

CONVERSION OF SYNGAS TO MIXED ALCOHOLS OVER K-Mo-S/ACTIVATED CARBON

Nguyen Tien Thao^{1*}, Christopher W. Jones²

¹*Faculty of Chemistry, Hanoi College of Science, Vietnam National University (VNU)*

²*School of Chemical & Biomolecular Engineering, Georgia Institute of Technology*

Received 20 May 2011

Abstract

The present work reported the catalysts were prepared from activated carbon impregnated with K_2CO_3 and MoO_x and investigated for the synthesis of mixed alcohols from syngas. Two catalyst samples have different MoO_x loadings of 15 - 30 wt%. The solids were characterized by XRD, SEM, H_2 -TPR and BET techniques. An increased Mo loading results in a decreased surface area of the solid. After sulfidation with H_2S/H_2 , the catalysts are tested for the synthesis of alcohols from syngas and show a high CO conversion at values of 10-23%. The predominant product is ethanol with the selectivity of 25-45% at typical reaction conditions.

1. INTRODUCTION

As crude oil becomes increasingly scarce, the search for petroleum free routes to chemical products intensifies. Alternative fuels containing alcohols is known as the most promising vehicle fuels since other oxygenated compounds (MTBE, ETBE...) are prohibited. Mixtures of methanol and higher alcohols (C_2^+OH) have the potential for providing a gasoline- blending stock compared with that of straight-run methanol or ethanol [1]. The development of catalysts and processes that can directly synthesize the alcohol mixtures from syngas is an interesting subject of both academic and industrial interest. Accordingly, molybdenum-based catalysts are of a special interest due to their resistance to sulfur poisoning [2]. However, the catalytic activity and selectivity to mixed alcohols over Mo catalysts were remarkably dependent on several variables (support, additives, reaction condition) [3]. Catalysts based on activated carbon possess many advantages as compared with silica- and alumina-based catalysts. In addition, interaction between the support and the active material is limited to a large extent by the inertness of the graphitic surface. In many cases, this can result in an optimized utilization of the metals/support catalysts [4]. The thermostability of activated carbon in inert environments at elevated temperatures is indicated and no significant sintering of the support is observed up to 1500°C [5]. Another benefit of using activated carbon as a support is its stability in caustic and acidic/basic solutions.

Synthesis gas has substantial appeal because it can be a product of biomass and/or coal gasification – two sources of minimal cost. To this end, the conversion of synthesis gas to higher hydrocarbons and alcohols over supported molybdenum sulfide catalysts is a topic of contemporary interest [6, 7].

This publication presents the characteristics and preliminary catalytic activity of a molybdenum sulfide catalyst supported on Norit activated carbon impregnated with potassium carbonate. The catalysts were prepared by impregnating the activated carbon with molybdenum salt, addition of potassium carbonate, followed by calcinations. The resultant oxide catalyst was sulfided ex-situ in flowing H_2S , and then used for the catalytic conversion of synthesis gas to higher alcohols and hydrocarbons in a fixed bed reactor.

2. EXPERIMENTAL

2.1. Catalyst preparation and characterization

A solution containing a desired amount of ammonium heptamolybdate and deionized water was stirred at 65°C for 2 hours. Then, the Norit carbon was added to the preheated solution. The resultant mixture was dried in an oven at 105°C overnight and then heated in a ½ inch diameter quartz tube at 500°C for 2 hours (5°C/min, 50 ml/min of nitrogen). The heated solid was then added into deionized water containing a quantity of K_2CO_3 at room temperature. The wet solid was dried in an oven at 105°C overnight, and then calcined in a

½ inch diameter quartz tube at 400°C for an hour (5°C/min, 50 ml/min of N₂).

Nitrogen physisorption analysis was done at 77 K using a Micromeritics ASAP 2010. Powder X-ray diffraction (XRD) patterns were obtained on a Philips X'pert diffractometer equipped using CuK α radiation. Scanning electron microscope (SEM) images of the catalysts were acquired on a Hitachi S-800 operating at 10 kV. The TPR experiments were conducted on an AutoChem II 2920. 0.05 grams of sample was placed in a quartz U-tube reactor. The reactor was heated using the furnace, which was controlled by the temperature programmer. The exit gas stream from the reactor passed through a cold trap filled with a mixture of dry ice and isopropanol and then to a thermal conductivity detector where the H₂ content of the stream was monitored.

2.2. Catalytic test

Catalytic measurement was carried out in a tubular reactor consisting of a quarter inch stainless steel tube (316 SS) with the catalyst loading of 0.20 grams. Premixed hydrogen, carbon monoxide, and nitrogen feed gases from cylinders are compressed and regulated at the reaction pressure. The feed gas mixture contains hydrogen and carbon monoxide at the desired molar ratio of 1/1 with about 10 percent

by volume of nitrogen serving as an internal standard, and about 50 ppm of H₂S. The feed gas then flows at the stated hourly space velocities through the fixed bed reactor kept at the stated reaction temperature and 1500 psig. The reactor effluent is fed into a gas chromatograph to analyze the product distribution.

3. RESULTS AND DISCUSSION

3.1. Characteristics of catalysts

The morphological analysis was observed by SEM at different magnifications and presented in figure 1. The 7.5%K₂CO₃ + 15%MoO_x/activated carbon particles are irregularly shaped and randomly sized. SEM images show the spongy like texture of the catalyst and random orders of carbon material instead of long-range crystalline order. In addition, there are many large empty spaces between the catalyst particles and no ordered porous structure was observed at this magnification. Moreover, figure 2 presents the XRD pattern of the two K₂CO₃/MoO_x/Activated carbons with two very broad reflections at 2-theta of 22.5 and 44° corresponding to the micrographic structure characteristic of activated carbon [8].

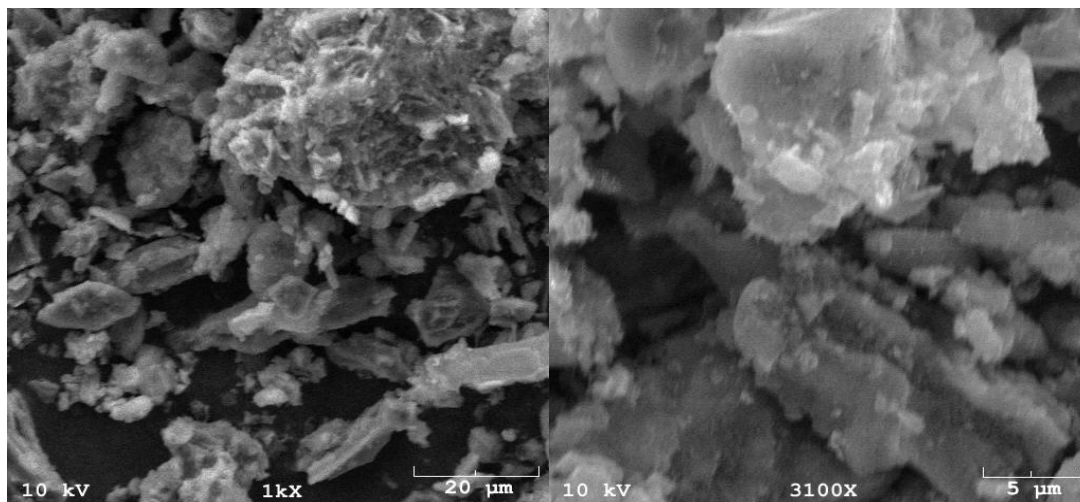


Figure 1: SEM of 7.5%K₂CO₃ + 15%MoO_x/Norit carbon

For the purpose of comparison, we also collected a MoO₃ reference pattern. As seen in figure 2, there is no observable reflections of the prepared solids are matched with those of MoO₃ reference, suggesting that the MoO₃ was not formed by the decomposition of (NH₄)₆Mo₇O₂₄·4H₂O precursor under nitrogen flowrate at a high temperature. Under impregnation condition, molybdenum oxide reacted

with K₂CO₃ to produce more stable salt of polymolybdate or was reduced to lower oxidation states. The oxidation of Mo moieties may be elucidated as considering the H₂-TPR experiments. H₂-TPR pattern for the representative sample is shown in Figure 3. H₂-TPR profile shows two well-resolved reduction peaks as seen from figure 3. The maximum H₂-consumption in the first peak is

posited at 435°C while the second one centers around 685°C, but the reduction of molybdenum

oxide is incomplete since the signal is not reached the base line at a high temperature (900°C).

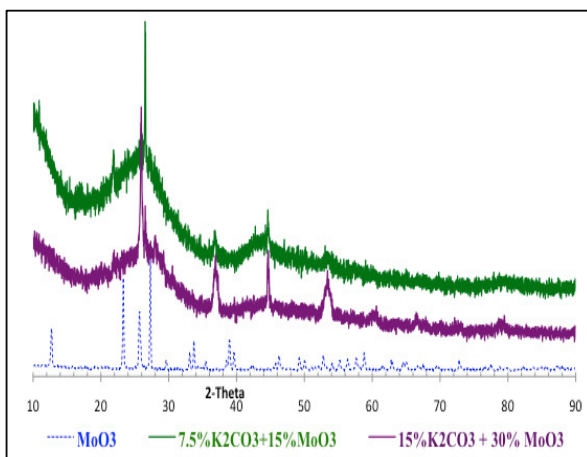


Figure 2: XRD patterns of catalysts

In view of the oxidation/reduction, potassium is unable to be reduced itself under these conditions, but it has significantly modified the reducibility of other components in the catalysts [9]. So, the two peaks are firmly contributed to the reduction of differently coordinated Mo sites on the support. Xianguo Li et al. [10] suggested that the low- and high- temperature peaks are respectively assigned to the reduction of octahedrally and tetrahedrally coordinated Mo species [11-13], indicating that the Mo species in C-supported Mo-based catalyst may be present in the polymolybdate salts. The low-temperature peak is responsible for the conversion of molybdenate(s) to Mo(IV) [11,13]. Therefore, H₂-TPR result let us choose the optimal sulfidation of catalyst in order to convert MoO_x into MoS₂ at 450°C.

3.2. Catalytic activity

The alcohol synthesis was carried out in the tubular reactor under the reaction conditions after an *in-situ* pretreatment of K₂CO₃+MoO_x/carbon precursors at 450°C in 20 vol.% H₂S/H₂ for 2 hours. The catalytic activity is monitored at 310°C. Figure 4 presents the CO conversion versus time on stream. The catalysts approach the steady state after 15 hours-on-stream and no significant deactivation was monitored for 2 days. The CO conversion curves reach almost plateaus at relative values of 10.5 and 22.5% over the two examined samples, indicating the strong stability of a potassium carbonate-molybdenum sulfide catalyst supported on activated carbon in the synthesis of mixed alcohols from syngas [14]. An increased Mo loading results in a

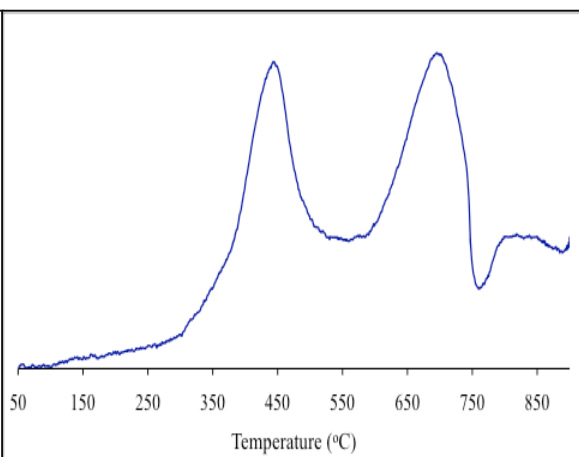


Figure 3: H₂-TPR profile of 7.5%K₂CO₃ + 15%MoO_x/Activated carbon

higher CO conversion (Fig. 4), but a lower total alcohol selectivity (Fig. 5). This may be correlated with the dispersion of MoS₂ active phase on the different surface area [14]. In order to elucidate this issue, we have measured the specific surface area of the two examined samples. For the lower Mo and K⁺ loading sample, 7.5%K₂CO₃ +15%MoO_x both are dispersed on Norit activated-carbon, leading to a remarkable decrease in the specific surface area of the support from 1200 m²/g to 624 m²/g.

As increasing the loading of K₂CO₃ and MoO_x to 15 and 30 % respectively, the surface area of the latter catalyst dramatically falls to 387 m²/g. Thus, a high Mo loading sample is presumably to have a lower dispersion of Mo species which may decrease the ability of CO adsorption. This leads to a lower selectivity to alcohols (Fig. 5). Meanwhile, the low Mo-loading catalyst shows a rather higher selectivity to total alcohols of 78-82% and a very low selectivity to hydrocarbons (18-22%).

Among the mixture of linear primary alcohols produced, ethanol is always formed as the predominant product with the selectivity of 20-45% over both catalysts. The selectivity of such ethylic alcohol is proportional with total oxygenated product selectivity as seen in figure 5, implying a rational fraction in the product distribution. Except for C₁OH (methanol), the selectivity to higher (C₂⁺OH) alcohols decreases in the orders of ethanol > n-propanol > n-butanol > n-pentanol and therefore product distribution obeys an Anderson-Schur-Florry calculation [9, 15]. The formation of a higher alcohol is following the insertion of CH_x moiety into carbon skeletal intermediates to produce a longer carbon chain product [6, 7, 9, 15].

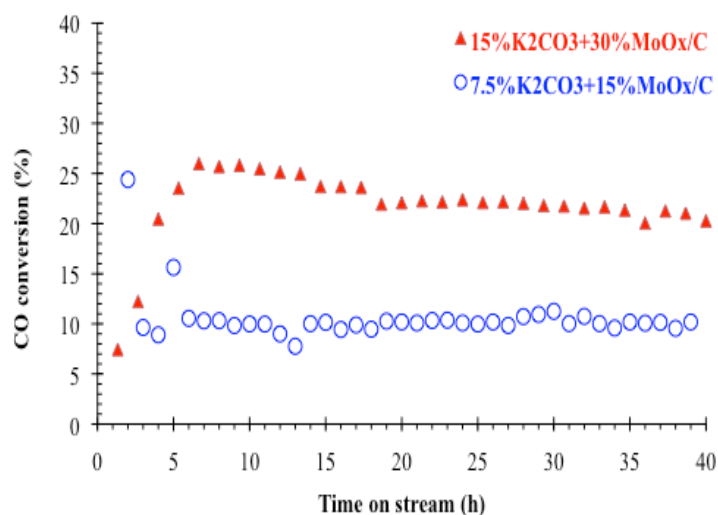


Figure 4: CO conversion at 310°C, 1500 psi, H₂/CO = 1, 4000 h⁻¹

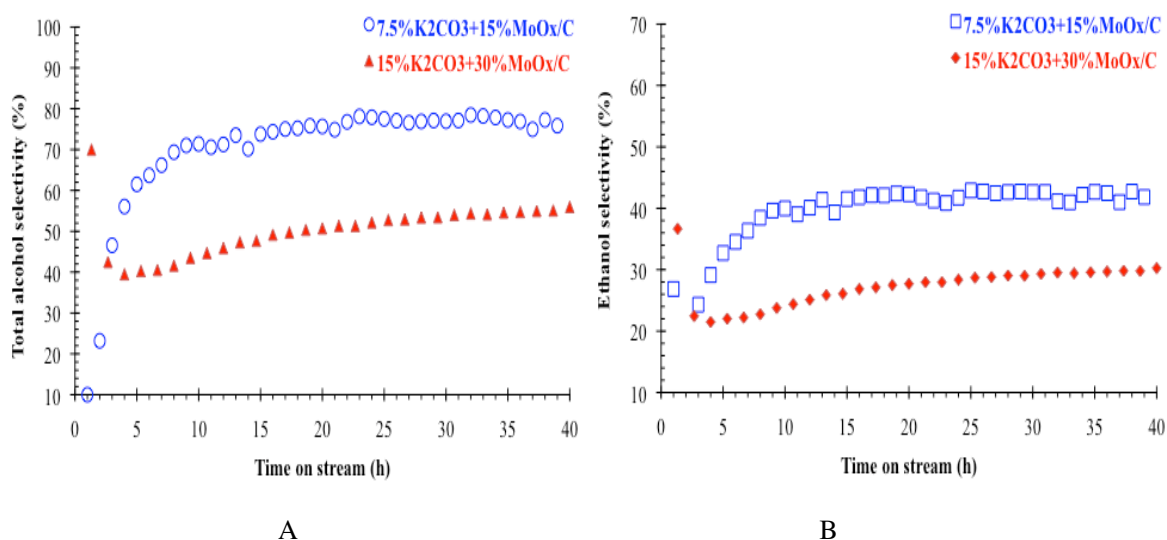


Figure 5: Total alcohol (A) and ethanol (B) selectivities at 310°C, 1500 psi, H₂/CO = 1, 4000 h⁻¹

4. CONCLUSIONS

Potassium carbonate and molybdenum sulfide supported on activated carbons were prepared through sulfidation of K₂CO₃/MoO_x/support precursor under typical conditions. The catalyst characterization was investigated by XRD, SEM, nitrogen physisorption, H₂-TPR. The catalysts were tested for the synthesis of alcohols from syngas. Under the reported conditions, the supported molybdenum sulfide catalyst showed high ethanol selectivity with low methanol and hydrocarbon selectivity. Additionally, an ethanol selectivity of 45% at CO conversion of 10-23% suggests that the prepared catalyst is a promising candidate material for ethanol synthesis from synthesis gas.

REFERENCES

1. A. A. Abdel-Rahman and M. M. Osman, *Experimental investigation on varying the compression ratio of SI engine working under different ethanol-gasoline fuel blends*, International Journal of Energy Research, **21**(1), 31-40 (1997).
2. J. Bao, Y. Fu, Z. Sun and C. Gao, *A highly active K-Co-Mo/Co catalyst for mixed alcohol synthesis from CO + H₂*. Chem. Comm., 746-747 (2003).
3. G. A. Cochran, B. Murchison, B. Craig, J.G. Quarderer and R. R. Stevens, *Preparation of ethanol and higher alcohols from lower carbon number alcohols*, U.S. Patent 4,825,013 (1989).
4. J. C. Duchet, M. E. van Oers, J. H. V de Beer, and R. Prins, *Carbon-supported sulfide catalyst*, J. Catal., **80**, 386-402 (1983).

5. R. Moene, F.W. Tazelaar, M. Makkee, and J.A. Moulijn, *Nickel-Catalyzed Conversion of Activated Carbon Extrudates into High Surface Area Silicon Carbide by Reactive Chemical Vapour Deposition*, *J. Catal.*, **170**, 311-324 (1997).
6. Kegong Fang, Debao Li, Mingguo Lin, Minglin Xiang, Wei Wei, Yuhuan Sun, *A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas*, *Catal. Today*, **147**, 133-138 (2009).
7. R.G. Herman, *Advances in catalytic synthesis and utilization of higher alcohols*, *Catal. Today*, **55**, 233-245 (2000).
8. C. S. Castro, M. C. Guerreiro, L. C. A. Oliveira, M. Goncalves, A. S. Anastácio, M. Nazzarro, *Iron oxide dispersed over activated carbon: Support influence on the oxidation of the model molecule methylene blue*, *Appl. Catal. A* **367**, 53-58 (2009).
9. Nguyen Tien-Thao, M. Hassan Zahedi-Niaki, Houshang Alamdari and Serge Kaliaguine, *Effect of alkali additives over nanocrystalline Co-Cu based perovskites as catalysts for higher-alcohol synthesis*, *J. Catal.*, **245**, 348-357 (2007).
10. Xianguo Li, Lijuan Feng, Lijun Zhang, Dady B. Dadyburjor and Edwin L. Kugler, *Alcohol Synthesis over Pre-Reduced Activated Carbon-Supported Molybdenum-Based Catalysts*, *Molecules*, **8**, 13-30 (2003).
11. F. E. Massoth. *Characterization of molybdena catalysts*. *Adv. Catal.*, **27**, 265-310 (1978).
12. S. Rajagopal, H. J. Marini, J. A. Marzari, R. Miranda. *Silica-alumina-supported acidimolybdenum catalysts-TPR and XRD characterization*. *J. Catal.*, **147**, 417-428 (1994).
13. P. Arnoldy, M. C. Franken, B. Scheffer, J. A. Moulijn. *Temperature-programmed reduction of cobalt monoxide-molybdena/alumina catalysts*, *J. Catal.*, **96**, 381-395 (1985).
14. Jamshid Iranmahboob, Hossein Toghiani, Donald O. Hill, *Dispersion of alkali on the surface of Co-MoS₂/clay catalyst: a comparison of K and Cs as a promoter for synthesis of alcohol*, *Appl. Catal. A* **247**, 207-218 (2003).
15. Debao Li, Cheng Yang, Ning Zhao, Huijie Qi, Wenhui Li, Yuhuan Sun, Bing Zhong, *The performances of higher alcohol synthesis over nickel modified K₂CO₃/MoS₂ catalyst*, *Fuel Processing Technology*, **88**, 125-127 (2007).

Corresponding author: **Nguyen Tien Thao**

Faculty of Chemistry, Hanoi University of Science, (VNU)
 19 Le Thanh Tong, Hoan Kiem, Hanoi, Vietnam
 Email: nguyentienthao@gmail.com