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Tuning of higher alcohol selectivity and productivity in CO hydrogenation reactions over K/MoS_2 domains supported on mesoporous activated carbon and mixed MgAl oxide

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ABSTRACT

Higher alcohol synthesis from syngas is studied over K/MoS_2 domains supported on mesoporous carbon (C), mixed MgAl oxide (MMO), or mixtures thereof. While the carbon support offers high ethanol productivity, the MMO support yields enhanced $C_{3+}OH$ selectivity. MoKMMO-C, whereby Mo is initially contained on MMO then ground with carbon, behaves similar to the parent MoKMMO catalyst, as Mo on MMO has limited mobility during reaction. In contrast, on MoKC-MMO, significant Mo migrates from C to MMO during reaction, giving reactivity associated with Mo species on both supports (high $C_{3+}OH$ selectivity and productivity). MoS_2 domain structures are correlated with the selectivity of the catalysts ($C_{3+}OH$ selectivity ~ double MoS_2 layers, total hydrocarbon selectivity ~ single MoS_2 layers). This study advances the understanding of the support's effect on structure–reactivity relationships for this family of catalysts and introduces a new catalyst composition with desirable reactivity.

1. Introduction

Even though U.S. oil production has boomed in recent years due to hydraulic fracturing, the need for petroleum-free routes to value-added chemicals will continue to intensify in the future when carbon building blocks become increasingly scarce. Lower olefins (C_2–C_4), primarily produced today by steam cracking, are key building blocks in the chemical industry, with ethylene being the largest volume petrochemical produced worldwide at approximately 80 million metric tons per year [1]. Another versatile petrochemical is propylene, with 40 million metric tons produced every year. The demand for olefins will continue to increase, with propylene demand expected to exceed production capacity, inevitably requiring the development of alternative routes to olefins.

Syngas is a versatile chemical feedstock that can be produced from coal, biomass, methane, and mixtures thereof, with commercial technologies. Syngas-based processes to olefins include long-chain hydrocarbon cracking, methanol-to-olefin conversion (MTO), and higher alcohol (C_2–C_4) dehydration. Two of these building blocks are currently commercially produced from syngas: methanol over Cu-based catalysts [1] and long-chain hydrocarbons over Fischer–Tropsch (FT) catalysts [2]. However, there is no commercially viable catalyst to produce higher alcohols from syngas.

Higher alcohol synthesis has been investigated with different families of heterogeneous catalysts including noble metal Rh-based catalysts [3–11], modified Cu-based methanol synthesis catalysts [12–16], and modified FT catalysts based on Co, Ru, and Fe [5,8,17–19]. A particularly promising non-noble metal family of catalysts, MoS_2-based catalysts modified with potassium [20,21], has been widely studied due to its resistance to sulfur poisoning, less severe coke deposition, and ability to form higher alcohols with a high selectivity to ethanol. However, MoS_2-based catalysts are less active than noble metal catalysts and require higher pressures to achieve reasonable productivities.

Supported MoS_2 catalysts have also been widely studied as means to improve higher alcohol selectivity and productivity using SiO_2, TiO_2, MgO, Al_2O_3, CeO_2, and a variety of carbons as supports [22–25]. Further studies were performed with activated carbon [26–32] and multi-walled carbon nanotubes (MWCNT)

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[17–19,33–36] as supports that enhanced productivity due to higher dispersion of MoS_2 domains. These studies showed that catalytic activity is enhanced by dispersing the MoS_2 over a support and that Mo–support interactions can affect the reactivity and product distribution of the catalyst by facilitating alcohol reaction pathways. Recently, Morrill et al. [37,38] developed new potassium promoted MoS_2 catalysts supported on a mixed Mg/Al oxide (MMO) support, derived from a hydrotalcite, that strongly perturbed the product distribution toward higher alcohols. The intrinsically basic properties of the support were suggested to promote alcohol-forming reactions, unlike common acidic γ-alumina [39–42] known to promote alcohol dehydration and subsequent hydrocarbon formation. The studies indicated that MMO supports yielded high $C_{3+}OH$ selectivity influenced by Mo–MMO interactions, but generally also yielded low catalytic productivity. It has further been shown that the Mo:MMO ratio greatly affected the reaction selectivity, while catalyst preparation methods had little impact on this parameter [38].

It was also observed that low Mo loading, resulting in enhanced higher alcohol selectivity, could be correlated with highly dispersed, smaller MoS_2 domains with few stacked layers. Chianelli et al. previously investigated the effect of the degree of MoS_2 stacking on selectivity for hydrodesulfurization (HDS) reactions [43]. The proposed "Rim-Edge model" described the catalyst as a stack of several disks, with the top and bottom disks associated with rim sites and the disks in between associated with edge sites. The results showed that hydrogenation reactions occurred on rim sites only, whereas HDS reactions occurred on both rim and edge sites. Based on this model, it is hypothesized that CO hydrogenation reactions over K/MoS_2 supported on MMO should primarily occur on rim sites.

Furthermore, Morrill et al. noted that carbon supports yielded high methanol and ethanol selectivities [37]. Previous work on mesoporous carbon, prepared at Oak Ridge National Laboratory (ORNL), yielded catalysts with greater alcohol productivity than similar catalysts supported on a commercial activated carbon [32,44,45]. In this work, we seek to evaluate the hypotheses that molybdenum supported on a mixed support comprised of MMO and mesoporous activated carbon may allow for elevated higher alcohol productivity (due to MoS_2 domains on the carbon support) and good higher alcohol selectivity (due to MoS_2 domains on the MMO support), with an emphasis on understanding the MoS_2 structure–reactivity relationships over the carbon/MMO composite supported catalysts. A particular focus is placed on determining the effect of the support on MoS_2 structure, as well as the mobility of Mo species on the two supports under reaction conditions.

2. Experimental section

Mesoporous activated carbon was prepared via a published procedure developed at ORNL. Mesoporous carbon was synthesized by carbonization of nanostructured polymers, obtained by self-assembly of block copolymer and phenolic resin under acidic conditions *via* soft-template method, under flowing N_2 at 850 °C for 2 h. The mesoporous carbon was then activated with KOH and subsequently washed by dilute HCl to remove residual KOH. For KOH activation, a physical mixture of solid KOH (16 g) and mesoporous carbon (4 g) was loaded to a quartz tube in a nickel crucible and heated under flowing N_2 to 900 °C and held for 2 h. The resulting material was washed with deionized water and then mixed with a ~0.2 M HCl solution that was then heated up to 80 °C with stirring for 30 min. The activated mesoporous activated carbon was collected by filtration, washed with deionized water, and dried at 100 °C [46]. MMO was synthesized using the same method described in our previous studies [37,38] by coprecipitation of magnesium nitrate hexahydrate (Alfa Aesar, 98–102%), and aluminum nitrate nonahydrate (Alfa Aesar, 98–102%) aqueous solutions with a Mg:Al molar ratio of 7:3 (0.6 M in metal ions) together with a 1.2 M NaOH (EMD, 97.0%) and 0.15 M Na_2CO_3 (Aldrich, 99.5+%) at 65 °C and a pH of 9.5. The resulting solution was stirred for 48 h, filtered, washed with deionized water, dried overnight at 105 °C, and then calcined at 450 °C for 2 h.

A set of four catalysts using a mixture of mesoporous activated carbon (C) and MMO supports was synthesized with an approximate Mo loading of 5 wt.%, K loading of 3 wt.%, and a molar ratio of Mo:K of 1. The parent catalysts in this study, which are derived from a single support, are referred to as MoKMMO and MoKC. The mixed supported catalysts in this study are referred to as MoKC-MMO and MoKMMO-C, where the parent catalyst is first prepared and is ground with the bare secondary support in a mass ratio of MMO:C of 3.6 to yield the final precatalysts (Fig. 1). $Mo_{0.15}K_{0.09}C$ was used as the parent catalyst for MoKC-MMO, and $Mo_{0.06}K_{0.04}MMO$ was used as the parent catalyst of MoKMMO-C, so that when ground with the secondary support the desired Mo and K loadings were achieved. The precatalysts were then pressed into pellets for catalyst testing in the fixed bed reactor. MoKMMO was pelletized to ~3000 psig, whereas mixed supported catalysts (MoKMMO-C and MoKC-MMO) were pelletized at ~6000 psig to obtain self-supporting pellets. In Table S1 in the Supporting Information, it is shown that upon pelletization the MMO and MMO-C supports lose ~20% of their surface area, and ~10% of their pore volume. Therefore, there is no considerable decrease in porosity upon pelletization.

Mo was added to the supports via incipient wetness impregnation using ammonium molybdate tetrahydrate (AMT) (Sigma–Aldrich, ACS Reagent) dissolved in DMSO for the MMO support (the solution was stirred for 12 h until AMT was dissolved) and water for the carbon support. DMSO was used as the impregnation solvent for MMO instead of water to limit the recrystallization of the hydrotalcite phase, which can be induced by water, thereby "burying" the potassium promoter [14,47,48]. The resulting materials were dried in open atmosphere at 135 °C for 12 h for the MMO support and at 100 °C for 12 h for the carbon support, and then placed in a quartz tube, whereby the AMT was decomposed via heating to 200 °C for 6 h at 5 °C/min, followed by further heating to 450 °C for 2 h at 5 °C/min under 40 mL/min of flowing N_2. After the decomposition step, the parent oxide precatalysts were

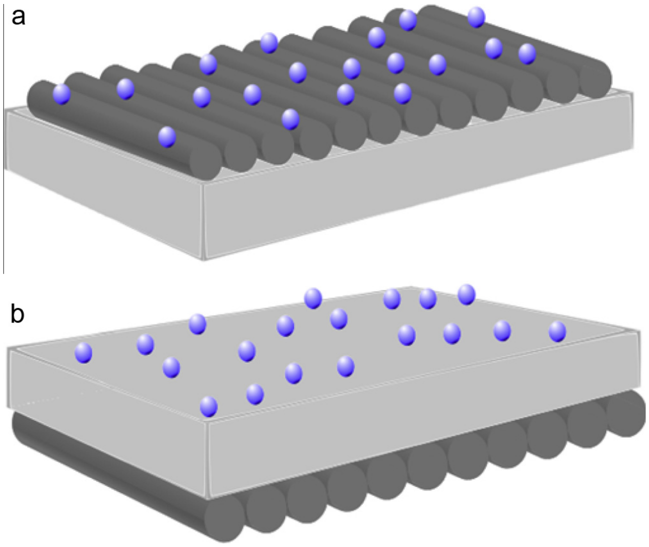

Fig. 1. Catalyst schematic for (a) MoKC-MMO and (b) MoKMMO-C precatalysts with Mo oxide domains represented by spheres, mesoporous activated carbon represented by cylinders, and MMO represented by a rectangular box.