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Use of infrared spectroscopy and density functional theory to study the influence of rubidium on alumina-supported molybdenum carbide catalyst for higher alcohol synthesis from syngas

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ABSTRACT

Molybdenum carbide nanoclusters supported on alumina were promoted by Rb_2CO_3 and tested for higher alcohol synthesis from syngas. At 573 K and 30 bar syngas ($H_2/CO = 1$), the promoted catalyst demonstrated 63% selectivity to alcohols (on a CO_2-free basis), with hydrocarbons and ethers as side products. In contrast, the alcohol selectivity of an unpromoted Mo_2C/Al_2O_3 catalyst was very low. DRIFTS of adsorbed CO on Mo_2C/Al_2O_3 revealed a significant red shift in the CO band with added Rb promoter, which correlated to a decrease in hydrocarbon production rate and therefore an increase in alcohol selectivity. A quantum chemical description of CO adsorbed on a model Mo_2C surface identified several possible binding modes of the CO. Both reactivity studies and DRIFTS of adsorbed CO demonstrated that mobility of the Rb promoter was enhanced in the presence of water vapor, which facilitates dispersion of Rb across the catalyst surface and effectively neutralizes acid sites that are deleterious to alcohol selectivity.

1. Introduction

Limited crude oil reserves and competition with the food industry associated with fermentation-based biofuel production inspire new research efforts on effective catalytic transformations of alternative carbon sources to produce energy carriers and chemical feedstocks. Synthesis gas ($CO + H_2$) can be derived from coal, natural gas, or renewable biomass and is a platform for the synthesis of fuels and chemicals.

Fischer–Tropsch synthesis (FTS) of hydrocarbons has received growing attention as a source of low-sulfur diesel fuel because of the uncertainty of crude oil prices. However, higher alcohol (C2+ alcohols) synthesis from synthesis gas, as a source of chemical feedstocks, might be more commercially attractive. For example, Celanese Corporation reported an expected ethanol price of $1.4/gallon with their new coal-to-ethanol technology via acetic acid [1,2], and E.I. du Pont de Nemours and Company and BP have a stated goal for a butanol price of $1/gallon with their bio-based process currently under development [3]. Considering that methanol is currently produced from natural-gas-based syngas at the world scale, it is reasonable to expect a comparably low price for higher alcohols produced by a similar catalytic process, assuming production and selectivity achievements are realized.

Because of methanol's low solubility in gasoline, it needs to be further converted to another molecule such as methyl *tert*-butyl ether (MTBE) before being used as a gasoline blend. However, MTBE is being phased out as a fuel additive due to environmental concerns. Higher alcohols, on the other hand, have mutual solubility with gasoline and ethanol has been widely used in the US as a gasoline additive. Since almost all the ethanol used for fuel is produced from fermentation, there is still a need for a more efficient catalytic process for the production of ethanol (and other higher alcohols).

An effective catalyst for the production of higher alcohols from syngas is necessarily multifunctional since CO activation, hydrogenation, carbon chain growth, and potentially alcohol coupling processes are all important steps in the reaction. Thus, no single-component transition metal catalyst has been discovered to effectively catalyze higher alcohol synthesis.

Exploratory research on higher alcohol synthesis has discovered some promising candidates [4–8]. Rh-based catalysts are effective for the formation of ethanol and other C2-oxygenates from syngas [9–11], but the very high cost of Rh likely prohibits its large-scale utilization. Several non-precious metal catalysts for higher alcohol synthesis have thus been evaluated and include, for example, Cu–Co, Cu–Zn–Al and Zn–Cr–K [5], but improvements in the

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overall catalytic activity, alcohol selectivity, and long-term stability of these catalytic materials for higher alcohol synthesis are still needed.

Molybdenum-based catalysts have been widely used in many hydro-treating processes because of their high activities in desulfurization and denitrogenation with H_2. When promoted by alkali metals, Mo-based catalysts also show encouraging properties for higher alcohol synthesis from CO hydrogenation. Both supported and unsupported MoS_2-based catalysts have been heavily investigated for higher alcohol synthesis [12–15] since it was firstly developed by The Dow Chemical Company in the 1980s [16–20]. However, trace amounts of H_2S in the feed were required to sustain the performance of the MoS_2-based catalysts [17]. Moreover, small amounts of sulfur may enter the carbon skeleton of the products, which is problematic as the world moves toward the use of very-low-sulfur fuels. Thus, there is a need for a non-sulfided alternative for MoS_2-based catalyst in this process, among which molybdenum carbide has demonstrated some promise when properly promoted [21–25]. Early transition metal carbides are also recognized as potential substitutes to precious metal catalysts because of their similar surface electronic properties [26–28].

The selectivity toward alcohols over alkali-metal-promoted MoS_2-based and Mo_2C-based catalysts in the syngas reaction was reported to be low initially but increased significantly with time onstream over a period of several hours to several days [23,29–31]. Lee et al. suggested that the promotional effect of alkali metal species on MoS_2 [13] and Mo_2C [32] catalysts for alcohol formation during CO hydrogenation was mostly the result of the surface sites being blocked from adsorbing reactants. By using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Koizumi et al. claimed that syngas adsorption on a $MoS_2/\gamma\text{-}Al_2O_3$ catalyst for CO hydrogenation was significantly suppressed by K species and the K-promoted Mo species were likely more oxidized than those on K-free MoS_2 [33]. Muramatsu et al. also studied the role of a K promoter on a Mo oxide catalyst for alcohol production from syngas and concluded that K inhibits both dehydration of alcohols to alkenes and the hydrogenation of alkenes to alkanes [34]. For supported MoS_2-based catalysts, interactions between K promoters and Mo begins with the oxidized catalyst precursors [12,29,35,36] and that some K–Mo–S and/or K–Mo–S–O species are formed after sulfidation. However, it is still unclear whether the promoters enhance the activity of the catalysts for higher alcohol synthesis. Although CO adsorption has been used to probe the surfaces of MoS_2-based [37–42] and Mo_2C-based [43–47] catalysts, few of these studies addressed the promotional influence of the alkali metals on higher alcohol synthesis. X-ray absorption spectroscopy of Rb-promoted Mo_2C/MgO catalysts demonstrated that the local environment around the Rb_2CO_3 promoter was structurally modified during reaction [23], but the actual structural form of the working promoter is not yet known.

The present study uses diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO combined with density functional theory (DFT) to investigate the interactions between Rb and supported-Mo_2C particles. Results from DRIFTS and DFT are used to interpret observed reactivity trends of working catalysts.

2. Methods

2.1. Catalyst synthesis

Incorporation of Mo onto the alumina support (Mager Scientific, >99.98%, predominantly γ-phase, $S_{BET} = 76\ m^2\ g^{-1}$) was accomplished by incipient wetness impregnation of an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.98%, Aldrich) followed by drying in air for 12 h at 400 K and calcining in flowing air for 5 h at 773 K to produce a supported molybdenum oxide, denoted here as MoO_3/Al_2O_3. Carburization of MoO_3/Al_2O_3 was performed in a quartz tube by heating at a rate of $5\ K\ min^{-1}$ from room temperature to 573 K and at a rate of $1\ K\ min^{-1}$ from 573 K to 1033 K in 20 vol.% CH_4 (GTS-Welco, 99.997%) and 80 vol.% H_2 (GTS-Welco, 99.999%) at a total gas flow rate of $75\ cm^3\ min^{-1}$ (STP). After ramping to 1033 K in CH_4/H_2, the temperature was maintained at 1033 K for 1 h. The catalyst was subsequently cooled to 673 K in flowing He (GTS-Welco, 99.999%, additionally purified by a Sigma–Aldrich OMI-2 purifier) and held at 673 K for 5 h in flowing purified H_2 at a flow rate of $60\ cm^3$ (STP) min^{-1}. The catalyst was then cooled to room temperature in flowing purified He before passivation in a $20\ cm^3\ min^{-1}$ (STP) stream of 1.04 vol.% O_2/N_2 mixture (GTS-Welco) at room temperature for 12 h. The alkali-metal-promoted Mo_2C/Al_2O_3 samples were prepared by grinding Rb_2CO_3 (99.975%, Alfa Aesar) together with passivated Mo_2C/Al_2O_3 in a mortar and pestle.

2.2. Hydrogenation of carbon monoxide

Hydrogenation of CO was conducted in a fixed-bed stainless steel reactor (BTRS Jr., Autoclave Engineers) with about 1.25 g catalyst (0.025 g nominal Mo_2C). The catalysts were tested at nominally identical conditions of 573 K, 30 bar total pressure, syngas (H_2 + CO) flow of $10\ cm^3\ min^{-1}$ (STP), and $H_2/CO = 1$. Additional experimental details can be found in our previous works [23,25].

In another series of studies on representative samples, water was introduced to the catalyst by flowing N_2 (GTS-Welco, 99.999%, additionally purified by a Sigma–Aldrich OMI-2 purifier) to the fixed-bed reactor through a saturator with liquid water at 300 K. The samples were sequentially treated at ambient pressure with $50\ cm^3\ min^{-1}$ (STP) H_2O/N_2 at 300 K for 2 h and with $50\ cm^3\ min^{-1}$ (STP) H_2 (GTS-Welco, 99.999%) at 573 K for 12 h prior to syngas reaction.

In control experiments without water, the samples were pretreated with $50\ cm^3\ min^{-1}$ (STP) H_2 (GTS-Welco, 99.999%) at 573 K for 12 h prior to syngas reaction.

2.3. Catalyst characterization

The X-ray diffraction patterns were obtained on a Scintag XDS 2000 diffractometer using Cu Kα radiation. Scans were collected over a range of 2θ from 5° to 90° at a rate of $2°\ min^{-1}$ for bulk materials and $0.8°\ min^{-1}$ for supported catalysts.

Elemental analyses of representative samples were performed by Galbraith Laboratories (Knoxville, TN). The loading of molybdenum and rubidium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the loading of carbon was evaluated by combustion and coulometric measurements.

X-ray absorption spectroscopy (XAS) was performed on beam lines X23A2 and X18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The storage ring was typically operated at 2.8 GeV with a ring current of about 300 mA. The XAS data were obtained in the transmission mode at the Mo *K* edge (20 keV) with a spot size of 0.5 mm × 5 mm. The Mo *K* edge spectra were measured at room temperature with Mo foil (Goodfellow) as a reference. The air-free handling protocols for the non-passivated, unpromoted catalyst before reaction and the Rb-promoted catalyst after syngas reaction have been discussed in our previous work [25]. The XAS data were processed using the Athena [48] software for background removal, post-edge normalization, and X-ray absorption near edge structure (XANES) analysis. The value of E_0 was assigned here as the energy at the half-step height. Metallic Mo foil, MoO_2 (99%, Aldrich) and MoO_3 (99.99%, Aldrich) were used as standard references for Mo in various oxidation states. Standard