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Alcohol Synthesis from CO and H₂ over Molybdenum Sulfide. The Effect of
Pressure and Promotion by Potassium Carbonate.

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Abstract

Molybdenum Disulfide is an active catalyst for the formation of alkanes from $\text{CO} + \text{H}_2$. Addition of K_2CO_3 as a promoter greatly increases the selectivity to alcohols. The alcohol production is also dependent on the pressure, higher pressures of either CO or H_2 lead to significant increases in the alcohol yield. In particular, at 2000 p.s.i.g. and 250°C , a catalyst with 30% by weight K_2CO_3 produces a total alcohol yield of 90%, mostly methanol.

I. Introduction

Recently, molybdenum sulfides have been reported to produce methane, other alkanes¹⁻², and alcohols³ under a variety of experimental conditions. The purpose of our investigation is to explore the catalytic behavior of molybdenum sulfide for this important reaction using well characterized catalysts. Compounds of the early transition metals Mo, W, V, Nb and Cr have not been explored as possible catalysts for the selective production of hydrocarbons from CO and H₂ to the same extent as the late transition metals Cu, Zn, Ni, Ru, Pd, and Rh. References 4-17 provide an overview of the large volume of work that has been done on the latter metals and their compounds.

In this paper we report the preparation and characterization of a K₂CO₃ promoted MoS₂ catalyst for alcohol formation from CO and H₂. In addition to the K₂CO₃ promotion, the dependence of this catalyst's selectivity upon pressure is demonstrated. We find that the alcohol selectivity is very sensitive to both K₂CO₃ promotion and total pressure. Increases in either K₂CO₃ concentration or total pressure greatly increase the alcohol selectivity.

II. Catalyst Preparation and Characterization

MoS₂ was prepared by thermally decomposing (NH₄)₂MoS₄, obtained from Alfa Chemical Co., in a tube furnace with flowing nitrogen at 350°C for three hours. The following reaction occurs under these conditions;

X-ray diffraction patterns of the product give the same peak positions as that of a commercially obtained MoS_2 , but the peaks were much broader, as shown in Figure 1. The lack of sharp diffraction features indicates that either our product is MoS_2 with small particle size or that it lacks uniform composition. Further studies are needed to better characterize the catalyst's bulk properties. It is clear, however, that the near surface region of our catalyst is actually MoS_2 . This is shown by the Mo 3d and S 2p XPS spectra that are displayed in Figures 2 and 3. In both cases the spectra for our product agree with those of commercial MoS_2 . B.E.T. measurements indicate that the catalyst has a surface area of 6.9 m^2/g .

Promoted MoS_2 catalysts were prepared by impregnating MoS_2 with a 0.2% K_2CO_3 solution and drying at $110^\circ\text{--}120^\circ\text{C}$ for several hours. The catalysts were then ground before using.

III. Experimental

High pressure catalytic reactions were carried out in a 280 ml steel autoclave which is equipped with a stirrer. The walls of the autoclave have negligible catalytic activity for CO hydrogenation in comparison with the MoS_2 catalysts.

Each experiment was performed using about 0.1 gram of catalyst. After placing the catalyst in the autoclave it was flushed with several atmospheres of Ar and heated to the reaction temperature. The H_2 and CO were introduced sequentially to initiate the reaction. The products were analyzed by a gas chromatograph equipped with a flame ionization detector. A Chromosorb 102 column was used to separate the product alkanes, alkenes, and alcohols. Experiments were conducted over a total pressure range of

500 to 2000 p.s.i. The reaction temperature was 250° C and the H₂:CO ratio was 1:1 for the experiments reported here.

IV Results and Discussion

Our experiments show that MoS₂ has a high catalytic activity for CO hydrogenation to hydrocarbons, but very little alcohol formation is apparent. The total selectivity to alcohol for the unpromoted MoS₂ is less than 5%. Note that all selectivities quoted in this paper refer to those at one hour reaction time, unless otherwise noted. The conversion at one hour was very low (< 0.01) which allowed us to operate far from thermodynamic equilibrium.

The turnover rate of methane production of our MoS₂ catalyst is approximately 10⁻³ sec⁻¹, at 250°C, 1000 p.s.i., and a CO:H₂ ratio of 1:1. This is in the same range as reported for the more common Group VIII Ru, Ni, and Fe catalysts by Vannice¹⁸. This number also falls within the range reported for supported MoS₂ and Mo-C catalysts¹⁹.

After adding K₂CO₃ to MoS₂ the product distribution shifts dramatically to selective alcohol formation. In Figure 4 we compare the selectivity of MoS₂ and a K₂CO₃ promoted MoS₂. The experimental conditions were 250°C, CO:H₂ ratio of 1:1, reaction time 1 hour, and a total pressure of 1000 p.s.i. The addition of K₂CO₃ promoted both the production of CH₃OH and C₂H₅OH, with CH₃OH selectivity peaking at about 55% and C₂H₅OH at about 10%. The CH₄ selectivity drops from about 50% to 35%, C₂H₆ and C₃H₈ selectivities decline from 25% and 15% respectively to essentially zero. Note that the promoted catalyst has a total of only 10% C₂+ products as opposed to about 40% for the unpromoted catalyst.

By K₂CO₃ promotion alone the selectivity to alcohol for this catalyst

is increased from about 2% to 65%. This effect appears to level off at a loading of approximately 0.3g K_2CO_3 / g MoS_2 catalyst. It should be noted here that the addition of K_2CO_3 does not change the conversion significantly, only the selectivity is shifted greatly.

In addition to K_2CO_3 , other alkaline compounds can also promote MoS_2 to increase the selectivity of CO hydrogenation to alcohol. Table 1 gives a comparison of the effects for several promoters. The results show that KOH has a promotion effect similar to K_2CO_3 . NaOH, Na_2CO_3 also show promoter effect but not to the extent of either K_2CO_3 or KOH. A detailed study of the behavior of these different promoters has not yet been completed .

The effect of alkali promoters on our catalyst is to increase the selectivity to alcohols. This behavior was also reported by Quarderer and Cochran³. Their catalyst was supported MoS_2/K_2CO_3 with about 10% K_2CO_3 loading by weight. Their results are in qualitative agreement with ours. Similar catalysts were also used by Murchison and Murdick²⁰. In their experiments a catalyst with a much lighter loading of K_2CO_3 gave no alcohol. The result was an enhancement of C_2-C_5 yield.

The addition of high concentrations of alkali compounds to MoS_2 is necessary to promote alcohol formation. The reasons for this have yet to be determined. The high levels necessary to achieve this effect suggest the formation of an alkali overlayer or compound with MoS_2 . Perhaps with this amount of alkali carbonate on the surface weaker interactions of molecular CO with the overlayer, that lead to its direct hydrogenation, dominate other reaction channels and the catalysis no longer occurs on the MoS_2 . Much more work is necessary to determine the nature of this effect.

We were also able to increase greatly the alcohol selectivity by increasing the pressure. Increases in either the total pressure or of the H_2 pressure led to significant increases in the alcohol selectivity of the K_2CO_3 promoted MoS_2 catalyst. In Figure 5 we show the effect of increasing the H_2 pressure upon alcohol selectivity. The figure shows that the selectivity to alcohol increases from 65% to 90% for a catalyst that is 0.6g K_2CO_3 / g MoS_2 . These experiments covered a pressure range of 500 to 1500 p.s.i. H_2 with a constant CO pressure of 500 p.s.i.. This increase is entirely due to the increased production of CH_3OH . As a result of this and a lack of a concomitant increase in the production of C_2H_5OH , the C_2H_5OH selectivity decreases. Note that the increase in CH_3OH production was continuous for the pressure range tested. In contrast, note Figure 6 where we show that the pressure has very little influence on the selectivity of the unpromoted MoS_2 catalyst.

Figure 7 shows that the selectivity to alcohols can also be increased by increasing the total pressure and keeping the $CO:H_2$ ratio constant. This is also accompanied by a decrease in CH_4 formation. At a total pressure of 500 psi, CH_4 is favored over CH_3OH by a margin of 60% to 28% of the total products. At 2000 psi this has reversed to 75% CH_3OH to 15% CH_4 . In both the aforementioned experiments the amount of C_2H_5OH stayed relatively constant and equal to 10%.

Experiments that monitored the selectivity as a function of the CO pressure were performed. The results showed that again higher pressures led to increased alcohol production. However, severe catalyst deactivation during these experiments did not allow us to quantify this trend.

These studies show the alcohol selectivity of the promoted catalyst

is increasing with pressure. The unpromoted catalyst was insensitive to pressure. This variation with pressure could be due to the enhancement of a reaction pathway that exists only on the promoted catalyst. As mentioned earlier, the reaction to form the alcohol might occur on the alkali overlayer. Possibly this layer stabilizes an intermediate to alcohol formation. This species, possibly a weakly bound formate, would be present in much higher concentrations at high pressures.

The residence time of the products in this batch reactor can also influence the selectivity of the K_2CO_3 / MoS_2 catalyst. In Figure 8 we show the effect of increasing reaction time. The selectivity shifts away from CH_3OH to CH_4 . The selectivity to CH_3OH shifted from 58% at 60 minutes to 30% at 300 minutes. Correspondingly, the selectivity to CH_4 increased from 35% to 60%. The production of C_2H_5OH also dropped, however less than 1% of the final products were C_2H_6 . These changes are due, as shown in Figure 9, to a secondary reaction of CH_3OH that produces the decomposition products of CH_4 , H_2O , and CO_2 . In this experiment we monitored the decomposition of CH_3OH in Ar at $250^\circ C$, and 1000 psi total pressure.

V. Conclusions

We show the effects of K_2CO_3 promotion and increased pressure upon alcohol synthesis from carbon monoxide and hydrogen over a molybdenum disulfide catalyst. Increasing K_2CO_3 concentrations greatly enhances the selectivity of the reaction to methanol.

Similar results from experiments with other oxygenated promoters Na_2CO_3 , $NaOH$, and KOH suggest an alkali oxide or alkali/oxygen compound with MoS_2 is the surface site responsible for the formation of the alcohol.

The other major conclusion of this work is that K_2CO_3 promotion makes the product distribution pressure dependent. The product distribution of the CO/H_2 reaction over the MoS_2 catalyst did not show any dependence on either total or hydrogen partial pressure. However, when the catalyst is promoted with K_2CO_3 we see a large pressure dependence; increased total pressure yields increased selectivity to methanol.

Finally, we have shown that CH_3OH decomposes on the catalyst. This reaction becomes more significant with increased reaction time, as the concentration of the alcohol increases in the batch reactor.

More detailed study of this catalytic system is warranted. Experiments are in progress to better characterize the pressure and temperature dependences of the rates. The effects of alkali addition on the bonding of CO , CH_3OH , and H_2 are being investigated.

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TABLE I

A COMPARISON OF ALCOHOL SELECTIVITIES FOR DIFFERENT PROMOTED CATALYSTS

(250°C, 1000 psi, CO:H₂ = 1:1, 1 hour)

CATALYST	WT. MoS ₂ :WT. PROMOTER	ALCOHOL %
MoS ₂	-	2.7
MoS ₂ /K ₂ CO ₃	1:0.6	65.0
MoS ₂ /KOH	1:0.6	64.8
MoS ₂ /NaOH	1:1	61.8
MoS ₂ /Na ₂ CO ₃	1:1	29.7

Figure Captions

- Figure 1 - X-Ray Diffraction Patterns of MoS_2 prepared from thermal decomposition of MoS_2 and of Alfa Co. MoS_2 .
- Figure 2 - Mo 3d X-Ray Photoelectron Spectra of Alfa Co. MoS_2 , and of MoS_2 prepared in our lab before and after reaction.
- Figure 3 - S 2p X-Ray Photoelectron Spectra of Alfa Co. MoS_2 , and of MoS_2 prepared in our lab before and after reaction.
- Figure 4 - The product distribution of the MoS_2 catalyst as a function of K_2CO_3 loading.
- Figure 5 - The H_2 pressure dependence of the $\text{K}_2\text{CO}_3/\text{MoS}_2$ catalyst's selectivity.
- Figure 6 - The H_2 pressure dependence of the MoS_2 catalyst's selectivity.
- Figure 7 - The total pressure dependence of the $\text{K}_2\text{CO}_3/\text{MoS}_2$ catalyst's selectivity.
- Figure 8 - The effect of increasing the reaction time upon the selectivity of the $\text{K}_2\text{CO}_3/\text{MoS}_2$ catalyst.
- Figure 9 - The decomposition of CH_3OH as a function of reaction time over $\text{K}_2\text{CO}_3/\text{MoS}_2$ catalyst.

X-Ray Diffraction Patterns

XBL 858-6527

(Fig. 1)

XPS Spectra of MoS₂

XBL858-6526

(Fig. 2)

XPS Spectra of MoS₂

XBL858-6525

(Fig. 3)

Effect of K₂CO₃ Content on Product Distribution of Promoted MoS₂ Catalyst

XBL 856-6370

(Fig. 4)

Effect of Pressure on Product Distribution of
 K_2CO_3/MoS_2 Catalyst

XBL856-6369

(Fig. 5)

XBL 658-6523

(Fig. 6)

Effect of Total Pressure on Selectivity of
 K_2CO_3/MoS_2 Catalyst

XBL 856-6368

(Fig. 7)

Time Dependence of Selectivity

XBL 858-6524

(Fig. 8)

CH_3OH Decomposition on K_2CO_3/MoS_2 Catalyst

XBL 856-6367

(Fig. 9)

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