each co-feed experiment was conducted with fresh catalysts.

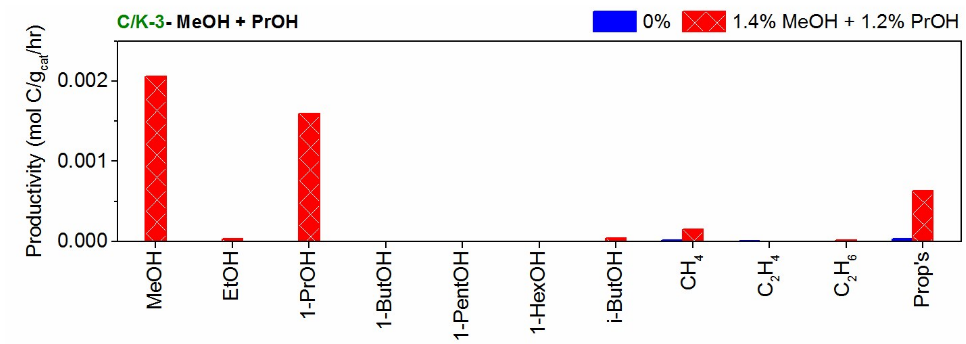

Fig. S9 Minor products for the Mo-free C/K-3 material for mixed methanol, 1-propanol co-feed experiment.

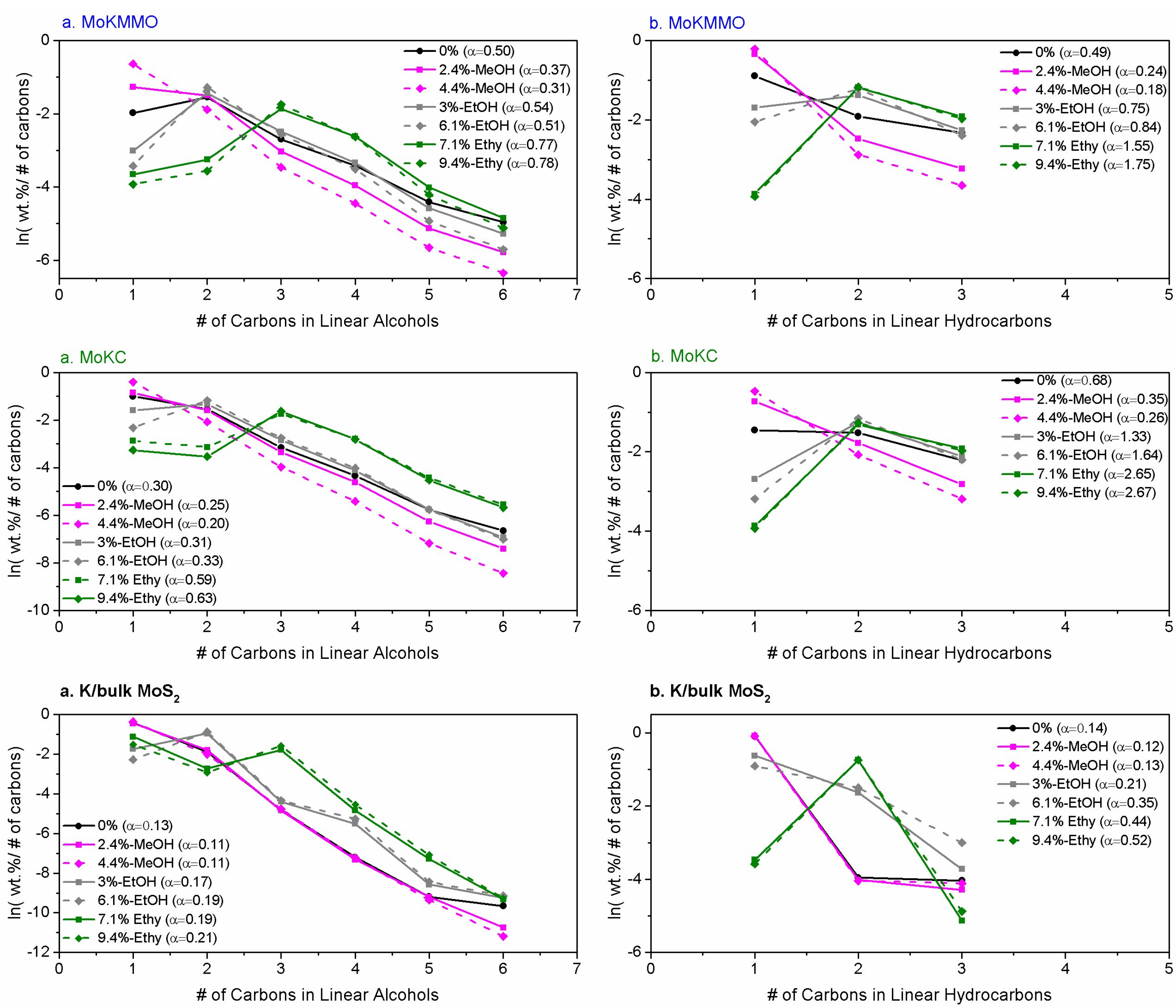

Fig. S10 Anderson-Shulz Flory distribution for linear alcohols (a) and hydrocarbons (b) for the MoKMMO, MoKC, and K/bulk-MoS_2 catalysts.

Note: The probability of chain growth for linear alcohols includes unreacted co-fed methanol and ethanol for their respective co-feed experiments. Similarly, the probability of chain growth for linear hydrocarbons includes unreacted co-fed ethylene. Their inclusion does not greatly affect the probability of chain growth.

It is important to note that for ethanol and ethylene co-feed experiments, methane (produced in negligible amounts) nonetheless strongly perturbs the ASF distribution, resulting in alpha values greater than one (which is physically impossible). The weight fraction for methane approaches zero and therefore makes the ln(methane wt.% / 1) (where 1 is the # carbons in methane) a large negative number that does not follow the ASF distribution. However, if methane is not included in the probability of chain growth, the influence of co-feed on hydrocarbon product distribution would not be accurately represented.

MoKMMO shows the largest influence in C_{3+} alcohol formation with methanol, ethanol, and ethylene co-feed experiments, as the probability of chain growth over MoKMMO is larger than over MoKC and K/bulk MoS_2. This suggests that Mo-K-MMO sites facilitate higher alcohol formation. The probability of hydrocarbon chain growth over MoKC is significantly higher compared to MoKMMO and K/bulk MoS_2 with ethanol and ethylene co-feeds, suggesting that MoKC favors C_{2+} hydrocarbon over C_{3+} alcohol formation.

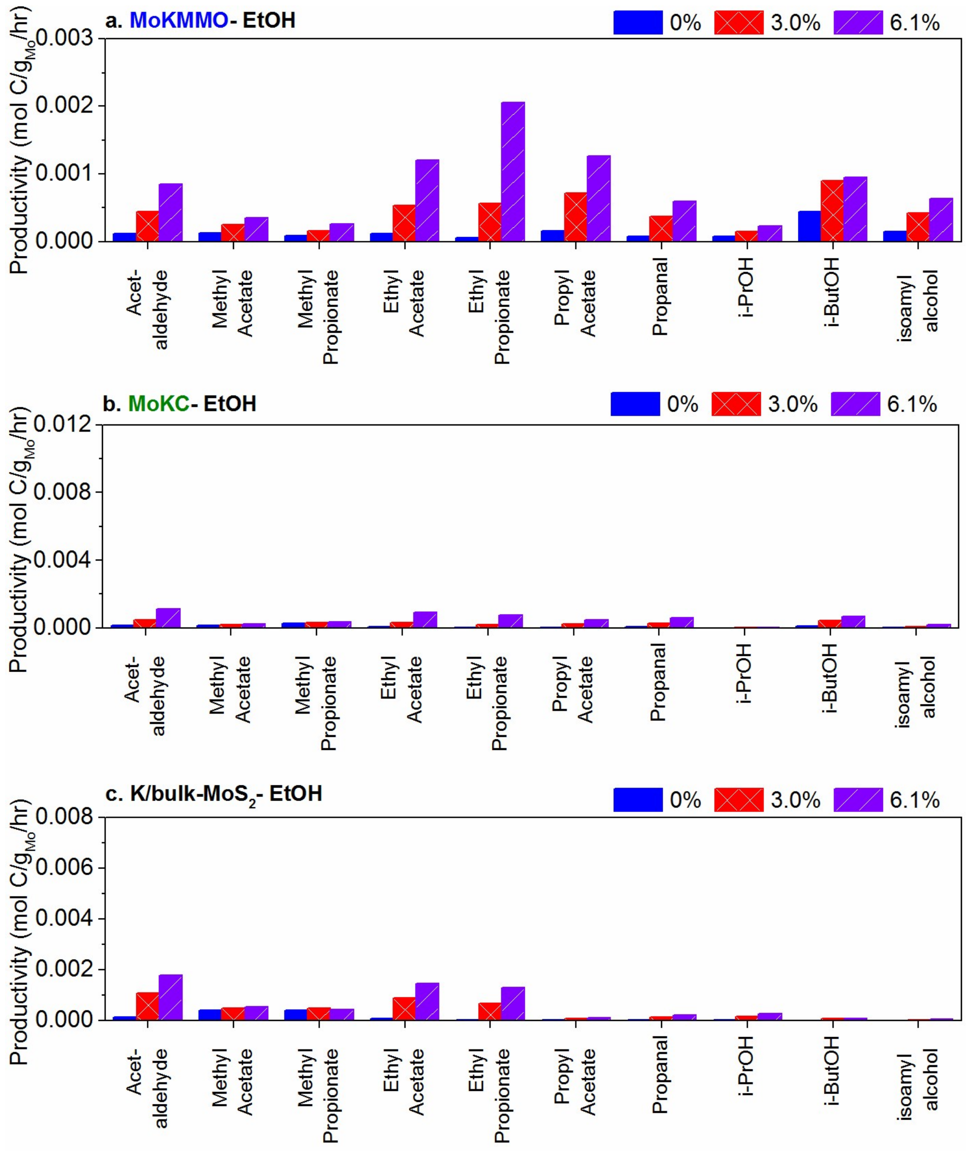

Fig. S11 Minor products for ethanol co-feed experiments for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

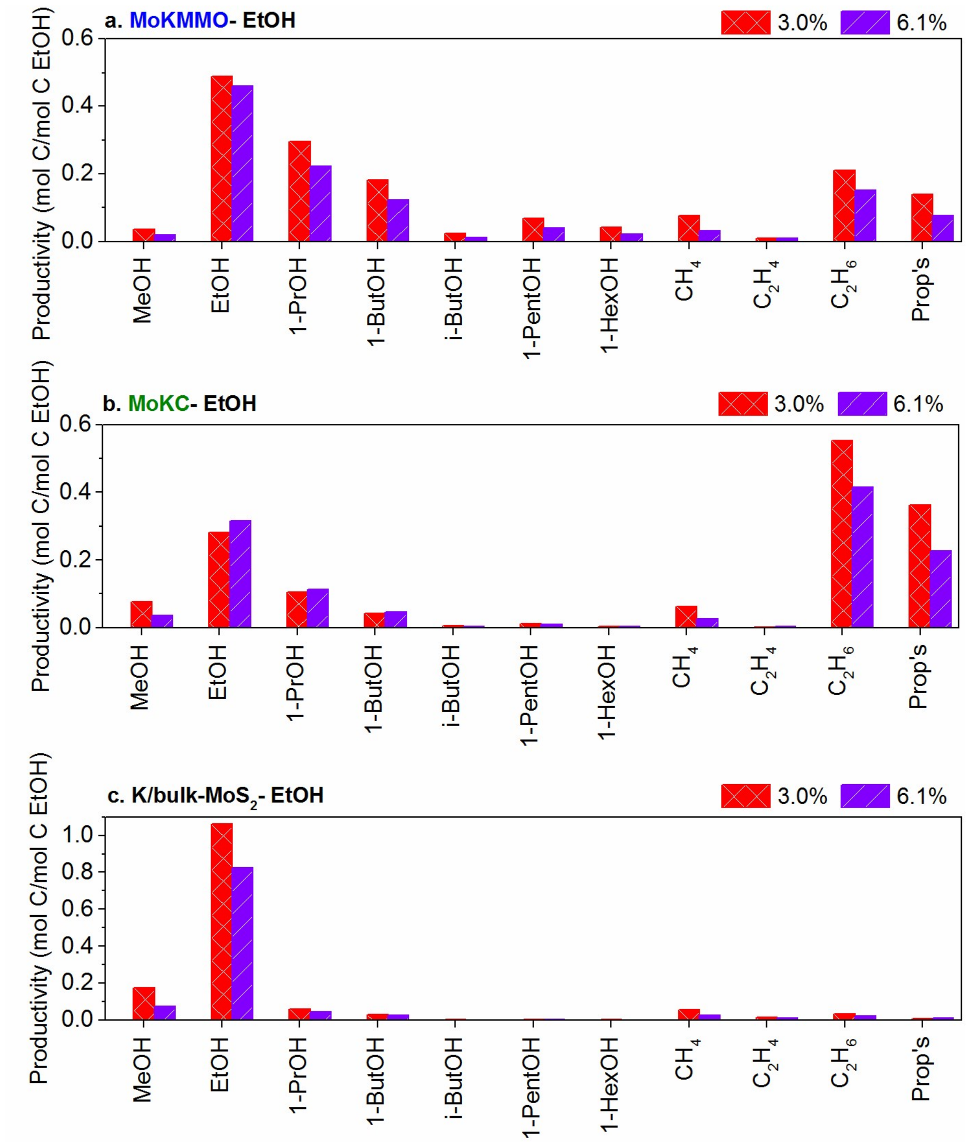

Fig. S12 Normalized major products (by co-fed mol carbon from ethanol) for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

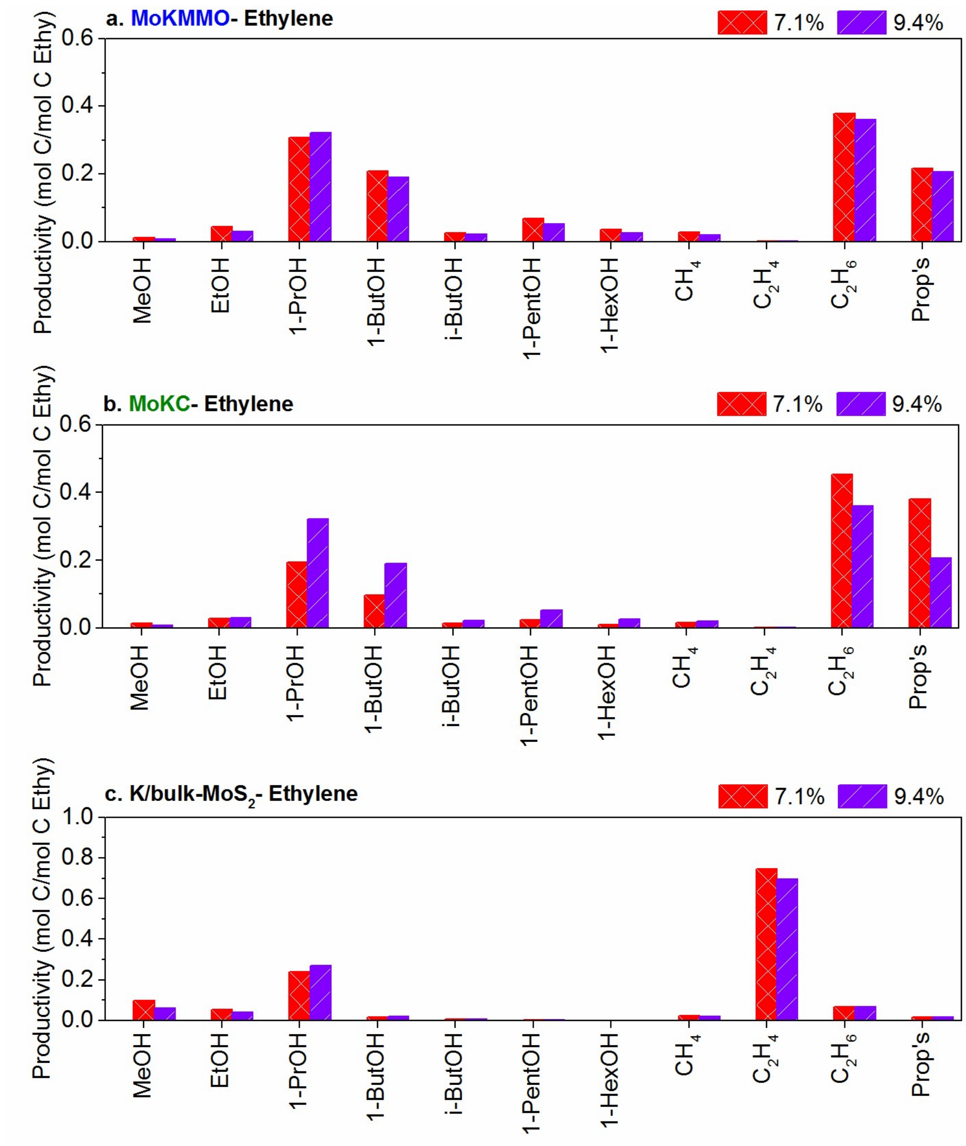

Fig. S13 Normalized minor products (by co-fed mol carbon from ethylene) for the for (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS_2 catalysts.

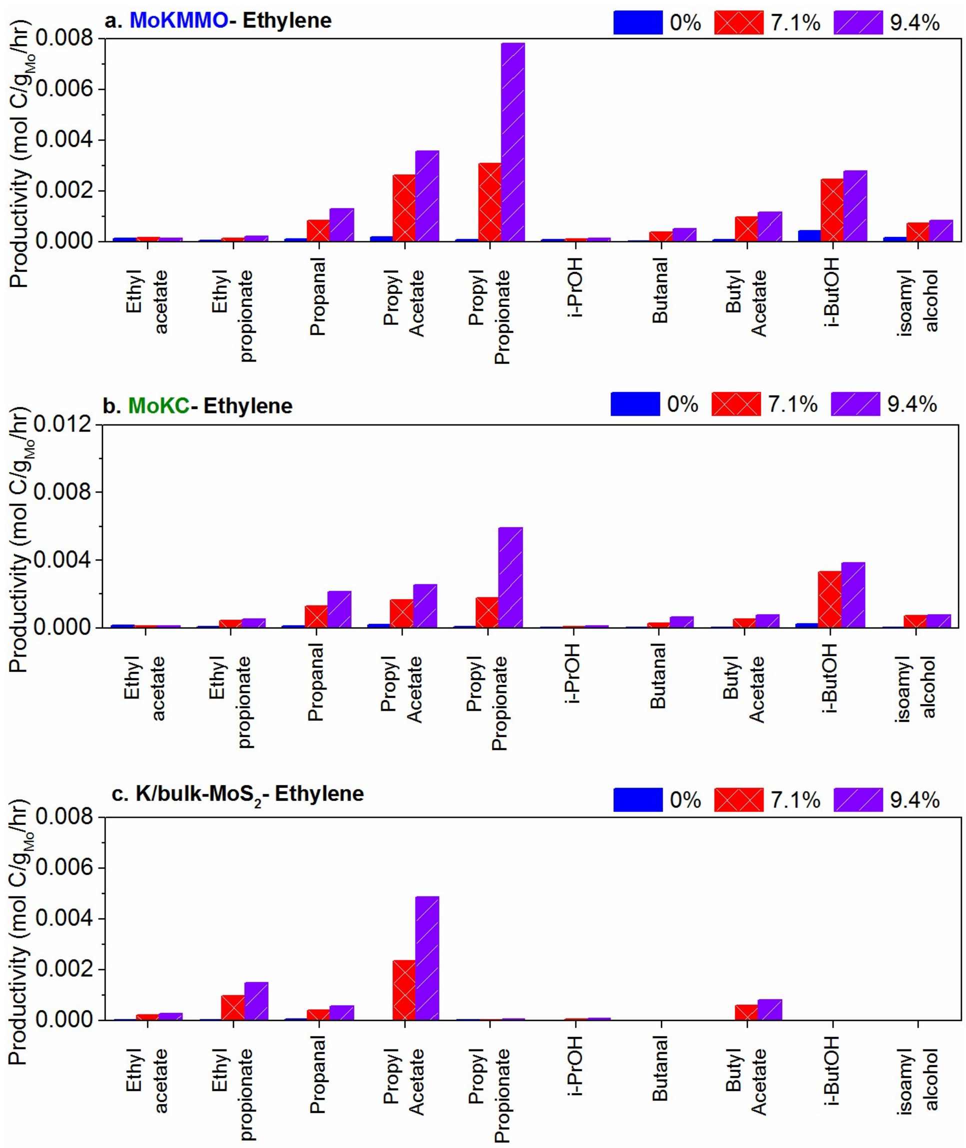

Fig. S14 Minor products for ethylene co-feed experiments for the (a) MoKMMO, (b) MoKC, and (c) K/bulk-MoS$_2$ catalysts.