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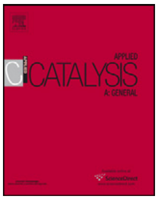

Thermal decomposition of bulk K-CoMoS$_x$ mixed alcohol catalyst precursors and effects on catalyst morphology and performance

Martin J. Menart[1], Jesse E. Hensley*, Kellen E. Costelow[2]

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)$^{-1}$ h^{-1} 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_2, CO_2, 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$_x$) 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$_x$ 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$_x$ 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$_x$ precursors and its relationship to catalyst performance.

The literature is not completely devoid of these studies. Bulk MoS_2 has traditionally been prepared through the thermal decomposition of ammonium tetrathiomolybdate (ATTM, $(NH_4)_2MoS_4$) [6]. Cobalt sulfides form simultaneously with MoS_2 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

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* Corresponding author. Tel.: +1 303 384 7914; fax: +1 303 384 7951.
E-mail addresses: martinmenart@gmail.com (M.J. Menart), jesse.hensley@nrel.gov (J.E. Hensley), kcostelow@gmail.com (K.E. Costelow).

[1] 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.

[2] Present address: Suncor Energy, 3801 Brighton Blvd., Commerce City, CO 80022, United States. Tel.: +1 303 374 8908.

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difference in catalyst morphology and selectivity to various HDS reactions [7]. The presence of organic sulfur during decomposition further altered the morphology of MoS_2 [8]. Dianis et al. and Gang et al. showed that the atmosphere in which decomposition takes place impacts final catalyst performance (inert vs. reducing vs. sulfiding) [9,10]. Tsyganenko et al. studied the thermal decomposition of ATTM in vacuum using FTIR and postulated the following reaction sequence [11]:

$$(NH_4)_2MoS_4 \xrightarrow{\Delta} 2NH_3 + H_2S + MoS_3 \xrightarrow{\Delta} MoS_2$$

where the first decomposition occurs below 150 °C to form ammonia, hydrogen sulfide, and molybdenum trisulfide, and the second decomposition occurs below 300 °C to form molybdenum disulfide (identified via inductively coupled plasma chemical analysis). Heating to 400 °C was shown to sinter the MoS_2, resulting in a lower surface area material.

Preparation of K-$CoMoS_x$ catalysts varies in the literature, but a popular procedure includes the formation of a wet precipitated $CoMoS_x$ precursor derived from ATTM, followed by rapid heating in N_2 to 500 °C, finished with a soak at 500 °C for 1–5 h and cooling to room temperature [12–15]. Others have found slightly lower temperatures to also be effective [16,17]. The resulting catalysts are intrinsically amorphous, but higher temperatures do contribute to the formation of crystalline sulfide phases [6]. Potassium is traditionally applied by blending the finished sulfide powder with K_2CO_3 crystals under inert conditions. We suggest that simpler techniques, like washing catalyst precursors with aqueous salts, are also possible.

Beyond this, the literature is sparse in K-$CoMoS_x$ preparation studies; especially for materials synthesized specifically for mixed alcohol synthesis. This is surprising given the rich detail available in the HDS literature for $CoMoS_x$ catalysts used for desulfurization (notably, desulfurization occurs at much different conditions than mixed alcohol synthesis). Given the results above from Tsyganenko and Chianelli and the rather extreme decomposition conditions used to produce many of the K-$CoMoS_x$ catalysts studied to date, we developed the hypothesis that K-$CoMoS_x$ catalyst performance might be impacted by the thermal decomposition procedure alone. In this paper we determine the temperatures at which decomposition events occur for both K-promoted and non-K-promoted precursors. We then show the catalyst morphologies that result from different thermal treatments and the improvements in catalyst activity that are possible by using milder decomposition procedures. Next we show evidence for segregation of Co during the heating step and suggest implications of that phenomenon. Finally, we consider a thermal treatment wherein sulfur is made available in the gas phase and comment on the changes in morphology that result.

2. Experimental

2.1. Catalyst precursor synthesis

Catalyst precursors were made via co-precipitation of Mo and Co sulfides. Ammonium tetrathiomolybdate (ATTM, $(NH_4)_2MoS_4$, AAA Molybdenum Products #1008) was added to distilled water at 35 °C to form a 0.08 kg L^{-1} solution. The solution was filtered on #2 Whatman filter paper to remove insoluble material, which was then dried and weighed to calculate an absolute mass of dissolved ATTM. Pure ATTM solution was confirmed via UV–Vis spectroscopy as taught elsewhere [18], with the absence of the $MoOS_3^{2-}$ 'oxo' species at 396 nm confirmed. Cobalt acetate tetrahydrate crystals ($C_4H_6CoO_4{\cdot}4H_2O$, 98%, Alfa Aesar) were added to the stirred ATTM solution steadily over a period of 10 min to form a solution with nominal atomic ratios of 3:1 Mo:Co. As Co was added a black precipitate formed. Following Co addition, sulfuric acid (H_2SO_4, 2.5 mol L^{-1}, Spectrum Chemicals) was added drop-wise until the solution pH fell below 3.0, resulting in full precipitation of remaining ATTM and evolution of H_2S gas. The resulting precipitates were vacuum filtered on a Buchner funnel with Whatman Sharkskin paper and washed four times with distilled water. To K-promote the catalyst at the precursor stage, a solution of potassium carbonate (K_2CO_3, 99.94%, Spectrum Chemicals) was dissolved in enough distilled water to displace one volume of water from the precipitate 'cake' and used to wash the precipitate a final time. Upon addition of K solution, gases formed at the surface, presumably due to reaction between carbonate and residual acid. Precursors were immediately heat treated or placed in gas-tight bags, purged generously with N_2, and flash frozen in dry ice until ready for use. All precursors were used within two weeks of synthesis. Samples K-promoted at the precursor stage are termed 'salted' in the text that follows and samples washed only with water are termed 'unsalted.'

2.2. Temperature programmed decomposition (TPD) and calcination

TPD was conducted with the apparatus shown in Fig. 1. Frozen precursor was shattered to <0.005 m chunks and dispersed on a large quartz boat. The boat was then placed into a 0.025 m OD stainless steel tube within the isothermal zone (±5 °C consistency over full temperature range) of a horizontally mounted Barnstead/Thermolyne type F21135 tube furnace. A thermocouple was carefully positioned at the centerline of the tube directly above the surface of the precursor and the system sealed and purged with flowing N_2 at 0.5 L min^{-1}. The furnace was then heated to 100 °C and the precursor was allowed to dry for 2 h. Following this the furnace was heated at 10 °C min^{-1} to a sample temperature of 650 °C and then turned off to allow the sample to cool to room temperature. Preliminary experiments showed that temperatures above 650 °C did not provide additional decomposition data. In an additional experiment, nitrogen was bubbled through a vessel containing dimethyl disulfide (DMDS), after drying and during the temperature ramp, to introduce a saturated organic sulfur stream to the decomposing sulfides. Reactor effluent was sampled with a Pfeiffer QMG 220 Compact mass spectrometer (MS) system connected via heated capillary line. The MS featured a closed ion source operated at 70 V impact energy. A Pfeiffer QMA 220 Continuous Secondary Electron Multiplier (C-SEM) analyzer was used to detect ions having a mass to charge ratio (m/z) of 2–100. Effluent was not sampled during the drying step to preserve the filament of the MS. Capillary tubing was replaced after each test due to deposition of solid sulfur and propensity to plug in subsequent runs. Temperatures were correlated with MS signals using synchronized data loggers and the gas holdup time between sample and MS detector, measured separately with Ar pulses, was used to correct temperature/time data for MS signals. Thermal events were identified as the temperature at which an ion peak reached first inflection. In some experiments, precursors were held at the inflection temperatures of known decomposition events and expected ions were selectively measured at a scan rate of 0.05 s amu^{-1} until the ion signals decayed to baseline values, followed by additional temperature ramps and soaks. Once samples had cooled below 100 °C, they were passivated overnight in industrial-grade Ar (contains 0.5–1% O_2) and then transferred to an N_2-purged glove box for additional handling.

Larger samples (0.1–1 kg finished mass) were produced by moving catalyst precursor directly into a nitrogen-purged stainless steel rotary retort without freezing. The material was dried as described above, quickly heated to intermediate and final soak temperatures, and then held for a predetermined period before cooling to room temperature in

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