Tuning of Higher Alcohol Selectivity and Productivity in CO Hydrogenation Reactions over K/\(\text{MoS}_2\) Domains Supported on Mesoporous Activated Carbon and Mixed MgAl Oxide

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**Introduction**

A family of mesoporous activated carbon and MgAl oxide (MMO) were used as supports to tune higher alcohol selectivity and productivity for higher alcohol synthesis from syngas over K\(\text{MoS}_2\). Previous work showed that carbon supports yield high methanol and ethanol productivities.\(^1\) Specifically, mesoporous activated carbon (C), obtained through collaboration with Oak Ridge National Laboratory, showed improved higher alcohol productivity than commercial activated carbon, which was attributed to highly dispersed Mo species. Hydrotalcite-derived MgAl oxide (MMO) supports yield high \(\text{C}_1-\text{OH}\) selectivity influenced by small \(\text{MoS}_2\) domains of few stacked layers, but generally yield low productivity. It has been shown that Mo:MMO ratio greatly affects the selectivity of the catalyst, while the catalyst preparation method does not.\(^2\) Furthermore, it was observed that the nature of the precursor Mo phase (e.g., oxide vs. carbide), prior to sulfidation to create the \(\text{MoS}_2\) phase had no effect on the catalytic selectivity, suggesting that Mo species are highly mobile during sulfidation and reaction.\(^3\) This work probes the hypothesis that Mo supported on a family of MMO and C mixed-supports may facilitate tuning of higher alcohol selectivity (due to \(\text{MoS}_2\) domains on the MMO support) and higher alcohol productivity (due to \(\text{MoS}_2\) domains on the C support).

**Materials and Methods**

A set of four catalysts using single C or MMO supports (MoKMMO, and MoKC) and a mixture of C and MMO supports (MoKC-MMO, MoKMMO-C) was synthesized with an approximate loading of 5 wt.% Mo and 3 wt. % K with a Mo:K molar ratio of 1. For mixed supported catalysts the single supported catalyst was synthesized first and then it was physically ground with the second support with a mass ratio of MMO/C of 3.6. The support on which Mo was loaded is listed first in the sample name, with the Mo-free support added by grinding listed after the dash. The oxide precatalysts were reduced \textit{in situ} to the sulfide phase before reaction with syngas at 310 °C and 1500 psig at 700-6500 mL/g catalyst/h to reach 3-4 steady-state, isothermal CO conversions for a total of ~12 days on stream. \(\text{MoS}_2\) domains were characterized \textit{ex situ} by scanning electron microscopy (STEM), Raman spectroscopy, X-ray absorption spectroscopy.

**Results and Discussion**

The MoKC-MMO catalyst yields selectivity trends in between that of the MoKMMO and MoKC materials, suggesting that some Mo was able to migrate from the originally impregnated carbon support to the MMO support during sulfidation and reaction. Although not as selective towards higher alcohols as MoKMMO, Mo mobility is hypothesized to influence the improved higher alcohol productivity (more than two-fold increase) as compared to the MoKMMO and MoKC catalysts. On the other hand, MoKMMO-C yields selectivity trends similar to the MoKMMO material, suggesting that Mo species are more firmly held on the MMO support due to strong Mo-MMO interactions that limit the ability of Mo to migrate to the carbon support. \(\text{MoS}_2\) domain sizes of the catalysts studied, as determined by STEM, show a clear correlation with the selectivity of the catalysts. Specifically, \(\text{C}_1-\text{OH}\) alcohols are correlated with double \(\text{MoS}_2\) stacked layers, whereas total hydrocarbon selectivity is correlated with single \(\text{MoS}_2\) layers.

**Significance**

This study combines distinct complementary C and MMO supports to achieve desirable attributes of high \(\text{C}_1-\text{OH}\) alcohol selectivity and productivity (MoKC-MMO). This work advances the structure-reactivity relationship (\(\text{MoS}_2\) domain size vs. selectivity) for this family of catalysts and provides the basis for future investigations on reaction pathways over these catalysts.

References


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**Figure 1.** a) Layer distribution of \(\text{MoS}_2\) stacked layers (1, 2, 3, 3+ layers (L)) for the reaction-aged catalysts b\(\text{C}_1-\text{OH}\) selectivity (CO\(_2\)-free) vs. % double layers (solid line) and total hydrocarbon selectivity (CO\(_2\)-free) vs. % single layers (circles).