NEW SYNTHETIC METHODS TO ALTER CATALYTIC PROPERTIES OF

SUPPORTED K/MoS$_2$ CATALYSTS FOR

SYNGAS CONVERSION TO HIGHER ALCOHOLS

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New Synthetic Methods to Alter Catalytic Properties of

Supported K/MoS$_2$ Catalysts for Syngas Conversion to Higher Alcohols

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LIST OF ABBREVIATIONS

$Al(NO_3)_3 9H_2O$: aluminum nitrate nonahydrate

AMT: ammonium molybdate tetrahydrate

$Co(NO_3)_3 9H_2O$: cobalt nitrate nonahydrate

$Co(OAc)_2$: cobalt acetate

DMSO: dimethyl sulfoxide

EA: elemental analysis

GHSV: gas hourly space velocity

HC: hydrocarbon

K_2CO_3: potassium carbonate

$Mg(NO_3)_2 6H_2O$: magnesium nitrate hexahydrate

MMO: mixed metal oxide

Na_2CO_3: sodium carbonate

NaOH: sodium hydroxide

TPR: temperature-programmed reaction

XAFS: X-ray absorption fine structure

XANES: X-ray absorption near edge structure

XRD: X-ray diffraction

SUMMARY

The purpose of this study is to develop catalysts for conversion of synthesis gas (H_2 and CO) to higher alcohols, primarily ethanol and propanol. Crude oil is consumed at a rate of more than 20 million barrels a day in the United States, mainly for producing fuels and chemical feedstocks. However, the total amount of crude oil is limited, and alternative ways of producing alcohols as precursors for chemical feedstocks are desirable. In this study, using a known K/MoS_2/metal oxide catalyst as the starting point, two different approaches were explored to improve catalytic properties:

1) Co promotion on K/MoS_2/mixed metal oxide (MMO) catalysts, and

2) Preparation of K/MoS_2/metal oxide catalysts with molybdenum carbide as a precursor, instead of molybdenum oxide.

With respect to Co promotion on K/MoS_2/MMO catalysts, the effect of varying the Co content in the K/Mo-Co/MMO catalysts prepared by a co-impregnation method did not produce significant changes in catalytic acitivities or selectivities. It was due to the premature precipitation of cobalt molybdate during synthesis. Cobalt molybdate precipitation can generally be prevented by using water as a solvent,[1,2] but this approach is not appropriate for this study because of the use of hydrotalcite-derived mixed metal oxide as the support. Co loadings on K/Mo/MMO-Co catalysts did not change selectivities significantly, either. However, they changed catalytic activities, represented by gas hourly space velocity (GHSV) required to obtain 8% conversion while maintaining high selectivities for higher alcohols. As a result, C_{2+} alcohol productivities reached $0.01 g_{alcohol}/g_{catalyst}/hr$ with Co loadings higher than 8%.

With respect to using Mo_2C as the precursor of Mo species instead of MoO_3, comparisons between catalysts with different precursors for Mo species and different pretreatments were investigated. In this study, both K/Mo catalysts supported on MgO and α-Al_2O_3 showed similar tendencies of catalytic activities and selectivities. The highest C_{2+} alcohol selectivities and productivities were obtained on presulfided MoO_3 catalysts on both supports. In comparison of K/Mo_2C catalysts with different pretreatments, higher C_{2+} alcohol selectivities and lower MeOH selectivities were obtained on presulfided catalysts compared to non-pretreated catalysts.

CHAPTER 1: INTRODUCTION

Motivation

Over the past several decades, the demand for energy has grown significantly for

transportation, electricity generation and industrial processes. On top of these uses, the

world is currently heavily dependent on petroleum for syntheses of chemical feedstocks,

and it is becoming increasingly so. However, the security of the oil supply and the

negative impact of use of fossil fuels on the environment, such as the greenhouse effect,

have become more and more serious issues. Additionally, total amount of consumption

of crude oil and imported crude oil price have increased significantly. (Fig. 1.1)[3] Based

on these issues, the federal government of the United States passed laws in 2007 which

set the applicable volume of renewable fuels to be 36 billion gallons per year by 2022.[4]

In order to fulfill this requirement, bio-ethanol has been already commercially introduced

in many countries. However, bio-ethanol that is commercially available now is primarily

produced from sugar or starch,[5] which affects food supplies by switching crops and

croplands to biofuel production.[6] This issue also affects the price of bio-ethanol, which in

fact is keeping the cost of bio-ethanol at a competitive level. In order to solve these

issues, there is an increasing need for developing catalysts for conversion of syngas,

which can be produced from non-food related ingredients, to produce higher alcohols.
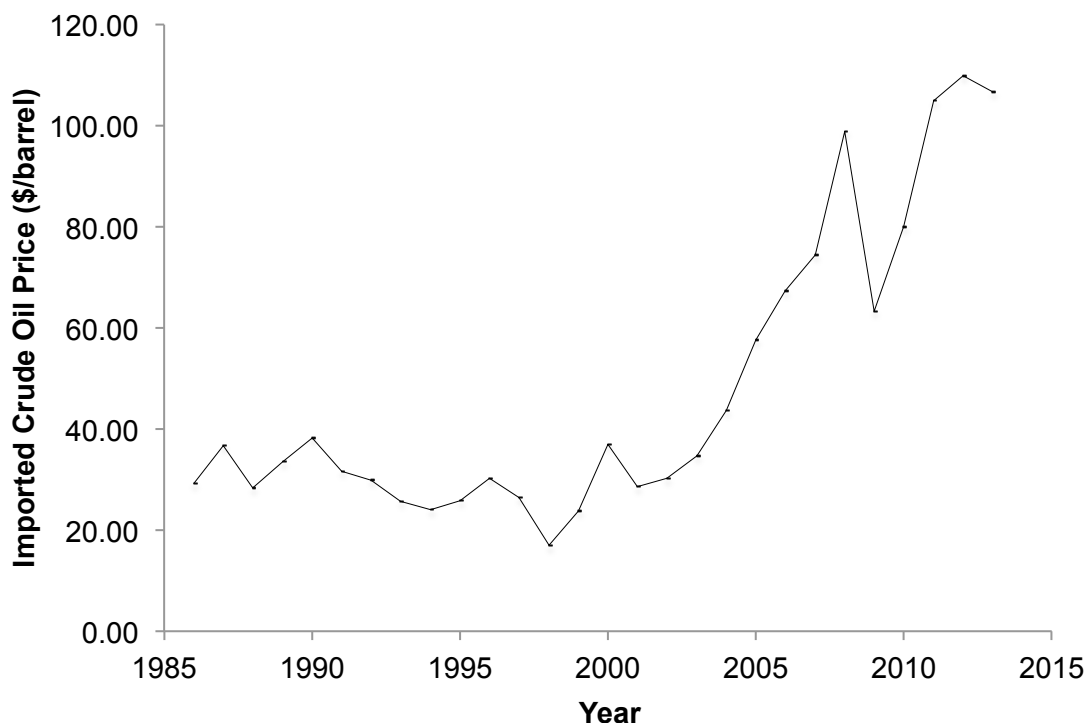
Figure 1.1 Price increase of imported crude oil[3]

Reported catalysts for alcohol synthesis from syngas

There are many catalysts reported for alcohol syntheses from syngas. Most are

heterogeneous catalysts, but there are some homogeneous catalysts reported as well.

Maitlis reports homogeneous catalysts in solution with soluble complexes of Co, Rh or

Ru that produce alcohols, glycols and formyls, with very little hydrocarbons (HC).[7]

However, most of the homogeneous catalysts for alcohol syntheses are for methanol

homologations.[8] Most of the catalysts reported for direct syntheses of alcohols from

syngas so far are heterogeneous catalysts. Those catalysts may be classified in four

types: Rh-based catalysts, modified methanol synthesis Cu-based catalysts, modified

Fischer–Tropsch type catalysts and modified Mo-based catalysts.[9]

Rh-based catalysts are reported for hydrogenation reactions for CO, CO_2 and a mixture of CO and CO_2. Especially to produce oxygenates by hydrogenation of CO, Rh is one of the most widely studied catalysts. Supported Rh catalysts have been studied for production of C_{2+} oxygenates for over 30 years.[10] It is also known that Rh catalysts may be significantly affected by promoters and supports. Promoters provide interaction sites for CO molecules with the catalyst surfaces, and supports affect the CO adsorption by affecting Rh domain dispersion.[9] It is reported that a 2.5% Rh/SiO_2 catalyst promoted by 0.05% Fe produces high ethanol selectivity of 31.4%, and a methanol and ethanol production rate of 50 g/$L_{catalyst}$/hr.[8]

Cu catalysts have been studied for methanol syntheses for a long time as well. Since the observation of an increase of higher alcohol yield obtained by the use of alkali during a catalyst preparation in 1920's, alkali-doped Cu/Zn catalysts have been studied for higher alcohol syntheses.[9] It is reported that $Cs/Cu/ZnO/CrO_3$ catalysts produce a yield of 0.95$g_{alcohol}$/$g_{catalyst}$/hr, at the conversion of 8.5% under reaction conditions of 340°C, 1100 psig and GHSV=18375 ml/$g_{catalyst}$/hr.[11]

Fischer-Tropsch catalysts also have a long history. Some major Fischer-Tropsch catalysts (Co, Ru and Fe-based catalysts) have been studied for oxygenate production and are now known to be active for higher alcohol syntheses with appropriate promoters.[9,12] It is reported by Kintaichi *et al*. that a C_{2+} alcohol selectivity of 19.3% was obtained using a Ir-Ru/SiO_2 catalyst under reaction conditions of 300°C, 711 psi, and GHSV of 2000 h^{-1}. This was the highest C_{2+} alcohol selectivity obtained during their study of all Pt group metal-based bimetallic catalysts supported by silica.[13] Moreover,

they reported that with promotion by Li, the total selectivity to C_{2+} alcohol increased to 23.9%.[13]

Mo-based catalysts have been widely studied as well. Just like other catalysts, alkali promotion is essential for shifting selectivities from hydrocarbons to alcohols.[14] This is because the sulfided K-Mo species are active for the formation of alcohols from CO hydrogenation, whereas the coordinatively unsaturated Mo sites are responsible for the formation of hydrocarbons. Also increasing K loadings increases Mo dispersion and active sites in MoS_2 domains.[15] With further promotions with Co, higher alcohol selectivities can increase even more.[9] Studies reported on Mo-based catalysts will be described later in this chapter.

Background on the main materials used in this present study

<u>Mixed metal oxide</u>

A Mg/Al mixed metal oxide, prepared by calcination of a synthetic hydrotalcite, has a general formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2](CO_3^{2-})_{x/2}-nH_2O$. It is a useful tool for the establishment of environmentally friendly technologies because of its high versatility and wide range of variables that is changeable in its preparation. Its versatility may be shown in various chemical and physical properties, such as high surface areas, solid base properties, and formation of various mixed metal oxides. In addition, the experimental conditions for synthesis are easy and mild. Generally hydrotalcites are prepared under atmospheric pressure, 60°C in aqueous solutions with pH of around 10.[16,17] Therefore, they have been widely studied and used in medicines, adsorbents and catalysts. As catalyst supports, mixed metal oxides have been studied for wide variety of reactions. For example, they have been studied for hydrocarbon reforming reactions, oxidation

reactions, and hydrogenation reactions such as production of higher alcohols from syngas.[18] For alcohol syntheses, MMOs composed of Zn, Cr, Cu and Al were used in most studies reported.[18] It has been pointed out that for alcohol syntheses it is essential that the catalyst and the support are basic, because acidic catalysts dehydrate and decompose alcohols.[19] Therefore, the less acidic the support is, the more selective the catalyst would likely be.[20] Study on the use of Mg-Al MMO as a support of the catalysts for alcohol syntheses from syngas was reported for the first time by Morrill *et al*.[21] According to that report, promotional effects similar to alkali, such as low MeOH selectivities and low catalytic activities, were obtained by using Mg-Al MMO, which is a basic support.

Molybdenum sulfide

Mo-based catalysts have been reported for various kinds of hydrotreating reactions, such as hydrodesulfurization[22–24] and hydrodenitrogenation,[25,26] in which they exhibit high activities. There are also many studies reported on Mo-based catalysts for alcohol syntheses from syngas.[15,20,27–33]

With respect to alcohol syntheses, it is reported that the sulfided K-MoO_3/γ-Al_2O_3 catalyst with potassium carbonate (K_2CO_3) loading of 18 wt% and MoO_3 loading of 24 wt% showed good catalytic activities, selectivities and stabilities.[28] Under reaction conditions of 385°C, 2030 psi and GHSV of 11000 h^{-1}, the obtained space-time yield was 416.7ml/$L_{catalyst}$/hr, and the alcohol selectivity was 82%. The stability was also excellent; it stabilized after the first 200 hours, and it did not decrease for the whole process of 1300 hours of reaction.[28] However, MoS_2 catalysts need H_2S in the feed gas to avoid losing sulfur during reaction.[34]

Jaras *et al.* reported that MoS_2 catalysts, when doubly promoted by K and Ni, decreased selectivities for alcohols and increased the ratios of long-to-short alcohol selectivities with an increase of conversion. These behaviors were observed in both of the cases where the conversions were increased by the increase of temperature and the decrease of space velocity.[35] This report suggests that shorter alcohols are the building blocks for longer alcohols. Moreover, hydrocarbons are produced by conversions of alcohols by secondary reactions.[35] According to Fujimoto *et al.,* between the range of 3-50% of Mo loadings, selectivities for alcohols increase with the increase of Mo loadings.[36] The main mechanism responsible for this reaction is activating CO and inserting it into metal-CH_x bond.[9,33]

Potassium carbonate promotion on Mo-based catalyst

In higher alcohol syntheses from syngas using MoS_2 catalysts, it is widely known that an alkali promotion is essential. It increases not only stabilities[37] but also higher alcohol selectivities.[9,32,36] From experimental studies, chain propagation promotion by K_2CO_3 is reported.[38] On K_2CO_3-promoted MoS_2 catalysts, carbon chains grow by CO insertions. Also from experimental studies, it is reported that the active site for alcohol formation is the alkali/oxygen compound with MoS_2 on the catalyst surface.[32] Alkali promotion is also effective in decreasing Mo particle sizes. It is reported by Surisetty *et al.* that as the K loading was increased from 3 to 9 wt% on 15 wt% Mo catalysts, the Mo particle sizes decreased from 20.6 to 12.2 nm.[15] In their study, the Mo (15 wt%)/K (9 wt%) catalyst supported on multi-walled carbon nanotube showed the highest alcohol yield, 0.11$g_{alcohol}$/$g_{catalyst}$/hr, with the total alcohol selectivity of 25.6% and conversion of 11%, under reaction conditions of 320°C, 1400 psi and GHSV of 3.6L/$g_{catalyst}$/hr.[15] It is

reported that the increase of the ratio of C_{2+} to C_1 over MoS_2 catalysts by potassium promotion indicates that the potassium promoters greatly reduce the hydrogenation functions of the MoS_2 catalyst.[35] Among other alkalis, potassium is known to be the most effective as a promoter.[9] With regard to catalytic stabilities, potassium is known to help the catalyst maintain catalytic activities and selectivities due to its resistance to sulfur poisoning and coking.[29] It was reported in a study of $K-MoS_2/\gamma-Al_2O_3$ catalysts under reaction conditions of 280°C, 580 psi, GHSV of 4500 h^{-1}, that the catalytic activities of the $K-MoS_2$ catalyst increased with an increase of the K/Mo atomic ratio until the K/Mo atomic ratio hits 0.8. In the same study, the alcohol selectivity also increased monotonically with the ratio in the range of K/Mo ratio of 0-1.5.[40] K_2CO_3 promotion on MoS_2 is also known to make the catalytic activities dependent on H_2 and CO pressures. Although on unpromoted MoS_2 catalyst alcohol yield was independent of feed gas pressures, when the catalyst was promoted with K_2CO_3, alcohol yields became higher with an increase in feed gas pressure.[32]

Klier *et al.* studied the reaction mechanism over alkali-promoted MoS_2 catalysts with injections of ^{13}C-labelled methanol into the reaction feed gas stream and analyzing the products by using ^{13}C-NMR spectroscopy.[41] Their results showed that the alcohol chain growth occurred via a CO insertion mechanism. This was indicated by the results in which they detected $^{13}CH_3CH_2OH$, $^{13}CH_3CH_2CH_2OH$ and $CH_3{}^{13}CH_2CH_2OH$, but not $^{13}CH_3{}^{13}CH_2CH_2OH$. This result suggests that carbon-carbon couplings of methanol molecules are not occurring, but only CO insertions are taking place in the alcohol chain growths.[41] They also reported that the addition of Co to the catalyst increased the rate of the alcohol chain growth step from C1 to C2.[41]

Cobalt promotion on MoS_2 catalyst

It is known that although alkali promotion of Mo-based catalysts shifts the selectivity for reactions of syngas from hydrocarbons to alcohols effectively, the effects on higher alcohol formation are limited when promotion is done only with K. Therefore promotions with transition metals are often used to improve C_{2+} alcohol selectivities and productivities.[9] Cobalt is well known as an effective promoter for $K-MoS_2$ catalysts for alcohol syntheses from syngas. Co is reported to improve C_{2+} alcohol productivities in several different ways: increase of C_{2+} alcohol selectivities,[41–43] increase of conversions,[44] and achievement of good alcohol selectivities even at high conversions.[31] The double promotion effects of cobalt and alkali on C_{2+} alcohol selectivities are known to be more effective than the solo promotion effects of cobalt and alkali.[9] These effects are due to Co addition to K-Mo catalysts increasing the number of surface Mo sites and promoting the reducibility of Mo.[29] This is a conclusion drawn by DRIFT spectroscopy measurements of CO adsorbed catalysts by Dalai *et al.*[29] They studied the active species in the sulfide form of the catalysts. With higher Co loadings, the intensities of bands on the Co-promoted Mo sites increased significantly. This result suggests that higher Co loadings cause the number of surface Mo sites to increase.[29] It is reported that the sulfided $Co_1Mo_1K_{0.3}$-10% catalysts supported by multiwalled carbon nanotubes produced a space-time-yield of total C_1-C_4 alcohols of $0.24g_{alcohol}/g_{cat}/hr$ with ethanol as the dominant product with 21.6% conversion. The reactions on these catalysts were under reaction conditions of 350°C, 725 psig, and a volume ratio of the feed gas of $H_2:CO:N_2$ = 60:30:10, and GHSV = 3600 $ml/g_{catalyst}/hr$.[45] There is another report on K-Co-MoS_2 catalysts supported by multiwalled carbon nanotubes with loadings of 9 wt% K, 15 wt% Mo and 6 wt% Co which states that this catalyst produces $0.21g_{alcohol}/g_{catalyst}/hr$ with 43.5% conversion under reaction condition of 320°C and 1200psig.[29]

Molybdenum carbide

Mo_2C catalysts are known to be selective mainly for hydrocarbons. However, with K_2CO_3 promotion, the selectivities are shifted to alcohols.[38] The effects of K_2CO_3 on Mo_2C catalysts are similar to the effects of K_2CO_3 on MoS_2 catalysts. With the promotion of K_2CO_3, an unsupported Mo_2C catalyst gives higher selectivities to C_{2+} alcohol and higher conversions compared to K_2CO_3-promoted MoS_2 catalysts.[46] According to Lee *et al.*, the K_2CO_3-promoted Mo_2C catalyst was analogous to MoS_2 catalyst doubly promoted by Co and K_2CO_3.[46] However, the downside of Mo_2C catalysts is that unlike MoS_2 catalysts, the catalytic activities and the selectivities for alcohols decrease over time when H_2S is added in the feed gas.[47] Sulfur tolerant catalysts are favorable, because H_2S is usually contained in biomass-derived raw syngas as one of the impurities.[47] It is reported by Lee *et al.* that under syngas flow containing H_2S, CO conversions and alcohol selectivities over sulfided Mo_2C catalyst were reduced, compared to under syngas flow without H_2S.[46] They also reported that H_2S in the feed gas over unsulfided Mo_2C catalyst reduces the selectivities for higher alcohols. According to their studies, the probability of chain growth for alcohols on the unsulfided Mo_2C catalyst decreased from 0.31 to 0.14 within 66 hours of reaction with feed gas containing H_2S.[46]

On molybdenum carbide catalysts, when Mo is partially reduced to a range of Mo^{2+} to metallic molybdenum, CO and H_2 molecules are known to be adsorbed on the molybdenum surface to form hydrocarbons, where chain growth happens. Then the hydrocarbons migrate to Mo^{4+} where CO inserts into hydrocarbons and form acyl species.[33]

<u>Effect of H$_2$S in the reaction feed gas</u>

H$_2$S is one of the impurities that are naturally contained in biomass-derived syngas.[47] The effect of H$_2$S in the reaction feed gas is mainly the promotion of chain growth for both alcohols and hydrocarbons.[39] It is known from experimental results that within the range of 0-200ppm, higher H$_2$S concentration in the reaction feed gas produces improved higher-alcohol-to-methanol ratios (wt/wt).[39] Although it does not have much effect on K-Mo-Co catalysts, the increase of selectivities for higher alcohols is significant on K-Mo catalysts.[42] It is reported that on a K$_2$CO$_3$/Co/MoS$_2$/C catalyst, high H$_2$S concentration in the feed gas stabilizes the catalytic activities fairly quickly, whereas when there is low or no H$_2$S concentration in the feed gas, the stabilization is much slower.[39] Also, when sulfur is lost from the catalyst to the gas flow, it may cause catalyst deactivation.[48] H$_2$S in the feed gas also contributes to the catalytic activities in this situation, by preventing loss of sulfur of the MoS$_2$ into the gas flow. Containing H$_2$S in the reaction feed gas over MoS$_2$ catalyst keeps the C$_{2+}$ alcohol selectivities at a high level.[46]

Target of this project

In this study, the goal was to develop catalysts with high catalytic activities and high C$_{2+}$ alcohol selectivities. Catalytic activities were represented by the GHSV required to obtain 8% conversion. The higher GHSV is, the higher the catalytic activity is. By using supported sulfided K$_2$CO$_3$/MoO$_3$ catalysts as the standard composition, the effects of promotion by Co and the effects of use of Mo$_2$C as the precursor for MoS$_2$ were investigated. Catalysts were tested for alcohol syntheses from syngas, and were characterized by using elemental analyses, X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) techniques, among others.

Cobalt is one of well-known promoters for K-MoS_2 catalysts for higher alcohol syntheses from syngas. It is known to be effective in producing catalysts with high alcohol selectivities even at high conversions.[31] In this study, Co promotion was done in two ways: 1) co-impregnating a Co precursor with a MoO_3 precursor on calcined MMO supports, and 2) co-precipitating a Co precursor with the hydrotalcite support precursors.

Mo_2C was investigated as the precursor for MoS_2. Using MgO and α-Al_2O_3 as supports, Mo_2C catalysts were investigated for higher alcohol syntheses from syngas. The catalysts were pretreated with i) 10% H_2S/H_2 gas and ii) H_2 gas. Both pretreated catalysts were tested for catalytic activity, along with catalysts with no pretreatment. For comparison, MoO_3 was also impregnated on the supports and the catalytic activities were tested after pretreatment with 10% H_2S/H_2 gas.

CHAPTER 2: Co-PROMOTED K$_2$CO$_3$/MoS$_2$/MMO

INTRODUCTION

Cobalt is one of the well-known promoters for K-MoS$_2$ catalysts for higher alcohol syntheses from syngas. It is known to be effective in obtaining high alcohol selectivities even at high conversions.[31] In this chapter, effects of Co promotion on sulfided K$_2$CO$_3$/MoO$_3$/MMO catalyst were investigated. Co promotion was done in two ways: by co-impregnating a Co precursor with a MoO$_3$ precursor on calcined MMO and by co-precipitating a Co precursor during hydrotalcite-based support synthesis. Catalysts were tested for alcohol syntheses from syngas and were characterized by multiple techniques.

EXPERIMENTAL

<u>Catalyst preparation</u>

Materials

Sodium carbonate (Na$_2$CO$_3$): Aldrich, granular, A.C.S. reagent, 99.5+%

Magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$6H$_2$O): Alfa-Aesar, 98.0-102.0%

Aluminum nitrate nonahydrate (Al(NO$_3$)$_3$9H$_2$O): Alfa-Aesar, 98.0-102.0%

Cobalt nitrate nonahydrate (Co(NO$_3$)$_3$9H$_2$O): Alfa-Aesar, 98.0-102.0%

Cobalt acetate (Co(OAc)$_2$): Sigma-Aldrich, A.C.S. reagent, 98+%

Sodium hydroxide (NaOH): EMD Chemicals

Dimethyl sulfoxide (DMSO): Alfa-Aesar, A.C.S., 99.9+%

Ammonium molybdate tetrahydrate (AMT): Sigma-Aldrich, A.C.S. reagent, 81.0-83.0% (MoO$_3$ basis)

Potassium carbonate (K$_2$CO$_3$):Aldrich, 99%

Methods

Mg-Al and Co-Mg-Al hydrotalcites were prepared by co-precipitation from aqueous solutions of suitable metal nitrates: magnesium nitrate hexahydrate ($Mg(NO_3)_2 6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 9H_2O$) and cobalt nitrate nonahydrate ($Co(NO_3)_3 9H_2O$). A 7 M solution of the mixed metal nitrates was added to a vigorously stirred 0.3M solution of Na_2CO_3. The pH was maintained constant at 9.5 by drop-wise addition of 1.2M NaOH solution, and the temperature was maintained constant at 65°C. Precipitates were kept in suspension at 65°C for 48 hours under vigorous stirring, followed by filtration, washing with distilled water and drying overnight at 100°C. Finally, prepared hydrotalcites were calcined at 450°C for 2 hours to make the MMO (Mg-Al mixed metal oxide) and MMO-Co (Co-Mg-Al mixed metal oxide) supports.

Cobalt for K/Mo-Co/MMO catalysts and Mo for all catalysts were added by the incipient wetness impregnation method. For K/Mo-Co/MMO catalysts, AMT and $Co(NO_3)_3 9H_2O$ were each dissolved in DMSO separately, and they were mixed after they were both well-dissolved. For K/Mo/MMO-Co catalysts, only AMT was dissolved in DMSO. The solution was slowly added with occasional stirring. After drying at 135°C overnight, it was treated at 200°C for 4 hours and then at 450°C for 2 hours under N_2 flow.

K_2CO_3 was added to the samples by grinding. The catalysts were then pelletized, crushed, and sieved to get fractions of particles 425-850µm and they were treated in-situ at 450°C for 2 hours under 20 ml/min of 10% H_2S/H_2 gas flow to create metal sulfides.

<u>Activity measurement</u>

The catalytic reaction was conducted under these conditions: feed gas composition $N_2/H_2/CO=1:5:5$ (vol%) and H_2S concentration of 50ppm, under the pressure of 1500psi at 310°C. These reaction conditions were chosen to maximize alcohol productivities with MoO_3-derived MoS_2 catalysts. The temperature of 310°C is the optimal reaction temperature for supported K/MoS_2 catalysts in terms of maximizing alcohol productivities.[49]

The reactions were done in a high-pressure flow reactor setup, as shown in Fig. 2.1. Inside the reactor, ca. 1g of catalyst was loaded on top of 2.5g of commercial 45 mesh SiC granules which were sieved to obtain particles of <450μm. From separate N_2, H_2, CO and $0.03\%H_2S/He$ gas tanks, gas mixture with the chosen syngas composition was collected in a 1.5L low pressure tank. The composition ratio was controlled by using mass flow controllers for N_2, H_2 and CO gases and a needle valve for H_2S/He gas. From the low pressure tank, using a high pressure booster using backpressure from the building compressor, the gas mixture was transferred to a 0.5L high pressure tank. The high pressure tank was kept at 1700-3100 psi to keep the pressure in the reactors at 1500 psi. The gas in the high pressure tank then flowed through two reactors. The flow rates through reactors were controlled by mass flow controllers on the upstream of the reactors, but the actual flow rates were measured manually using bubble meters downstream of the reactors. The flow rates recorded and used to calculate C_{2+} alcohol productivities were measured manually downstream of the reactors.

The products were analyzed by an on-line GC (Agilent Technologies 7890A GC System) equipped with a TCD and FID.
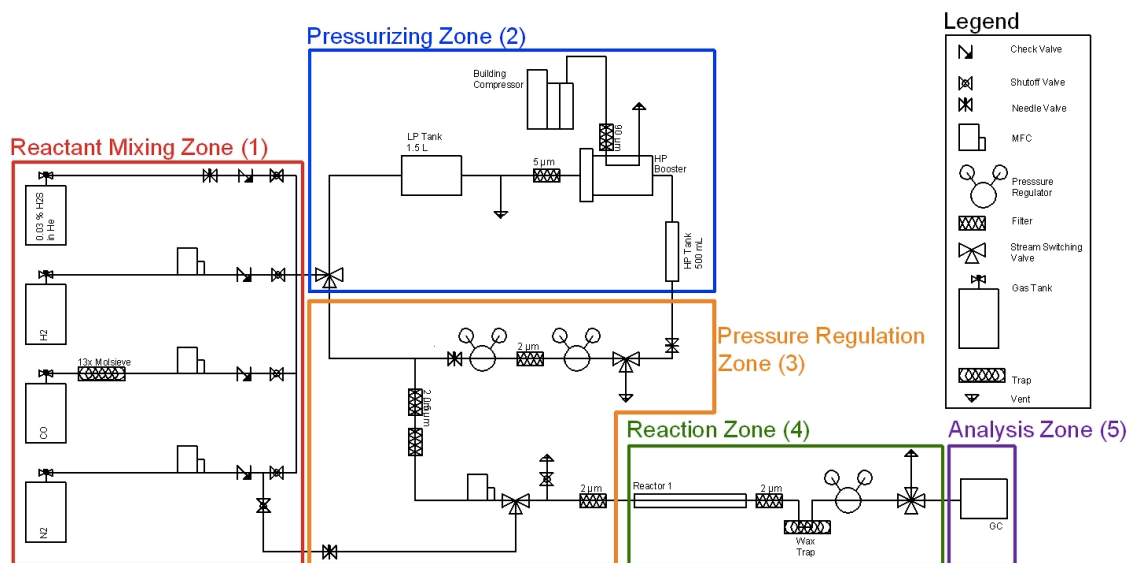
Fig. 2.1 Reactor setup (Drawn by Michael Morrill)

Characterization

X-ray diffraction (XRD)

Powder X-ray diffraction patterns of the samples were recorded using X-Pert PRO of PANalytical with Cu Kα radiation under the conditions of 40 kV and 40 mA.

Elemental analysis (EA)

Elemental analyses were done by a research coordinator at the Institute for Paper Science and Technology, using Inductively Coupled Plasma Optical Emission Spectroscopy on Perkin Elmer OPTIMA 7300 DV. For digestion, concentrated HNO_3 was mixed with the sample. It was heated to 95°C, followed by adding H_2O_2 and heating at 95°C for peroxide reaction. When effervescence subsided, concentrated HCl was added followed by heating at 95°C. The solution was filtered and was diluted with deionized water.

X-ray absorption fine structure (XAFS)

X-ray absorption spectroscopy (XAS) was carried out on beamline X-18B at the National

Synchrotron Light Source, Brookhaven National Laboratory by Michael Morrill. The data

were obtained in the transmission mode at the Mo K edge (20 keV).

RESULTS AND DISCUSSIONS

Co-impregnation methods of Mo and Co

At the first stage of the attempt to co-impregnate Co and Mo together, a problem arose

with premature precipitation, which presumably was cobalt molybdate. The precipitation

happened when $Co(NO_3)_39H_2O$ and AMT were added in DMSO and stirred to make a

solution. This was problematic because co-precipitation of cobalt molybdate before

impregnation would cause at least two major problems. One of the problems is that

cobalt-molybdenum domains would become much larger in the final catalyst, which

causes the catalytically active surface area to become too small. Additionally, the

molybdenum-support interactions would probably be different from the ones on cobalt-

free catalysts. Both of these issues would not only make it difficult to make appropriate

observations and comparisons of catalytic activities and characterization results between

Co-promoted and Co-free $K/MoS_2/MMO$ samples; they would also likely make the

catalytic activities lower than properly-made cobalt promoted MoS_2/MMO catalysts.

In order to avoid co-precipitation of $Co(NO_3)_39H_2O$ and AMT in DMSO solution, three

approaches were tried during co-impregnation. The first approach was to add aqueous

acetic acid solution to the Co and Mo solution. The second approach was to use

$Co(OAc)_2$ as cobalt precursor instead of $Co(NO_3)_39H_2O$, which produced less cobalt

molybdate. The third approach was to prepare DMSO solutions of $Co(NO_3)_3 9H_2O$ and AMT separately and not mix them until they were both dissolved in DMSO perfectly. With the third method, precipitation did not occur for the first several minutes after the mix, which was just long enough to perform impregnation on MMO supports

The first approach was investigated thoroughly. The required amounts of acetic acid solution of different concentrations for dissolving a specified amount of cobalt molybdate precipitant in DMSO are shown in Fig. 2.2. It shows that 20 wt% acetic acid solution works the best to minimize co-precipitation and water addition. It is desirable to minimize water because addition of water results in an unfavorable hydrotalcite memory effect. The hydrotalcite memory effect is an effect by water causing hydrotalcite domains to recrystallize from the MMO. It causes a non-homogeneous mixture of single metal oxide phases to form, instead of homogeneous mixed metal oxide phases.[16] It also affects the surface area to a great extent and interferes with proper dispersion of Mo and Co domains.
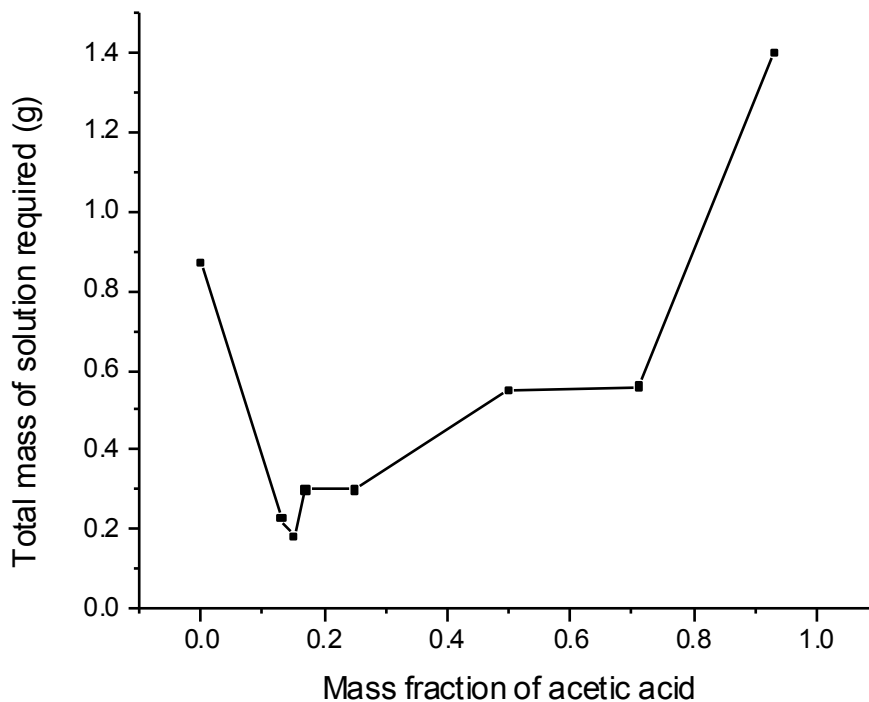
Fig. 2.2 Required amount of acetic acid solution for dissolving a specific amount of cobalt molybdate precipitant in DMSO with respect to concentrations of acetic acid

Although these trials allowed preparation of DMSO solution of $Co(NO_3)_39H_2O$ and AMT while minimizing premature precipitation before impregnation, it should be noted that some premature precipitation may have occurred before $Co(NO_3)_39H_2O$ and AMT have properly settled down on the MMO surface. For further investigation on Co-promoted $K/MoS_2/MMO$, in order to keep consistency and avoid MMO going back to hydrotalcite, the third approach was adopted.

The actual Co loadings on the K/Mo/MMO-Co catalyst prepared by co-precipitation method were verified by elemental analysis (EA), as shown in Fig. 2.3. The impregnation method does not have a washing step using solvents; thus any differences between intended and actual loadings can be attributed to non-uniform loading.
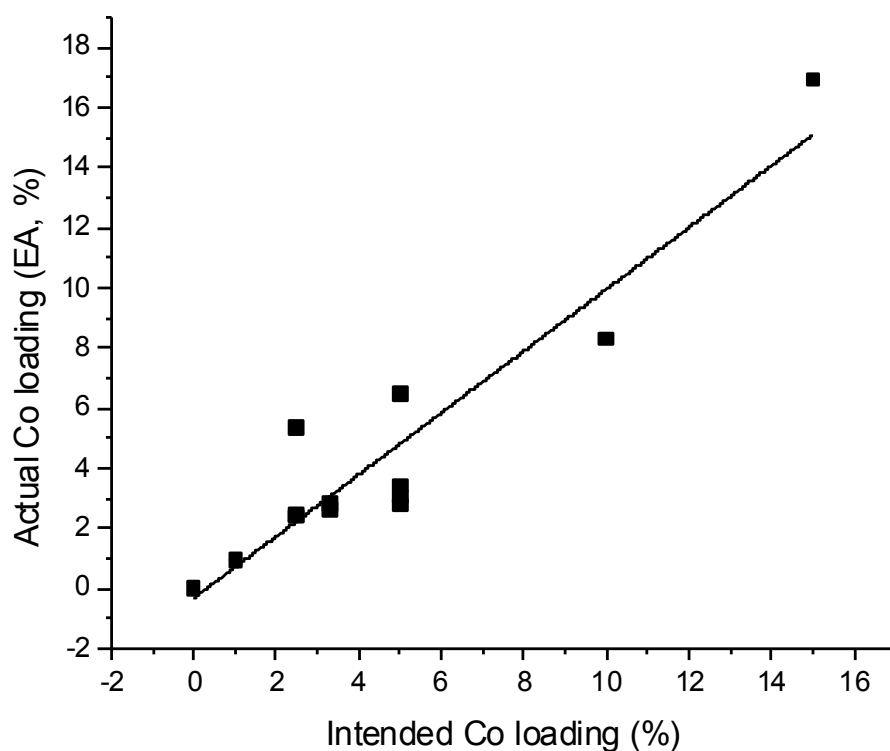
Fig. 2.3 Actual Co loadings of K/Mo/MMO-Co samples as determined by elemental analysis with respect to theoretical loading

The catalysts and control materials were characterized by X-ray diffraction. GT standard samples of CoMoS and Co_9S_8, prepared according to literature procedures,[34] appeared

amorphous based on XRD (Fig.2.4) so the composition may not be representative of a pure single phase.
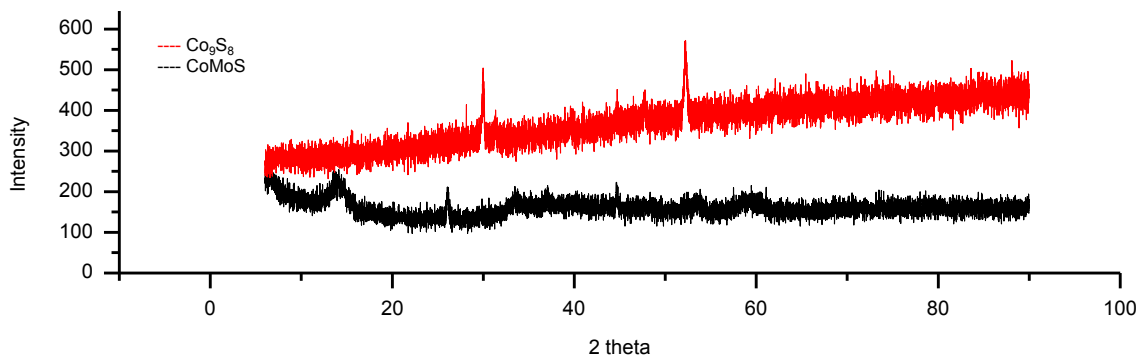
Fig. 2.4 XRD patterns of bulk Co$_9$S$_8$ and CoMoS.

K/Mo-Co/MMO catalysts and K/Mo/MMO-Co catalysts, along with standard samples, were characterized by using X-ray absorption near edge structure (XANES) to compare the oxidation states of Co with different Co loadings and different catalyst preparation methods. XANES data was also used to compare the changes in catalysts before and after sulfidation and reaction. Oxidation states are determined by the edge energies at the normalized absorbance of 0.3. Judging from XANES data shown in Fig. 2.5, 0.3 was chosen for determining Co oxidation states because edge energies of bulk Co standards with known oxidation states seem to be in a good correlation with known formal oxidation states. Previously, Davis and coworkers have correlated the electronic structure of Mo domains with Mo oxidation state using XANES.[50] Another noteworthy observation is the higher normalized absorbance intensities at the white line peaks (above an intensity of 1), present for the oxide samples. This feature can be used as being indicative of an oxide phase. The XAS results are shown in Fig. 2.5 – 2.8. Fig. 2.5 shows XANES data for various bulk cobalt compounds. In these results, sulfur-

20

containing samples showed edge energies between the Co-foil and the oxides. With these results, it is confirmed that Co sulfides have oxidation states of Co lower than Co oxides and higher than Co foil.

Fig. 2.6 shows XANES data for K/Mo-Co/MMO catalysts and K/Mo/MMO-Co catalysts with Co loading of 5% before and after presulfidation and reaction. In Fig. 2.6, it is observed that the edge energies at the normalized absorbance of 0.3 of catalysts after sulfidation and reaction are shifted lower compared to the catalysts before sulfidation and reaction. Also, the absorbance intensities at the white line peaks are lower after sulfidation and reaction. These data show that regardless of the methods of Co-promoted catalyst preparation, presulfidation and reaction reduce Co to some degree. This is not surprising since the reducing environment of the pretreatment gas and reacting syngas would result in a more reduced Co species. Co in the K/Mo-Co/MMO-Co catalyst seems to be more reduced or sulfided as compared to Co in K/Mo/MMO-Co materials, both before and after the sulfidation and reaction. From the preparation method of Co addition, for materials prepared by co-impregnation, Co is hypothesized to have stronger interactions with MoS_2 species than MMO supports. On the other hand, on K/Mo/MMO-Co catalysts prepared by co-precipitation, Co is hypothesized to be intercalated in the MMO structure, having stronger interactions with Mg and Al species in the support than MoS_2 domains. These differences explain differences in Co sulfidation observed in K/Mo-Co/MMO and K/Mo/MMO-Co. Also, both the edge energies at the normalized absorbance of 0.3 or the normalized absorbances at the white line peaks of catalysts after sulfidation and reaction did not go low enough to become completely the same as those of CoMoS or Co_9S_8 standards. These results suggest that although the oxidation states of both catalysts are lower than that of CoO after sulfidation and

reaction, both of them were not sulfided completely. This result implies that during reactions, there are mixtures of cobalt sulfide and cobalt oxide phases on the surface.

Fig. 2.7 shows XANES data of K/Mo-Co/MMO catalysts and K/Mo/MMO-Co catalysts with Co loadings of 2.5-10% before presulfidation and reaction. On as-prepared samples, both absorbance intensities at white lines and edge energies at the normalized absorbance of 0.3 were almost the same regardless of Co loadings and preparation methods. These data suggest that different Co loadings and different catalyst preparation methods do not affect the oxidation states. However, as shown in Fig. 2.8, the XANES data of the K/Mo-Co/MMO catalysts and K/Mo/MMO-Co catalysts with Co loadings of 2.5-10% after presulfidation and reaction show very different results. The data shows large differences in absorption at white lines and edge energies at the normalized absorbance of 0.3 between the K/Mo/MMO-Co catalysts and K/Mo-Co/MMO catalysts. These data suggest that different preparation methods of catalysts affect the oxidation states after sulfidation and reaction. The K/Mo/MMO-Co catalysts showed more oxide behavior, which suggest that the Co in K/Mo-Co/MMO becomes sulfided more easily than Co in K/Mo/MMO-Co.
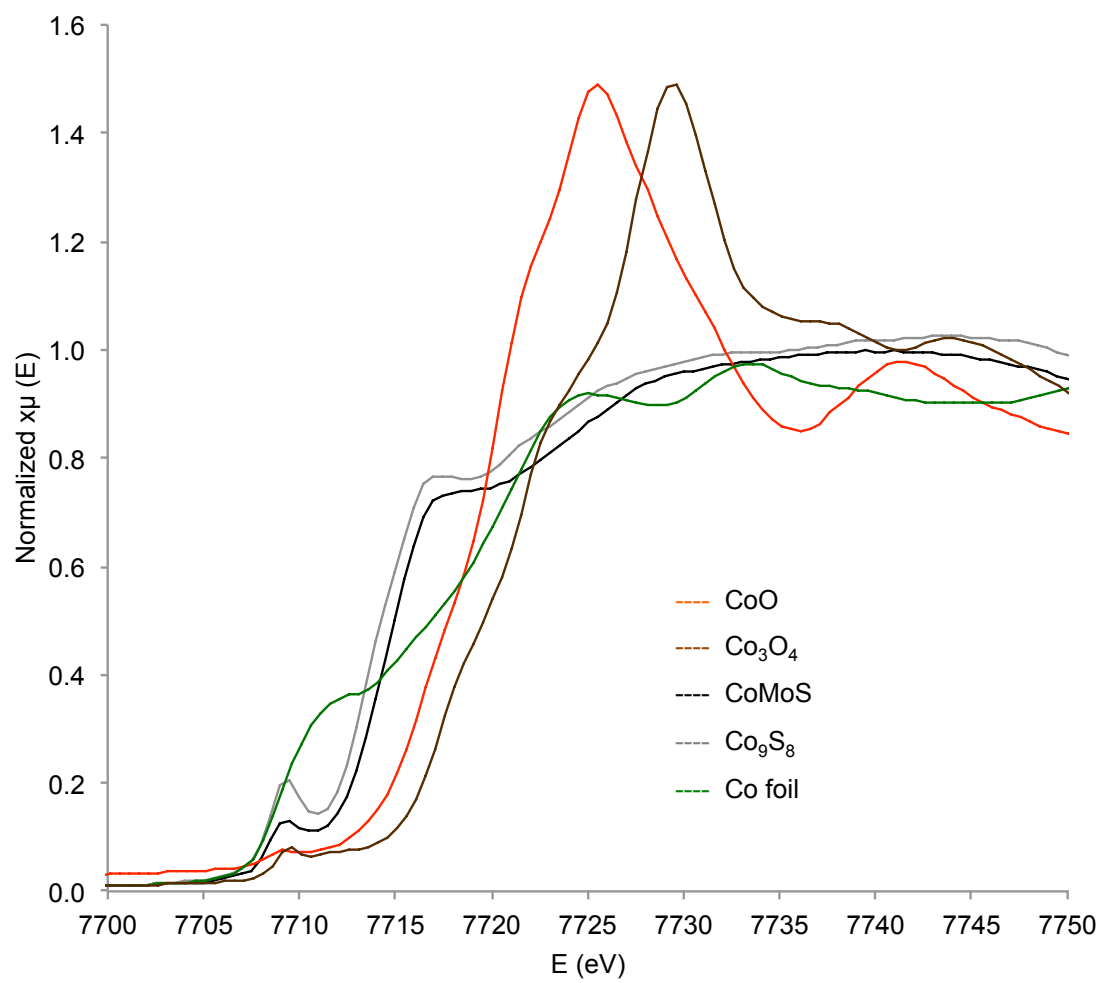
Fig. 2.5 XANES data of Co standards (Co K-edge)
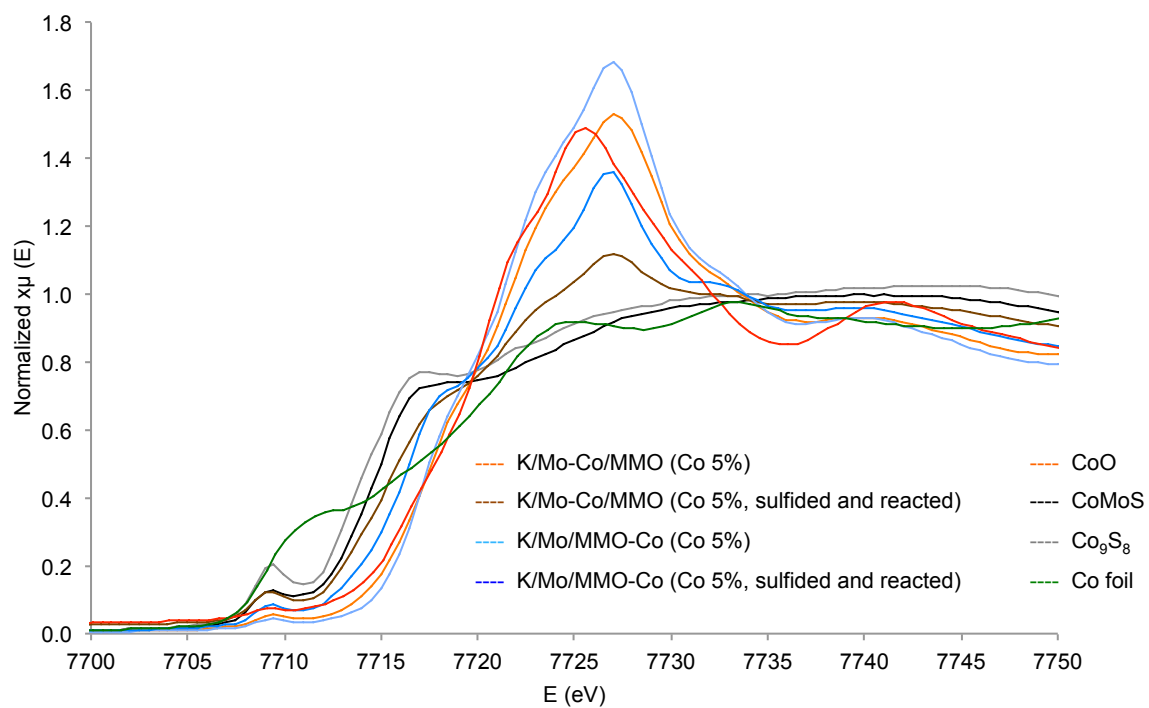
Fig. 2.6 XANES data of Co/MMO and MMO-Co samples; comparisons of sulfided and reacted samples and unreacted samples
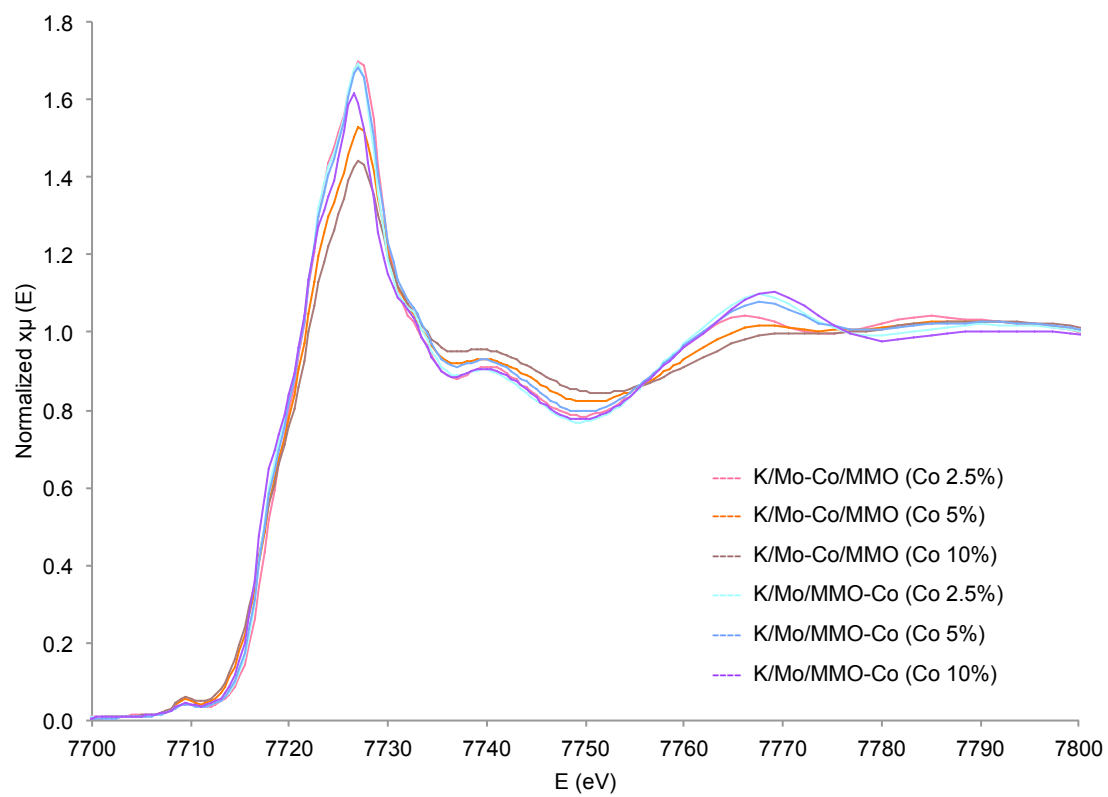
Fig. 2.7 XANES data of before sulfidation and reaction; comparison of Co/MMO samples and MMO-Co samples with different Co loadings
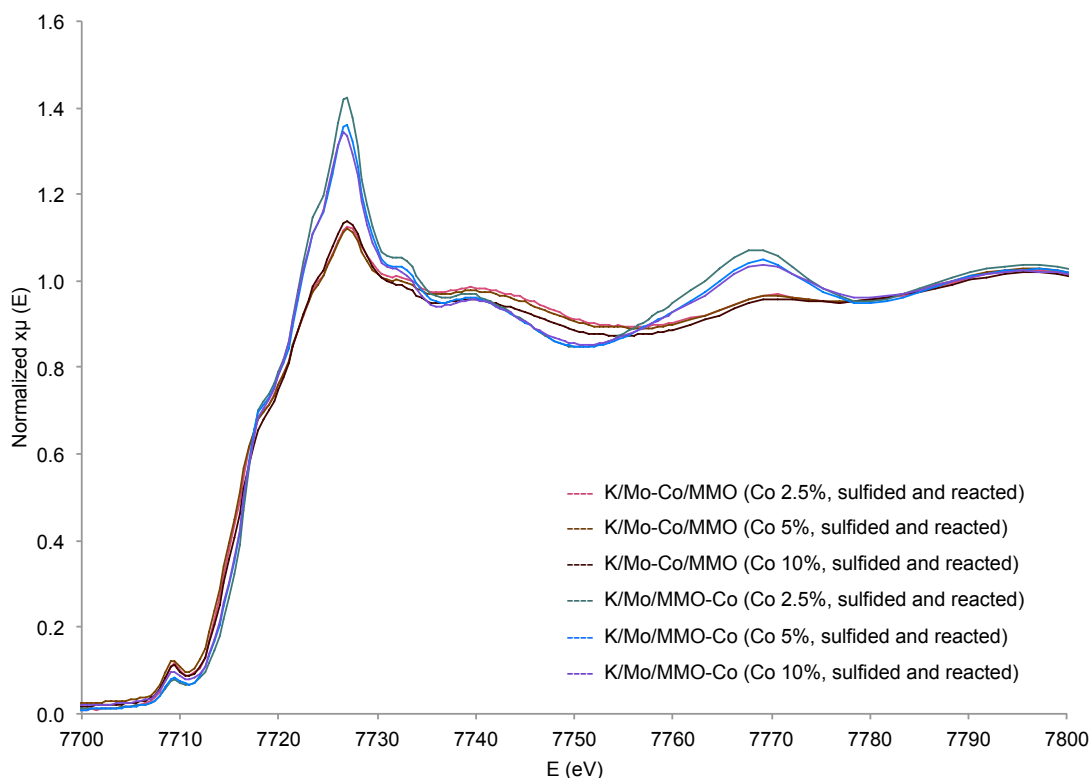
Fig. 2.8 XANES data of sulfided and reacted catalysts; comparison of Co/MMO samples and MMO-Co samples

Reaction results

The reaction results using catalysts prepared by the two synthetic methods are summarized in Table 2.1; the first approach involved using acetic acid whereas the second approach involved using different Co precursors, $Co(NO_3)_3 9H_2O$ and $Co(OAc)_2$. The results show that the use of pure water for impregnation makes the catalytic activity significantly lower as compared to catalysts in which impregnations were done by using DMSO as solvent. Similarly, use of acetic acid decreases catalytic activities on both catalyst precursors: $Co(NO_3)_3 9H_2O$ and $Co(OAc)_2$.

Table 2.1 Reaction results of K/Mo-Co/MMO (compositions: 7% Mo, 3% K) prepared by using different Co precursors (with and without use of acetic acid solution)

| | GHSV (ml/g/hr) | Organic Product Selectivity (Carbon % excluding CO_2) | | | | | | | | C_{2+}OH Prod. (g/g/hr) |
		Conv.	MeOH	EtOH	n-PrOH	C_4OH's	CH_4	Total OH	Total HC	
Co nitrate no acetic acid	1039	8.1	5.3	21.6	14.7	8.5	15	50.3	47.4	7.60E-03
Co nitrate 25% acetic acid (5.238g)	617	7.5	4.8	22.6	18.2	13.7	14.8	59.3	37.8	4.90E-03
Co acetate no acetic acid	859	8	4.8	26.8	21.5	12.8	11.9	66.1	31.5	8.50E-03
Co acetate 25% acetic acid (4.78g)	578	7.9	5	23.7	18.8	14.1	14.3	61.8	35.6	5.10E-03
Co nitrate Water as solvent	762	5.7	6.9	28	20.3	14.9	11.6	70.7	26	5.40E-03

The reduced catalytic activity when using water can be explained in two ways. It is known that when hydrotalcite-derived MMO is exposed to water, the layered structure of hydrotalcite recrystallizes, which is called the "hydrotalcite memory effect".[51] The hydrotalcite memory effect causes many changes in the structure of the final product of MMO, such as surface areas and homogeneity of metal oxide phases. The first reason for the reduced catalytic activity on catalysts in which water or aqueous solution of acetic acid was added is because of the possible decrease in surface area of the MMO during the impregnation procedure. Decreases in surface area generally occur due to the hydrotalcite memory effect, thus causing lower dispersion of Mo and Co domains. This would lower the number of accessible, catalytically active surface sites. Also, this decrease in MMO surface area is not recovered even after recalcination.[52] The second reason is that the recrystallization of hydrotalcite may cause segregation and make single metal oxide phases, instead of a uniform mixed metal oxide phase, after recalcination.[52] Consequently, recrystallization of hydrotalcite and recalcination could

yield non-homogeneous mixed metal oxides with low surface areas. It should be noted, however, that in some literature reports, it is claimed that by calcining the parent mixed metal oxide at higher temperatures, the hydrotalcite memory effect can be minimalized.[52,53] It also should be noted that the hydrotalcite memory effect induced by rehydration of the parent mixed metal oxide may result in an adverse effect in certain situations, yet in some other cases catalysts performance may be enhanced.[53] For example, Siffert et al. reports a study of Co impregnation using an aqueous solution of $Co(NO_3)_3 9H_2O$ on calcined hydrotalcite followed by another calcination. According to their report, this preparation method forms an active and selective catalyst for toluene oxidation composed of Co mixed oxide catalyst supported by calcined hydrotalcite. [53] Thus, whether the impregnation method using aqueous solution on calcined hydrotalcite produces a good catalyst depends on the desired catalytic properties and the specific chemical reaction.

Higher selectivities for higher alcohols were obtained by using $Co(OAc)_2$ as a precursor. When $Co(OAc)_2$ was used as precursor for Co, although premature cobalt molybdate precipitation was observed, the amount was much lower than when $Co(NO_3)_3 9H_2O$ was used as precursor. Similarly, when $Co(OAc)_2$ was used as a precursor with additional aqueous solution of acetic acid, because the amount of precipitation was less than that of $Co(NO_3)_3 9H_2O$, the required amount of aqueous solution of acetic acid was also less, causing the hydrotalcite memory effect to be minimalized.

As mentioned earlier, for further investigation on the effect of Co on K/Mo-Co/MMO catalysts, $Co(NO_3)_3 9H_2O$ was used as precursor, and no acetic acid solution was added. Instead, DMSO solutions of $Co(NO_3)_3 9H_2O$ and AMT were mixed only after both were thoroughly dissolved, and the mixed solution was impregnated on MMO quickly to

minimize the amount of premature precipitation of cobalt molybdate to the greatest extent possible.

The effect of varying Co content in the K/Mo-Co/MMO catalysts prepared by co-impregnation method without aqueous solution of acetic acid with $Co(NO_3)_3 9H_2O$ as a precursor did not produce significant changes in catalytic acitivities or selectivities as shown in Table 2.2.

Table 2.2 Reaction results of K/Mo-Co/MMO catalysts (compositions: 7% Mo, 3% K) prepared by co-precipitation method

| Co loadings (%) | GHSV (ml/g/hr) | Conv. | Organic Product Selectivity (Carbon % excluding CO2) | | | | | | | C2+OH Prod. (g/g/hr) |
			MeOH	EtOH	n-PrOH	C4OH's	CH4	Total OH	Total HC	
0	978	8.1	3.3	23.3	20.3	13.7	11.5	61.7	35.5	8.50E-03
0	976	8	4	24.3	18.7	11.8	13.1	59.5	37.7	8.50E-03
1	982	8	3.5	16.7	13	8.5	14.3	41.9	55.9	5.80E-03
2.5	819	7.9	4.4	21.5	17.2	10.8	14	54.1	43.8	6.30E-03
5	1039	8.1	5.3	21.6	14.7	8.5	15	50.3	47.4	7.60E-03
10	1175	7.9	5.8	20.8	13.2	6.8	15.4	46.8	50.7	7.90E-03

This was a surprising set of results, as it was different from what has been reported in the literature.[41,43,44,54] Authors report that Co-promoted catalysts (on various supports) result in an increase of C_{2+} alcohols. Klier *et al.* [41] and Christensen *et al.*[55] claim that the increased selectivities for C_{2+} alcohols on Co-promoted catalysts are because of the promotion of coupling reactions involving methanol. However, in this study, as shown in Table 2.2, Co promotion did not change selectivities for methanol, ethanol nor C_{2+} alcohols. This may be explained by premature precipitation of cobalt molybdate, and it suggests that by using this method of cobalt addition, cobalt promotion cannot make

appropriate contributions to catalytic activities or selectivities of MoS_2 catalysts.

Generally water is used as solvent during impregnation of metal precursors on catalyst supports.[1,2] With water as the solvent, premature cobalt molybdate would not precipitate, so there would be less possibility of aggregation of cobalt molybdate before or after impregnation. However using water as a solvent was not a viable option in this study because of the hydrotalcite memory effect. The results from Table 2.2 suggest that the promotional effects of MMO, similar to promotional effects of alkali, such as low MeOH selectivities,[21] are not affected by the use of water. However, these results suggest that the kinds of solvents to be used are limited on MMO supports in order to have additional metals perform their promotional effects properly. Another reason for Co not being effective in changing catalytic activities and selectivities is the optimal reaction temperature. Some scientists have reported that the optimal reaction temperature for Co-promoted catalysts is about 40°C higher than that for Co-free catalysts.[49,54] One of them even reports that at the optimal reaction temperature for Co-free catalysts, which is 310°C, Co-promoted catalysts show lower alcohol productivities compared to Co-free catalysts, although at the optimal reaction temperature for Co-promoted catalysts, which is 350°C, the alcohol productivities obtained by the Co-promoted catalyst are higher than that of the Co-free catalyst obtained at 350°C and 310°C.[49] If this is the reason for not obtaining higher alcohol selectivities and productivities by the use of Co promotion in this study, it is possible that the order of catalytic activities and selectivities inverts by increasing the reaction temperatures by 40°C. In this study, more emphasis was on comparing catalytic activities at the fixed reaction conditions with the temperature of 310°C, in order to make appropriate comparisons in catalytic activities and selectivities.

Another approach for Co promotion involved co-precipitation of $Co(NO_3)_3 9H_2O$ with $Mg(NO_3)_2 6H_2O$ and $Al(NO_3)_3 9H_2O$. Reaction results using K/Mo/MMO-Co catalysts

prepared by the hydrotalcite co-precipitation method are shown in Table 2.3 and Fig. 2.9. Co promotion in this way was not expected to contribute to the catalytic activities or selectivities as much as K/Mo-Co/MMO catalysts, since the amounts of Co available for cobalt-molybdenum sulfide domains would be less than that on K/Mo-Co/MMO catalysts. As expected, Co loadings on K/Mo/MMO-Co catalysts did not change selectivities significantly. However, they changed catalytic activities, represented by GHSV required to obtain 8% conversion, while maintaining higher alcohol selectivities greater than 40% in most cases. As a result, C_{2+} alcohol productivities reached $0.01 g_{alcohol}/g_{catalyst}/hr$ with Co loadings higher than 8%.
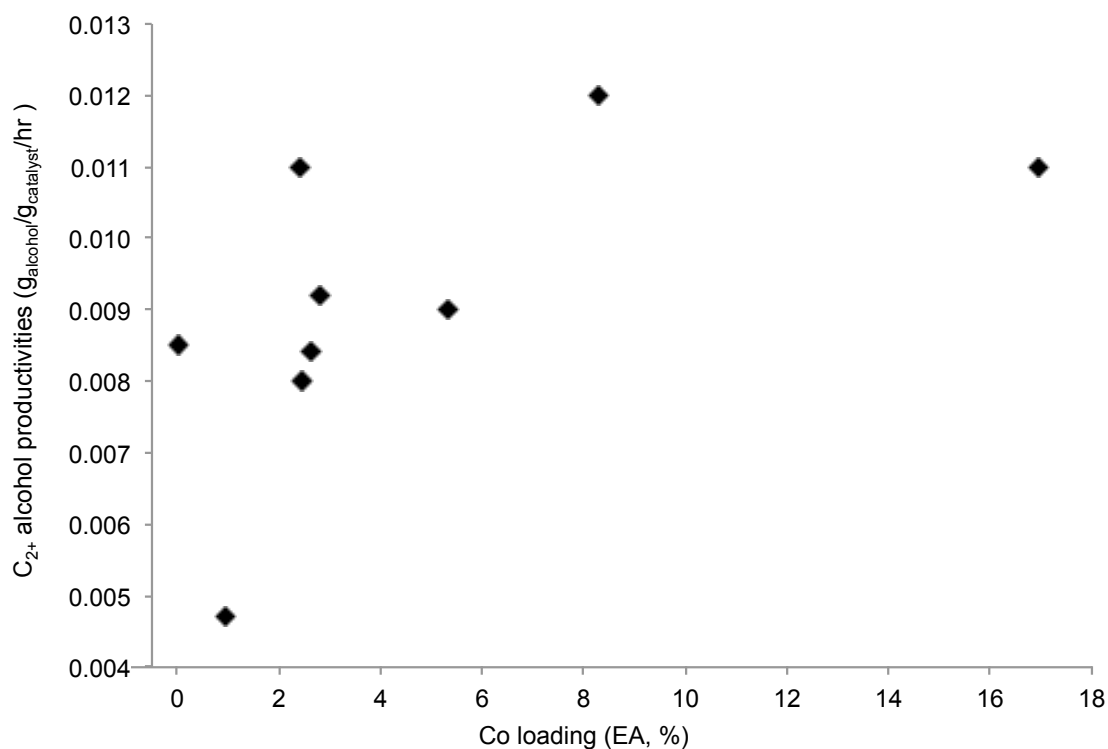
Fig. 2.9 C_{2+} alcohol productivities ($g_{alcohol}/g_{catalyst}/hr$) with respect to Co loading (%) using K/Mo/MMO-Co catalysts (compositions: 7% Mo, 3% K)

Mixed metal oxide catalysts derived from Co-Mg-Al hydrotalcites for synthesis of alcohols from syngas have not yet been reported. However, there are a few reports on catalytic activities for other reactions and adsorption/desorption studies on Co-Mg-Al hydrotalcite derived mixed metal oxides.[17,56–58] In these reports, all samples were prepared in a manner similar to the preparation method used in this study, which is the co-precipitation method using metal nitrates, Na_2CO_3 and NaOH, followed by calcination. In these literature studies, MMO-Co catalysts are referred to as being catalytically active for both reduction and oxidation reactions.[17,56–58]

Table 2.3 Reaction results of K/Mo/MMO-Co catalysts (compositions: 7% Mo, 3% K) prepared by co-impregnation method without aqueous solution of acetic acid with $Co(NO_3)_39H_2O$ as a precursor

| Co loadings(%) | GHSV (ml/g/hr) | Conv. | Organic Product Selectivity (Carbon % excluding CO2) | | | | | | | Total HC | $C_{2+}OH$ Prod. (g/g/hr) |
			MeOH	EtOH	n-PrOH	C4OH's	CH_4	Total OH	Total C_{2+} OH		
0	978	8.1	3.3	23.3	20.3	13.7	11.5	61.7	58.4	35.5	8.50E-03
0	976	8	4	24.3	18.7	11.8	13.1	59.5	55.5	37.7	8.50E-03
1	829	8	3.3	16.3	12.5	7.9	14.1	40.2	36.9	57.7	4.70E-03
1	1165	8	4	17.1	8.4	4.1	17.9	33.8	29.8	64.2	5.60E-03
2.5	1292	8	5.4	25.4	17	9.1	13.1	57	51.6	40.4	1.10E-02
2.5	1170	8	3.8	19.8	15.1	9	13.3	47.9	44.1	49.7	8.00E-03
2.5	1304	8	5.7	21.8	12	6.1	19.2	45.7	40	51.9	8.60E-03
3.3	1056	8.1	5.2	25.5	18.1	10.2	14.1	59.3	54.1	38.3	9.20E-03
3.3	1131	8	5.4	23.7	14.5	7.4	15.2	51.2	45.8	46.5	8.40E-03
5	1451	8	4.6	25.3	19.4	11.8	10.8	61.1	56.5	36.2	1.30E-02
10	1515	8	5.4	24	15.8	8.2	14.1	53.5	48.1	44.3	1.20E-02
15	1693	8	6.3	21.2	11.7	5.2	17	44.4	38.1	53.4	1.10E-02

The data shown in Table 2.3, in which K/Mo/MMO-Co catalysts obtained high alcohol productivities at higher Co loadings than 8%, are consistent with the literature.[17,56,58] However, it is not clear why the catalytic activities fell at the Co loading of 1%.

As shown in the XANES data of the K/Mo-Co/MMO catalysts and K/Mo/MMO-Co catalysts after presulfidation and reaction, very different amplitudes of absorption at white lines were obtained between K/Mo/MMO-Co catalysts and K/Mo-Co/MMO catalysts. (Fig. 2.8) It was suggested by the data shown in Fig. 2.8 that different preparation methods of catalysts affect the oxidation states during and after sulfidation and reaction, and thus may lead to different catalytic behaviors. This suggests that the Co in K/Mo-Co/MMO becomes sulfided more easily than Co in K/Mo/MMO-Co.

CONCLUSIONS

The effect of varying Co content in the K/Mo-Co/MMO catalysts prepared by the co-impregnation method without aqueous acetic acid solutions using $Co(NO_3)_39H_2O$ as a precursor did not produce significant changes in catalytic activities or selectivities. The lack of effect on catalytic activities and selectivities may be explained in two ways. First is the premature precipitation of cobalt molybdate. The precipitation ocurred when $Co(NO_3)_39H_2O$ and AMT were added in DMSO and stirred to make a solution. Thus, in order to prevent premature precipitation, impregnation steps for K/Mo-Co/MMO catalysts were done by dissolving $Co(NO_3)_39H_2O$ and AMT in DMSO separately and not mixing these solutions until just before impregnation. However, time for precipitation to occur was so short that it is possible that precipitation occurred before Co and Mo species developed physical/chemical interactions with the support. Cobalt molybdate precipitation is generally prevented by using water as solvent,[1,2] but that is not

appropriate for this study because hydrotalcite-derived mixed metal oxide was used as support. The second possibility is the optimal reaction temperature for Co-promoted catalysts was not used, which has been reported previously to be higher than the optimal reaction temperature for Co-free catalysts.[49] Further study on Co-promoted catalysts at higher temperatures is warranted. However in this study, more emphasis was on comparing catalytic activities at the fixed reaction condition at 310°C, in order to make appropriate comparisons in catalytic activities and selectivities.

On the other hand, although Co loadings on K/Mo/MMO-Co catalysts did not change selectivities significantly, they changed catalytic activities, while maintaining higher alcohol selectivities higher than 40% in most cases. Catalytic activities are represented by the GHSV required to obtain 8% conversion. As a result, C_{2+} alcohol productivities reached $0.01g_{alcohol}/g_{catalyst}/hr$ with Co loadings higher than 8%.

CHAPTER 3: Mo₂C AS A PRECURSOR FOR K₂CO₃/MoS₂ CATALYSTS SUPPORTED BY METAL OXIDES

INTRODUCTION

In this part of the study, Mo_2C was investigated as the precursor for supported MoS_2-based catalysts. Mo_2C samples were prepared on two different supports by collaborators at the University of Virginia. Using MgO and α-Al_2O_3 as supports, Mo_2C catalysts were investigated as precursors and catalysts for higher alcohol syntheses from syngas. The catalysts were pretreated with i) 10% H_2S/H_2 gas, ii) H_2 gas. Both pretreated catalysts were tested for catalytic activities, along with carbide-derived catalysts with no pretreatments. For comparison, MoO_3 was also impregnated on the supports and the catalytic activities were tested after pretreatment with 10% H_2S/H_2 gas. These samples were also characterized by using XRD, XAFS and elemental analyses.

EXPERIMENTAL

<u>Catalyst preparation</u>

Materials

α-Al_2O_3: Mager Scientific AP332 (100nm, $S_{BET} = 26m^2g^{-1}$)

MgO: UBE 500A ultrafine single crystal (>99.98%, 50nm, $S_{BET} = 35.7m^2g^{-1}$)

Ammonium molybdate tetrahydrate (AMT): Aldrich (99.98%)

Potassium carbonate (K_2CO_3): Aldrich, 99%

Methods

Supported Mo_2C Catalyst preparations were carried out by researchers at the University of Virginia as described previously.[50] A 6.7 wt% Mo_2C/MgO was prepared by carburization of MoO_3/MgO under 20 vol% CH_4/H_2 gas flow. AMT was first dissolved in water, and MoO_3 was loaded on to the supports by using incipient wetness method. The catalyst was dried overnight in air at 127°C and calcined at 500°C for 4 hours under air flow. Carburization was done by using temperature-programmed reaction (TPR) at temperatures between 400-700°C under 20 vol% CH_4/H_2 gas. The temperature was maintained at 700°C for 5 hours, followed by another 10 hours at 500°C. Then the temperature was quenched to room temperature under H_2 flow, followed by passivation in a stream of 1 vol% O_2/N_2 gas flow at room temperature for 12 hours before exposure to air.

Supported MoO_3 catalysts were prepared using the procedures outlined in Chapter 2. Mg-Al hydrotalcites were prepared by co-precipitation from aqueous solutions of suitable metal nitrates: $Mg(NO_3)_26H_2O$ and $Al(NO_3)_39H_2O$. A 7 M Solution of the mixed metal nitrates was added to a vigorously stirred 0.3M solution of Na_2CO_3. The pH was maintained constant at 9.5 by drop-wise addition of 1.2M NaOH solution, and the temperature was maintained constant at 65°C. Precipitates were kept in suspension at 65°C for 48 hours under vigorous stirring, followed by filtration, washing with distilled water and drying overnight at 100°C. Finally, the prepared hydrotalcites were calcined at 450°C for 2 hours to make MMO (Mg-Al mixed metal oxide).

Mo was added to the support by the incipient wetness impregnation method. First, AMT was dissolved in DMSO. The solution was slowly added to the MMO with occasional

stirring. After drying at 135°C overnight, it was treated at 200°C for 4 hours and then at 450°C for 2 hours under N_2 flow.

K_2CO_3 was added to the above catalyst by grinding. The catalysts were pelletized, crushed, and sieved to get fractions of particles 425-850 μm, and treated in-situ at 450°C for 2 hours under 20 ml/min of 10% H_2S/H_2 or H_2 gas flow.

Activity measurement

Catalyst activity measurements were carried out using the procedures outlined in Chapter 2. The reactor setup is shown in Fig. 2.1.

Characterization

XRD, XAFS and elemental analysis (EA) were carried out using the procedures outlined in Chapter 2.

RESULTS AND DISCUSSIONS

Characterization results

XRD data on $K/Mo_2C/\alpha-Al_2O_3$ are shown in Fig. 3.1. MoS_2 peaks were observed only after presulfidation and reaction, and no crystalline MoS_2 was observed when the catalyst was reacted without pretreatment.
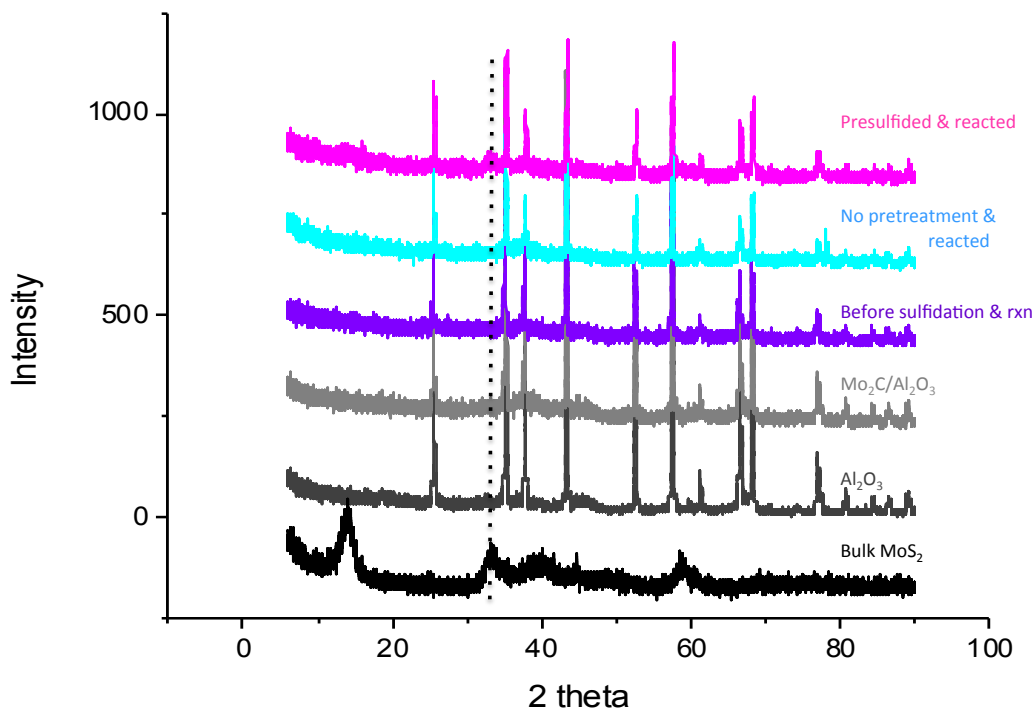
Fig. 3.1 XRD data of α-Al$_2$O$_3$ supported samples

These results agree with what has been reported previously by Oyama *et al.*, that Mo$_2$C is tolerant of sulfur.[59,60] In their studies on Mo$_2$C catalysts for hydroprocessing, XPS analyses on catalysts after reactions did not show indication of surface sulfidation, although the reactions were done at high temperatures (360°C and 370°C) and high pressures (2000 psi and 450 psi) with high contents of sulfur species (116 ppm, 810 ppm and 3000 ppm) compared to the work done here.[59,60] Thus, under the conditions used here, it is unlikely that MoS$_2$ domains would form on non-pretreated catalysts

The result shown in Fig. 3.1 suggests that Mo$_2$C catalyst does not get sulfided during syngas reaction with 50 ppm of H$_2$S at 310°C; this explains why the catalytic activities and selectivities did not change much with time during the first 7 days of reaction. Thus,

the reaction data presented below can be attributed to a Mo_2C-based catalyst, with perhaps some surface sulfidation.

XRD data on $K/Mo_2C/MgO$ are shown in Fig. 3.2. Similar to $K/Mo_2C/\alpha-Al_2O_3$, on $K/Mo_2C/MgO$, molybdenum sulfide peaks were not observed on presulfided catalysts and on catalysts pretreated under H_2 flow. However, after 5-6 days of reactions, both H_2S/H_2 pretreated $K/Mo_2C/\alpha-Al_2O_3$ catalyst and H_2 pretreated $K/Mo_2C/\alpha-Al_2O_3$ catalyst showed XRD peaks at $2\theta =54°$ and $33°$, which suggests the existence of $Mo_{21}S_8$.[61] It should be noted that this sulfide crystalline phase has not been observed in any work completed at GT on supported MoS_2 catalysts derived from MoO_3 as a precursor, and this result suggests that use of Mo_2C as a precursor may result in formation of different crystalline domains compared to the standard synthesis approach.
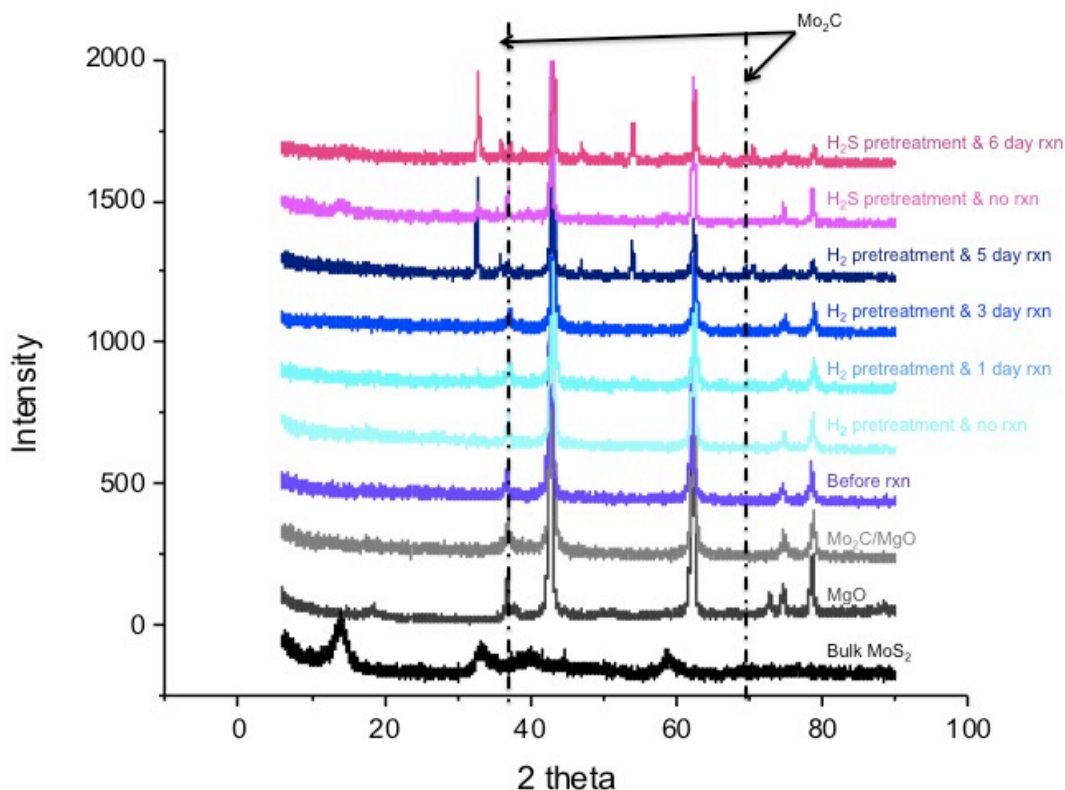
Fig. 3.2 XRD data of MgO supported samples

The reason why H_2 pretreated $K/Mo_2C/MgO$ catalyst was sulfided during syngas

reaction, although $K/Mo_2C/\alpha$-Al_2O_3 catalyst without presulfidation did not, is presumably

because the Mo species in H_2 pretreated $K/Mo_2C/MgO$ catalyst were reduced

significantly, perhaps all the way to metallic Mo, before the reactions began. Oyama et

al., who claim that Mo_2C is tolerant to sulfur, also ran reactions without pretreatment.[60]

This assumption may be supported by using XANES data from $K/Mo_2C/MgO$, shown in

Figures 3.3 and 3.4. In Fig. 3.3, Mo oxidation states are assessed by the edge energies

at the normalized absorbance of 0.5.[50] Judging from XANES data on Fig. 3.3, 0.5 was

chosen for determining Mo oxidation states because edge energies of bulk Mo

standards with known oxidation states seem to be in a good correlation with oxidation

states, as shown in Fig. 3.4. In order to calculate oxidation states shown in Fig. 3.4,

edge energies of bulk Mo standards and their oxidation states were correlated by a

linear regression. Oxidation states of other samples were extrapolated from the

regression based on their edge energies at the normalized absorbance of 0.5.[50]

Fig. 3.4 shows correlations of edge energies at the normalized absorbance of 0.5 of the

samples with the oxidation states along with those of Mo standards. In these figures, H_2-

pretreated catalysts are observed to be more oxidized than presulfided catalysts. The

only way Mo samples could have been oxidized in this way is by the exposure to the air

after reduction into a highly reactive form. Related work by our collaborators, Davis et

al. at the University of Virginia, has shown that simply exposing passivated Mo_2C to air

does not result in such a significant oxidation of the molybdenum. The data also show

that Mo in the H_2-pretreated samples was changed very little with time on stream with

exposure to syngas containing 50ppm of H_2S, suggesting that the sulfidation occurred at

the very early stage of reactions, with molybdenum sulfide domains large enough to

appear in the XRD patterns.
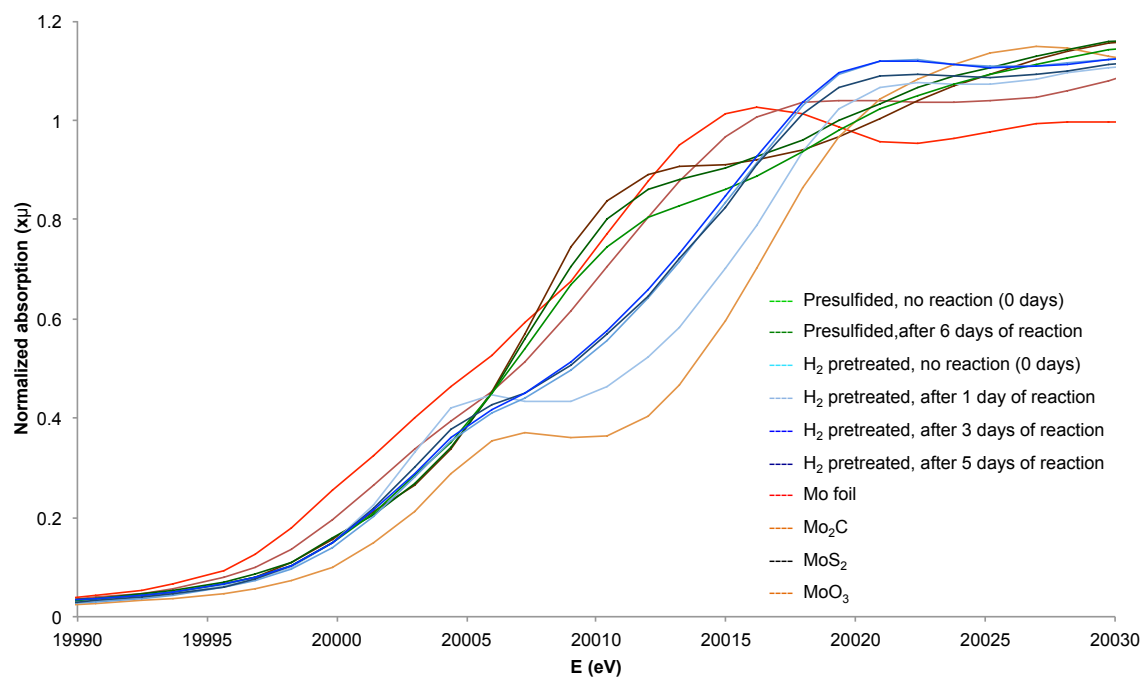
Fig. 3.3 XANES data of Mo$_2$C/MgO derived samples
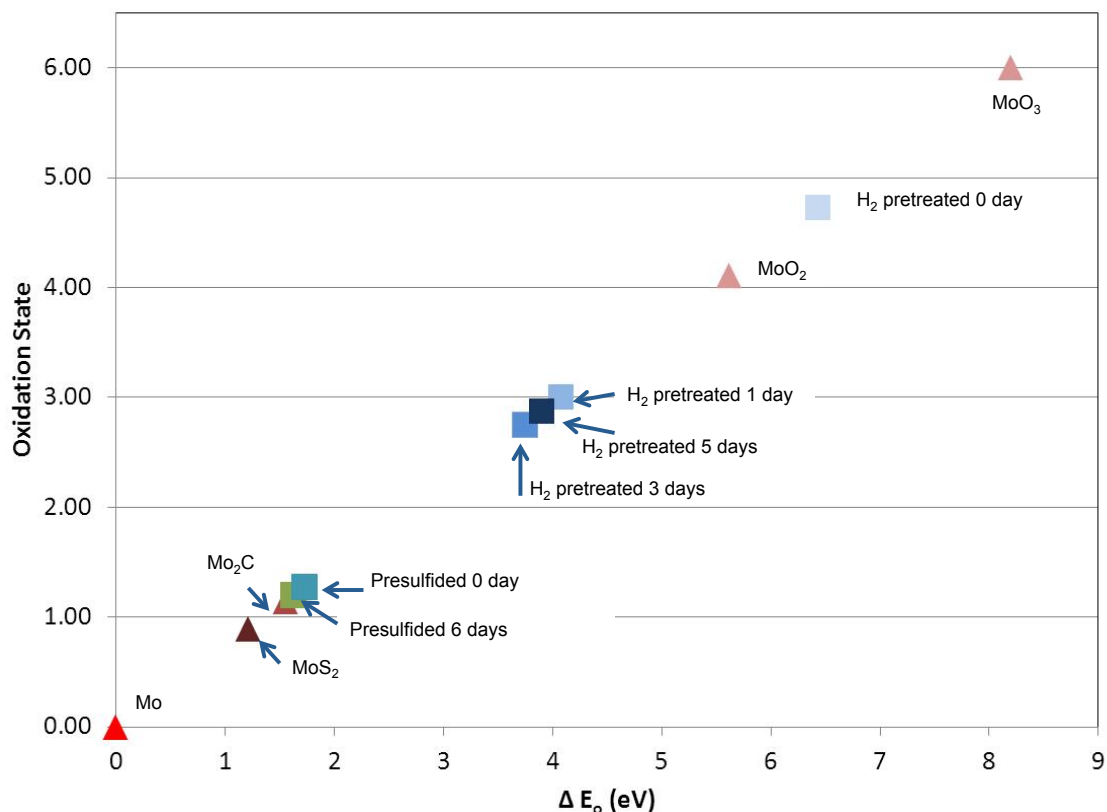
Fig. 3.4 Oxidation states of pretreated Mo$_2$C/MgO samples with respect to edge energy shift

<u>Reaction results</u>

Reaction results on K/Mo$_2$C/α-Al$_2$O$_3$ catalysts are shown in Table 3.1. Reactions were

done on K/Mo$_2$C/α-Al$_2$O$_3$ catalysts with H$_2$S/H$_2$ pretreatment and with no pretreatment.

Also, a reaction was run with the presulfided K/MoO$_3$/α-Al$_2$O$_3$ catalyst for comparison. In

the case of the catalyst without pretreatment, the catalyst was heated to 310°C in

syngas flow directly from room temperature and pressurized to start the reaction,

whereas in the case of catalysts with H$_2$S/H$_2$ pretreatment, the catalyst was first heated

to 450°C in H$_2$S/H$_2$ gas flow and kept at that temperature for 2 hours while being treated

with H_2S/H_2 gas flow, before being cooled down to 310°C and pressurized to start the reaction. It was expected that this set of experiments would allow a comparison of catalytic activities of Mo_2C, Mo_2C-derived MoS_2 and MoO_3-derived MoS_2.

Table 3.1 Reaction results of K/Mo$_2$C/α-Al$_2$O$_3$ (compositions: 7% Mo, 3% K), comparison of with and without presulfidation

Reaction ID #	Precursor/ Pretreatment	GHSV (ml/g/hr)	Conv. (% from prod.)	MeOH	EtOH	CH$_4$	C$_2$H$_6$	Total C$_{2+}$ OH	Total HC	C$_{2+}$OH Prod. (g/g/hr)	time (day)
							Organic Product Selectivity (Carbon % excluding CO$_2$)				
1	MoO$_3$ H$_2$S/H$_2$ (450°C, 2hrs)	1291	7.9	28.1	40.5	8.7	0.8	59.0	9.8	1.6E-2	2.8
1	MoO$_3$ H$_2$S/H$_2$ (450°C, 2hrs)	1098	7.7	26.8	40.9	10.5	0.7	57.9	11.9	1.3E-2	7.5
1	MoO$_3$ H$_2$S/H$_2$ (450°C, 2hrs)	1002	8.1	26.2	40.6	11.0	1.0	57.5	12.7	1.3E-2	9.3
1	MoO$_3$ H$_2$S/H$_2$ (450°C, 2hrs)	3942	3.2	39.8	37.5	3.7	0.3	53.4	4.6	2.0E-2	5.2
2	Mo$_2$C H$_2$S/H$_2$ (450°C, 2hrs)	951	7.8	27.3	39.0	14.6	0.6	52.1	16.0	1.0E-2	2.5
2	Mo$_2$C H$_2$S/H$_2$ (450°C, 2hrs)	645	7.6	17.4	40.5	15.7	1.7	59.3	19.0	7.1E-3	6.9
2	Mo$_2$C H$_2$S/H$_2$ (450°C, 2hrs)	2706	3.0	35.2	37.4	9.7	0.2	50.7	10.6	1.1E-2	3.9
3	Mo$_2$C No pretreatment	1241	7.7	38.7	19.5	23.7	0.8	26.8	27.6	6.8E-3	4.6
3	Mo$_2$C No pretreatment	1025	7.7	34.2	20.7	24.0	1.6	28.6	29.7	6.0E-3	16.7
3	Mo$_2$C No pretreatment	5030	3.2	62.9	12.2	13.3	0.7	16.0	17.1	8.1E-3	5.9

Mo_2C catalysts have not been investigated as catalysts for syngas conversion to synthesize alcohols as much as MoS_2 catalysts. In studies on Mo_2C catalysts for alcohol syntheses from syngas, it has been reported previously that selectivities for C_{2+} alcohols are higher for Mo_2C catalysts compared to MoS_2 catalysts, when both catalysts are

promoted with alkali.[46] In another report on Mo_2C by Rodriguez et $al.,$[62] the differences between Mo_2C and MoS_2 in chemical reactivities were attributed to differences in electronic properties of Mo in the domains.[62] It is also reported by Bussel et $al.$ that Mo_2C has a strong resistance to deep sulfidation.[63] This also suggests the possibility of obtaining a catalyst with mixed phases of sulfide and carbide. Since MoS_2 is supposed to be responsible for H_2 activation,[40] it was a reasonable expectation that a catalyst with mixture of Mo_2C and MoS_2 would yield good higher alcohol productivities.

As shown in Table 3.1, in this study, the presulfided $K/Mo_2C/\alpha-Al_2O_3$ catalyst had increased selectivities for higher total C_{2+} alcohols compared to the $K/Mo_2C/\alpha-Al_2O_3$ catalyst without pretreatment. In addition, the presulfided $K/MoO_3/\alpha-Al_2O_3$ catalyst produced the highest C_{2+} alcohol selectivities and thus the highest C_{2+} alcohol productivities. This result is in contrast to the study by Lee et $al.$[46] They reported that K_2CO_3-promoted Mo_2C catalysts produced higher selectivities for C_{2+} alcohols.[46] The reason for this discrepancy is not quite clear. One possible reason is the loading of K_2CO_3. Lee et $al.$ claim that the optimal K_2CO_3 loading for Mo_2C is >12% in their reports on studies on unsupported Mo_2C and MoS_2 catalysts. In their report, the comparisons of reaction results between Mo_2C and MoS_2 catalysts were done in the range of >12% loading of K_2CO_3, and the reaction results on MoS_2 catalysts with K_2CO_3 loadings of <12% were not given. The total C_{2+} alcohol selectivity for Mo_2C catalyst without alkali promotion is 1.3%, which is quite low; whereas the same catalyst with 12% loading of K_2CO_3 results in a total C_{2+} alcohol selectivity of 29%.[46] In the present study, the loading of K_2CO_3 is 5%. This suggests that MoS_2 catalysts are predominant in producing alcohols compared to Mo_2C catalysts at low loadings of K_2CO_3, but the trend may be reversed as the K_2CO_3 loadings increase, based on literature reports.[46] As shown in Table 3.1, non-pretreated $K/Mo_2C/\alpha-Al_2O_3$ catalyst produced significantly higher MeOH

selectivities compared to the presulfided $K/Mo_2C/\alpha-Al_2O_3$ catalyst. Since it was

previously reported by Xiang et al. that K_2CO_3 is responsible for promotion of the chain

growth,[38] it is possible that with higher loadings of K_2CO_3, methanol produced on non-

pretreated $K/Mo_2C/\alpha-Al_2O_3$ catalyst could be converted more efficiently into higher

alcohols.

Both presulfided and non-pretreated $K/Mo_2C/\alpha-Al_2O_3$ catalysts produced higher

selectivities for total C_{2+} alcohol and hydrocarbons, and lower selectivities for methanol

at higher conversions. Also, both presulfided and non-pretreated $K/Mo_2C/\alpha-Al_2O_3$

catalysts changed very little in selectivities, except for methanol, after several days of

reaction at 8% conversion (Fig. 3.5). In Fig. 3.5, changes in selectivities for major

products with respect to conversion on the presulfided $K/Mo_2C/\alpha-Al_2O_3$ catalyst are

shown. Between 2.5 days and 6.9 days after the start of the reaction, MeOH showed the

largest change at similar conversions of around 8%. With 10% drop of MeOH

selectivities, increases of 7% of total C_{2+} alcohol selectivities and 3% of total

hydrocarbon selectivities were observed. These results imply that C_{2+} alcohols and HCs

are produced from secondary reactions of MeOH.[35]
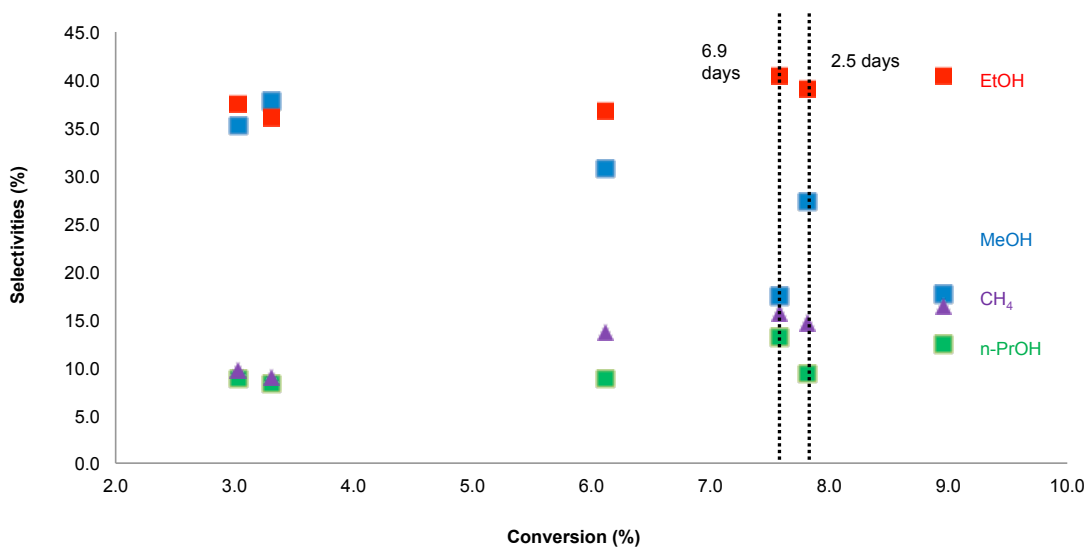
Fig. 3.5 Reaction results of presulfided K/Mo$_2$C/α-Al$_2$O$_3$ catalyst

Another set of reactions was carried out on K/Mo$_2$C/MgO catalysts. Reactions were done using K/Mo$_2$C/MgO catalysts with H$_2$S/H$_2$ pretreatment, H$_2$ pretreatment and no pretreatment at all. Also a reaction was run with a K/MoO$_3$/MgO catalyst with H$_2$S/H$_2$ pretreatment. Reaction results are shown in Table 3.2.

With respect to comparison of reaction results on K/Mo$_2$C/MgO catalyst with H$_2$S/H$_2$ pretreatment, without pretreatment and with H$_2$ pretreatment, the major tendencies in catalytic activities and selectivities were similar to those obtained for K/Mo/α-Al$_2$O$_3$ catalysts. Presulfided K/MoO$_3$/MgO catalyst provided the highest C$_{2+}$ alcohol selectivities and thus the highest C$_{2+}$ alcohol productivities. The sulfided K/Mo$_2$C/MgO catalyst provided higher C$_{2+}$ alcohol selectivities and lower methanol selectivities compared to K/Mo$_2$C/MgO catalyst without pretreatment. These results suggest that the supports do not affect the fundamental chemical properties of the K$_2$CO$_3$ and Mo species.

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Reactions were also run with H_2 pretreatment for $K/Mo_2C/MgO$ catalyst. The main

intention was to compare differences in catalytic activities invoked by using two different

pretreatments (H_2S/H_2 and pure H_2). Both pretreatments were done at 450°C under

atmospheric pressure for 2 hours. H_2 pretreatment was done in order to prepare the

catalyst with pretreatment at the same temperature and similar gas, except for H_2S, and

thus determine the role of H_2S on the reactivity. The presulfided catalyst yielded higher

C_{2+} alcohol selectivities and slightly higher total hydrocarbon selectivities compared to

catalysts pretreated with H_2 gas flow.

Table 3.2 Reaction results of K/Mo/MgO (compositions: 7% Mo, 3% K), comparison of use of different precursors for Mo species and pretreatments

| Reaction ID # | Precursor/ Pretreatment | GHSV (ml/g/hr) | Conv. (% from prod.) | Organic Product Selectivity (Carbon % excluding CO_2) | | | | | | | | | $C_{2+}OH$ Prod. (g/g/hr) | time (day) |
				MeOH	EtOH	n-PrOH	$C_4OH's$	CH_4	C_2H_6	C_3H_8, C_3H_6	Total $C_{2+}OH$	Total HC		
1	MoO_3 H_2S/H_2	1717	8.3	10.5	34.6	22.1	11.6	12.5	3.4	2.1	68.6	18.9	2.4E-2	3.7
1	MoO_3 H_2S/H_2	1794	7.5	12.4	34.5	21.5	11.0	11.5	3.0	2.6	67.4	17.9	2.3E-2	5.9
1	MoO_3 H_2S/H_2	862	7.2	13.1	35.0	22.2	8.8	11.0	2.4	1.5	66.4	17.1	1.1E-2	9.6
1	MoO_3 H_2S/H_2	3746	3.3	19.8	36.4	17.8	7.1	8.6	2.9	1.4	61.5	14.1	2.0E-2	8.1
2	Mo_2C H_2S/H_2	1245	3.2	12.5	27.5	16.5	6.3	14.5	5.3	5.6	51.1	30.2	4.6E-3	3.8
2	Mo_2C H_2S/H_2	628	5.6	9.0	24.7	19.1	7.7	18.1	6.5	5.7	52.5	33.4	4.1E-3	5.3
3	Mo_2C no pretreatment	1490	3.1	54.0	17.5	7.0	1.7	14.6	1.1	1.2	26.3	16.9	3.6E-3	11.5
4	Mo_2C H_2	1201	3.4	31.3	19.2	12.5	3.8	21.2	1.1	2.6	35.9	28.1	3.80E-03	0.9
5	Mo_2C H_2	1374	2.9	33.7	18.8	13.3	3.3	23.0	1.3	1.4	35.5	27.4	3.70E-03	2.8
6	Mo_2C H_2	1328	2.3	43	13.6	10.2	2.1	24.8	1.2	0.9	25.8	28.3	2.20E-03	4.7

These observations are significantly different from previously reported results on syntheses of alcohols from syngas using metallic Mo, MoO_2 and MoS_2 by Anderson *et al.*[64] and Barrault *et al.*[65] From their results, it is reported that both conversion of CO and hydrocarbon selectivities increase with the reduction of Mo species. Also, Barrault *et al.* claim that the more molybdenum is reduced, the less methanol is formed.[65] These reports are quite different from the results obtained in this study, which obtained significantly higher selectivities for methanol with the catalyst pretreated under H_2 gas flow compared to presulfided catalysts. However, it may be that methanol produced on the sulfide catalyst has undergone coupling or degradation reactions, thus producing higher C_{2+} alcohols.[55] If this assumption were true, then the initial amount of methanol produced should have been larger on the sulfide catalyst than that on the H_2 pretreated catalyst. This assumption is based on a previous report by Jensen *et al.* who studied alkali-promoted cobalt molybdenum sulfide catalysts for syntheses of alcohols from syngas, and claim that coupling of alcohols occurs on the catalysts to accomplish chain growth.[55] Their conclusions were drawn from experimental studies in which they performed syngas reactions with methanol co-feed.[55]

Selectivities on the presulfided catalysts appeared to be independent of conversions between 3-6%. However, with the H_2 pretreated catalyst, although conversions are at the same level, selectivities for C_{2+} alcohols decreased after several days of reaction. This is consistent with previously reported work by Rodriguez *et al.* in which they claim that metallic Mo is not catalytically stable compared to other Mo species such as Mo_2C.[66,67]

Table 3.3 shows a summary of reaction results of supported presulfided K_2CO_3/MoO_3 catalysts. MMO supported catalysts produced the lowest MeOH selectivities but low catalytic activities, and MgO supported catalysts produced the highest C_{2+} alcohol

selectivities. These two results suggest that basic supports are promotionally effective in a similar manner as alkali promotion, as suggested by Morrill et al.[21] Activated carbon supported catalyst produced the highest catalytic activities, and resulted in highest C_{2+} alcohol productivities, however the C_{2+} alcohol selectivity was the lowest. Further study on correlating these catalytic activities and selectivities with basicities and surface areas of the catalysts are warranted.

Table 3.3 Summary of reaction results of supported presulfided K_2CO_3/MoO_3 catalysts (*Experiment done by Mike Morrill)

			Organic Product Selectivity (Carbon % excluding CO_2)						
support	GHSV (ml/g/hr)	Conv.	MeOH	EtOH	n-PrOH	CH_4	Total $C_{2+}OH$	Total HC	$C_{2+}OH$ Prod. (g/g/hr)
MMO	976	8.0	4.0	24.3	18.7	13.1	55.5	37.7	8.5E-3
α-Al$_2$O$_3$	1291	7.9	28.1	40.5	12.6	8.7	59.0	9.8	1.6E-2
MgO	1717	8.3	10.5	34.6	22.1	12.5	68.6	18.9	2.4E-2
AC*	3973	8.0	14.2	33.5	13.6	15.7	51.8	32.0	3.9E-2

CONCLUSIONS

Both K/Mo catalysts supported by MgO and α-Al$_2$O$_3$ showed similar trends for catalytic activities and selectivities when different precursors for Mo species were used and different pretreatments were done.

The highest C_{2+} alcohol selectivities and productivities were observed when reactions were run after pretreatment with H_2S/H_2 gas on a catalyst in which MoO_3 was used as the precursor for Mo species. In comparisons of K/Mo$_2$C catalysts with different pretreatments, when pretreatments were done with H_2S/H_2 gas, higher C_{2+} alcohol

selectivities and lower MeOH selectivities were produced on both MgO and α-Al$_2$O$_3$ supports. As shown in XANES data, presulfided Mo$_2$C catalysts contained MoS$_2$ species. However, in most cases, molybdenum sulfide species were not in crystallites large enough to be detected by XRD. Poorer catalytic activities of Mo$_2$C-derived MoS$_2$ catalysts compared to MoO$_3$-derived MoS$_2$ catalysts may have been due to incomplete sulfidation of Mo species.

K/Mo$_2$C/MgO catalysts showed that significantly higher selectivities for methanol were obtained with catalyst pretreated under H$_2$ gas flow compared to presulfided catalysts. Also, with H$_2$ pretreated catalyst, selectivities for C$_{2+}$ alcohols decreased after several days of reaction. These poor catalytic activities are anticipated to be due to Mo species having been reduced to metallic Mo, as suggested by XANES data.

CHAPTER 4: CONCLUSIONS

Co promotion on K_2CO_3/MoS_2/MMO catalysts

Varying the Co content in the K/Mo-Co/MMO catalysts did not produce significant

changes in catalytic acitivities or selectivities when prepared by the co-impregnation

method without aqueous acetic acid with $Co(NO_3)_3 9H_2O$ as a precursor. The lack of

effect on catalytic activities and selectivities may be explained in two ways. First is the

possible premature precipitation of cobalt molybdate. Cobalt molybdate precipitation is

generally prevented by using water as solvent,[1,2] but that was not appropriate for this

study because hydrotalcite-derived mixed metal oxide was used as the support. The

second possibility is the reaction temperature was too low, as the optimal reaction

temperature has been reported previously to be higher than the optimal reaction

temperature for Co-free catalysts.[49]

Co loadings on K/Mo/MMO-Co catalysts did not change selectivities significantly.

However, they changed catalytic activities, represented by GHSV required to obtain 8%

conversion, while maintaining higher alcohol selectivities. As a result, C_{2+} alcohol

productivities reached $0.01 g_{alcohol}/g_{catalyst}/hr$ with Co loadings higher than 8%.

Investigations on Mo_2C as a precursor for K_2CO_3/MoS_2 catalysts

Mo_2C as a precursor for K_2CO_3/MoS_2 catalysts supported by metal oxides was evaluated

on two supports. Both K/Mo catalysts supported on MgO and α-Al_2O_3 showed similar

trends for catalytic activities and selectivities when different precursors for Mo species

were used and different pretreatments were done. When reactions were run after

pretreatment with H_2S/H_2 gas on a catalyst in which MoO_3 was used as the precursor for Mo species, the highest C_{2+} alcohol selectivities and productivities were observed. In comparisons of K/Mo_2C catalysts with different pretreatments, the presulfided catalysts yielded higher C_{2+} alcohol selectivities and lower MeOH selectivities on both MgO and α-Al_2O_3 supports, compared to non-pretreated catalysts.

XANES data shows that sulfide Mo_2C catalysts contained MoS_2 species. However, in most cases, molybdenum sulfide species were not in crystallites large enough to be detected by XRD. Poorer catalytic activities of Mo_2C-derived MoS_2 catalysts compared to MoO_3-derived MoS_2 catalysts may have been due to incomplete sulfidation of Mo species.

RECOMMENDATIONS

To study more accurately the promotion effect of Co on $K/MoS_2/MMO$ catalysts, I recommend further research on preparation methods without any cobalt molybdate precipitation and thus improving dispersion of Co and Mo domains. As shown in Table 2.1, when $Co(OAc)_2$ was used as precursor, which produced less cobalt molybdate than $Co(NO_3)_3 9H_2O$, Co-promoted K/Mo-Co/MMO catalyst produced the highest C_{2+} alcohol selectivities among other K/Mo-Co/MMO catalysts with the same Co loading. This result suggests the possibility of good promotion effects of Co with an appropriate catalyst preparation method. Specifically, exploring other DMSO-dissolvable Co precursors and Co complexes may be effective, along with sequence impregnation method, in which AMT would be impregnated and treated under N_2 flow at 450°C, and then Co precursor would be impregnated followed by another N_2 treatment at 450°C. Also, by performing calcination of hydrotalcite with higher temperature to minimalize the memory effect of hydrotalcite,[52,53] use of water as solvent or use of additive aqueous acetic acid solution may produce good catalytic activities.

It is also reported that 350°C is the optimal reaction temperature for Co-promoted catalysts.[49] It would be worthwhile to run reactions at higher temperatures if the increase of higher alcohol productivities exceeds the increase of energy required for maintaining the reaction temperatures.

In this study, in comparisons of presulfided Mo_2C catalysts and presulfided MoO_3 catalysts, the reasons for presulfided Mo_2C catalysts producing lower C_{2+} alcohol selectivities and productivities are anticipated to be due to Mo_2C being resistant to deep sulfidation.[63] This is based on studies on catalytic activities of Mo_2C-based catalysts and

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MoO$_3$-based catalysts in hydrodesulfurization reactions reported by Bussel et al.[63] The differences of deep sulfidation and surface sulfidation in K/Mo$_2$C/α-Al$_2$O$_3$ and K/Mo$_2$C/MgO may be confirmed by characterization studies using X-ray photoelectron spectroscopy (XPS) and EA.

The reasons why non-pretreated Mo$_2$C catalysts produced the highest methanol selectivities and presulfided MoO$_3$ catalysts produced the highest C$_{2+}$ alcohol selectivities are not clear. It is reported that K$_2$CO$_3$ is responsible for chain growth.[38] It is also reported that for Mo$_2$C catalysts, the optimal K$_2$CO$_3$ loadings are >12%.[46] Also with promotion of K$_2$CO$_3$, unsupported Mo$_2$C catalysts are reported to give higher selectivities to C$_{2+}$ alcohols and higher conversions compared to K$_2$CO$_3$-promoted MoS$_2$ catalyst.[46] Given these reports and results, it is suggested that the optimal ratios of K$_2$CO$_3$ to Mo$_2$C should be studied on supported K/Mo$_2$C catalysts, along with the optimal loadings of Mo$_2$C.

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