



# Thermal decomposition of bulk K-CoMoS<sub>x</sub> mixed alcohol catalyst precursors and effects on catalyst morphology and performance

Martin J. Menart<sup>1</sup>, Jesse E. Hensley\*, Kellen E. Costelow<sup>2</sup>

National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, United States

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## ABSTRACT

Cobalt molybdenum sulfide-type mixed alcohol catalysts were synthesized via calcination of precipitated bulk sulfides and studied with temperature programmed decomposition analysis. Precursors containing aqueous potassium were also considered. Precipitates thermally decomposed in unique events which released ammonia, carbon dioxide, and sulfur. Higher temperature treatments led to more crystalline and less active catalysts in general with ethanol productivity falling from 203 to 97 g (kg cat)<sup>−1</sup> h<sup>−1</sup> when the calcination temperature was increased from 375 to 500 °C. The addition of potassium to the precursor led to materials with crystalline potassium sulfides and good catalytic performance. In general, less potassium was required to promote alcohol selectivity when added before calcination. At calcination temperatures above 350 °C, segregated cobalt sulfides were observed, suggesting that thermally decomposed sulfide precursors may contain a mixture of molybdenum and cobalt sulfides instead of a dispersed Co–Mo–S type of material. When dimethyl disulfide was fed to the precursor during calcination, crystalline cobalt sulfides were not detected, suggesting an important role of free sulfur during decomposition.

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## 1. Introduction

Alternative fuels continue to receive significant research focus, especially processes that can convert biomass, methane, or coal to liquid fuels through chemical or biological catalysis. Biomass-derived fuels present specific challenges including the food vs. fuel debate, high oxygen (and water) content, and smaller scale. In recent years, emphasis has been placed on the gasification of non-edible biomass to syngas (CO, H<sub>2</sub>, CO<sub>2</sub>, and contaminants) and conversion of that syngas to ethanol, evidenced by a multitude of cellulosic ethanol startups, government tax incentives for ethanol production, and federal research spending in the area.

While many catalysts and staged processes are capable of producing ethanol from syngas, potassium-promoted cobalt molybdenum sulfide (K-CoMoS<sub>x</sub>) catalysts have received significant attention due to their sulfur tolerance, relative indifference to ammonia [1], low price compared to precious metals, high selectivity to ethanol, low selectivity to hydrocarbons including methane, and commercial readiness [2,3]. A recent conceptual design of a

thermochemical biomass to ethanol plant employing K-CoMoS<sub>x</sub> catalysts suggested that the price of ethanol made via this route is similar to gasoline (energy equivalent basis) but that improvements in the specific activity of the K-CoMoS<sub>x</sub> catalyst are needed for the process to be competitive [4]. That is, more active catalysts must be developed without sacrificing selectivity to ethanol, increasing cost (of metals and manufacture), or adding additional capital. Alternatively, increases in material/capital/operating costs must be offset by even higher performing catalysts.

It is known that catalyst performance depends on many factors including elemental composition, catalyst/support interaction, crystal size, surface area, activation procedure, poisons, etc. and furthermore, most of those properties can be adjusted to some extent by changing the thermal history invoked in synthesis [5]. Therefore, a logical place to start when trying to improve a catalyst without increasing its cost is to consider the thermal conversion of catalyst precursors to finished materials. In this paper, we explore the thermal decomposition of *bulk* K-CoMoS<sub>x</sub> precursors and its relationship to catalyst performance.

The literature is not completely devoid of these studies. Bulk MoS<sub>2</sub> has traditionally been prepared through the thermal decomposition of ammonium tetrathiomolybdate (ATTM, (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>) [6]. Cobalt sulfides form simultaneously with MoS<sub>2</sub> when Co is incorporated into the precursor material. The structure and performance of the subsequent finished catalyst is understood to be dependent on the intensity of the thermal treatment. For example, Chianelli et al. varied a hydrodesulfurization (HDS) catalyst preparation by changing the annealing temperature and found a resulting

\* Corresponding author. Tel.: +1 303 384 7914; fax: +1 303 384 7951.

E-mail addresses: [martinmenart@gmail.com](mailto:martinmenart@gmail.com) (M.J. Menart), [jesse.hensley@nrel.gov](mailto:jesse.hensley@nrel.gov) (J.E. Hensley), [kcstelow@gmail.com](mailto:kcstelow@gmail.com) (K.E. Costelow).

<sup>1</sup> Present address: Swiss Federal Institute of Technology Zurich, Dept. of Chemistry and Applied Biosciences, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland. Tel.: +41 077 492 4029.

<sup>2</sup> Present address: Suncor Energy, 3801 Brighton Blvd., Commerce City, CO 80022, United States. Tel.: +1 303 374 8908.