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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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Pressure and Promotion by Potassium Carbonate.

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Abstract

Molybdenum Disulfide is an active catalyst for the formation of alkanes from CO + H₂. 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 H₂ 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 K_2CO_3 promoted MoS_2 catalyst for alcohol formation from CO and H_2 . In addition to the K_2CO_3 promotion, the dependence of this catalyst's selectivity upon pressure is demonstrated. We find that the alcohol selectivity is very sensitive to both K_2CO_3 promotion and total pressure. Increases in either K_2CO_3 concentration or total pressure greatly increase the alcohol selectivity.

II. Catalyst Preparation and Characterization

 MoS_2 was prepared by thermally decomposing $(NH_4)_2MoS_4$, 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;

 $(NH_4)_2MoS_4(s)$ $350°C,N_2 \\ ----- MoS_2(s) + (NH_4)_2S(g) + 1/2 S_2(g).$

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X-ray diffraction patterns of the product give the same peak positions as that of a commercially obtained MoS₂, but the peaks were much broader, as shown in Figure 1. The lack of sharp diffraction features indicates that either our product is MoS₂ 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 MoS₂. 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 MoS₂. 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 $110^\circ-120^\circ$ 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 MoS₂ 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

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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 MoS_2 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 MoS_2 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 MoS_2 catalyst is approximately 10^{-3} sec⁻¹, at 250°C, 1000 p.s.i., and a $CO:H_2$ ratio of 1:1. This 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.

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After adding K_2CO_3 to MoS_2 the product distribution shifts dramatically to selective alcohol formation. In Figure 4 we compare the selectivity of MoS_2 and a K_2CO_3 promoted MoS_2 . The experimental conditions were 250°C , $CO:H_2$ ratio of 1:1, reaction time 1 hour, and a total pressure of 1000 p.s.i. The addition of K_2CO_3 promoted both the production of CH_3OH and C_2H_5OH , with CH_3OH selectivity peaking at about 55% and C_2H_5OH at about 10%. The CH_4 selectivity drops from about 50% to 35% , C_2H_6 and C_3H_8 selectivites decline from 25% and 15% respectively to essentially zero. Note that the promoted catalyst has a total of only 10% C_2 + products as opposed to about 40% for the unpromoted catalyst.

By K₂CO₃ promotion alone the selectivity to alcohol for this catalyst

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is increased from about 2% to 65%. This effect appears to level off at a loading of approximately 0.3g K_2CO_3 / g MoS₂ 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, Na₂CO₃ 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 Cochran ³. 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 -C₅ 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.

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We were also able to increase greatly the alcohol selectivity by increasing the pressure. Increases in either the total pressure or of the H₂ 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 CH3OH. As a result of this and a lack of a concommitant 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 MoS2 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 CH₄ formation. At a total pressure of 500 psi, CH₄ is favored over CH₃OH by a margin of 60% to 28% of the total products. At 2000 psi this has reversed to 75% CH₃OH to 15% CH₄. In both the aforementioned experiments the amount of C₂H₅OH stayed relatively constant and equal to 10%. . 2

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

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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 / MoS₂ catalyst. In Figure 8 we show the effect of increasing reaction time. The selectivity shifts away from CH₃OH to CH₄. The selectivity to CH₃OH shifted from 58% at 60 minutes to 30% at 300 minutes. Correspondingly, the selectivity to CH₄ increased from 35% to 60%. The production of C₂H₅OH also dropped, however less than 1% of the final products were C₂H₆. These changes are due, as shown in Figure 9, to a secondary reaction of CH₃OH that produces the decomposition products of CH₄, H₂O, and CO₂. In this experiment we monitored the decomposition of CH₃OH in Ar at 250°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 Na₂CO₃, NaOH, and KOH suggest an alkali oxide or alkali/oxygen compound with MoS₂ is the surface site responsible for the formation of the alcohol.

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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/H₂ reaction over the MoS₂ 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 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, CH₃OH, and H₂ are being investigated.

We would like to acknowledge Ms. Chris Hong for her help in performing some of the experiments that comprise this work. We are also grateful for discussions with Dr. C. Murchison. The research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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TABLE I

A COMPARISON OF ALCOHOL SELECTIVITIES FOR DIFFERENT PROMOTED CATALYSTS

 $(250^{\circ}C, 1000 \text{ psi}, C0:H_2 = 1:1, 1 \text{ hour})$

CATALYST	WT. MoS2:WT. PROMOTER	ALCOHOL %	
MoS2	-	2.7	
MoS2/K2CO3	1:0.6	65.0	
MoS ₂ /KOH	1:0.6	64 •8	
MoS ₂ /NaOH	1:1	61.8	
MoS_2/Na_2CO_3	1:1	29 .7	

Figure Captions

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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 K_2CO_3/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 K_2CO_3/MoS_2 catalyst's selectivity.
Figure 8	8	-	The effect of increasing the reaction time upon the selectivity of the $K_2C0_3/\ MoS_2$ catalyst.
Figure '	9	-	The decomposition of CH3OH as a function of reaction time over K_2CO_3/MoS_2 catalyst.



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(Fig. 1)

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XPS Spectra of MoS₂

XBL858-6525

X8L 856-6370

(Fig. 4)

(Fig. 5)

X8L 858- 6523

(Fig. 6)

X8L856-6368

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X8L858-6524

(Fig. 8)

X8L856-6367

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