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Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Wu, Q., Chiarello, G. L., Christensen, J. M., Temel, B., Grunwaldt, J-D., & Jensen, A. D. (2012). Active carbon supported molybdenum carbides for higher alcohols synthesis from syngas. Abstract from SynFuel 2012, München, Germany.

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Active carbon supported molybdenum carbides for higher alcohols synthesis from syngas

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Summary : This work provides an investigation of the high pressure CO hydrogenation to higher alcohols on K₂CO₃ promoted active carbon supported molybdenum carbide. Both activity and selectivity to alcohols over supported molybdenum carbides increased significantly compared to bulk carbides in literatures. The optimal loadings of both molybdenum carbide and the K₂CO₃ promoter on active carbon have been investigated. The catalysts were characterized using BET surface area measurements, transmission electron microscopy and X-ray diffraction. Additionally, *in-situ* X-ray diffraction and *in-situ* X-ray absorption spectroscopy were applied for determining the carburization temperature and evaluating the composition of the carbide clusters of different samples through determinations of the Mo-C and Mo-Mo coordination numbers.

Keywords : active carbon; molybdenum carbides; higher alcohols; syngas;

Introduction

The synthesis of liquid fuels such as methanol, and higher alcohols from syngas have received a renewed attention for the production of fuels and fuel additives especially with syngas produced by gasification of biomass or coal [1-2]. Higher alcohols are more attractive as a fuels or fuel additive due to their better miscibility with hydrocarbon components, improved water tolerances and higher overall heating value compared to methanol [3]. Additionally, higher alcohols can be used as liquid carriers of hydrogen and dehydrated to olefin feedstocks used in the production of polymers. Alkali modified bulk molybdenum carbide has previously been shown to produce ethanol as the main alcohol product [4-5]. However, the bulk molybdenum carbide suffers from a low specific surface area, which results in low activity for CO hydrogenation [6]. It would therefore be interesting to identify a suitable support material for molybdenum carbide that can accommodate a larger specific surface area of the active material.

This work provides an investigation of the high pressure CO hydrogenation to higher alcohols on active carbon supported molybdenum carbide. The optimal loadings of both molybdenum carbide and the K₂CO₃ promoter on active carbon have been investigated. The catalysts are characterized using BET surface area, transmission electron microscopy (TEM), *in-situ* X-ray diffraction (XRD) and *in-situ* X-ray absorption spectroscopy (XAS).

Experimental

Molybdenum carbides supported on active carbon (AC) were prepared by temperature programmed reaction of supported molybdenum oxide precursors in a flow of 20 vol% CH₄ in H₂. These supported carbides were impregnated with an aqueous solution of K₂CO₃ with calculated amount. The performance of catalysts for the higher alcohol synthesis from syngas has been evaluated in a fixed-bed continuous-flow reactor with a GC-FID/TCD detection system (6890N from Agilent Technologies) [2,6]. A bubble flow meter was used for determination of the volumetric flow rate of the reaction effluent. Prior to the reaction, the supported carbides were *in-situ* treated with a 20% H₂ in N₂ flow (52 ml/min) at 350 °C for 2 h to remove a possible oxide passivation layer formed during air exposure. Typical reaction conditions were: P=100 bar; T=250-300°C; GHSV=5000 h⁻¹; Feed: H₂/CO=1 (v/v). To understand the carburization process *in-situ* XAS and XRD measurements at the Mo K-edge were performed at the HASYLAB/DESY and ESRF. The specific surface areas of both fresh and used catalysts were determined by N₂ adsorption at 77 K.

Results

Fig.1 shows the effect of the Mo₂C loading on the CO conversion and the CO₂-free selectivities at steady-state conditions. As mentioned above the bulk Mo₂C (100 wt% point in Figure 1) suffers from a low specific surface area, which results in low activity for CO hydrogenation [6]. The CO conversion and selectivities to different products varied with the Mo₂C loading on AC. 5.3 wt% Mo₂C/AC showed the highest methanol selectivity - up to 55.3 mol%. 21.2 wt% Mo₂C/AC exhibited the highest hydrocarbon (HC) selectivity. The selectivity

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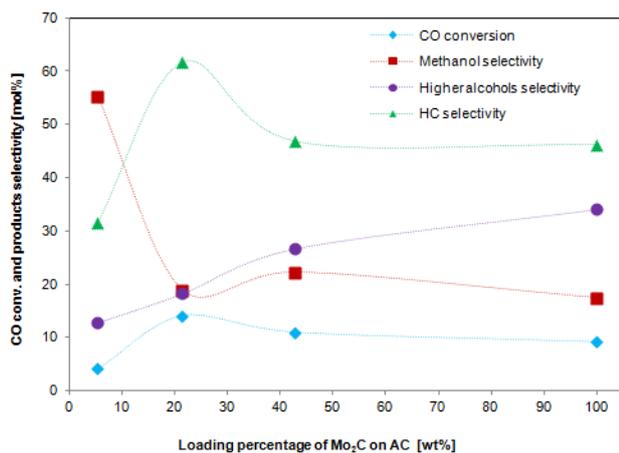


Fig. 1. The effect of Mo₂C loading (the molar ratio: K/Mo = 0.14) on CO conversion and the CO₂-free selectivity at steady state. P=100 bar; T=275°C; GHSV=5000 h⁻¹; Feed: H₂/CO=1 (v/v).

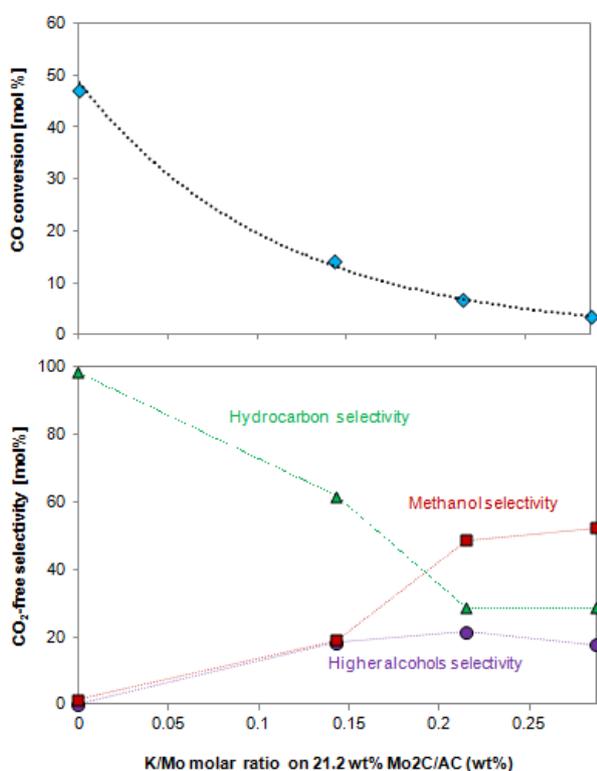


Fig. 2. The effect of K₂CO₃ loading on CO conversion and the CO₂-free selectivity at steady state, P=100 bar; T=275°C; GHSV=5000 h⁻¹; Feed: H₂/CO=1 (v/v).

to higher alcohols increased with increasing the Mo₂C loading on AC and reached a maximum with bulk carbides. The effect of the Mo₂C loading on the selectivity could be related to the composition of the supported carbide clusters. It was reported that MgO supported (5 wt%) Mo₂C showed higher coordination number (CN) of Mo-C(O) (CN = 5.1±1.7) than bulk Mo₂C (CN = 3) according to the results of *in-situ* extended X-ray absorption fine structure measurements [7]. The coordination numbers for active carbon supported clusters could thus be different from the CN's for the bulk carbide and this may be part of the explanation of the loading effect. The CO conversion showed a

maximum, when 21.2 wt% Mo₂C was loaded on active carbon. This indicated that this catalyst has the largest active surface area.

Additionally, for bulk Mo₂C it was observed that the selectivity to alcohols increased with increasing the K₂CO₃ content up to 10 wt% (the molar ratio: K/Mo = 0.14) and then stagnated [4]. Here, the molar ratios of K/Mo were kept as a constant 0.14 for all catalysts, but a dilution effect of the support should be considered. The amount of K₂CO₃ has a dramatic influence on the selectivity to different products, and the 21.2 wt% Mo₂C/AC catalyst exhibited the highest activity. Hence, the effect of the K₂CO₃ loading on the 21.2 wt% Mo₂C/AC catalyst as well. This is shown in Fig.2. Unpromoted Mo₂C/AC exhibited a high activity for CO conversion with HCs as the dominant products (>99 mol%). Upon addition of K₂CO₃ the overall CO conversion was reduced, while the product distribution shifted dramatically from HCs to alcohols. The increase in alcohol selectivity at the expense of HCs continued until the molar ratio of K/Mo = 0.22, where both the selectivity to higher alcohols and to alcohols in general reached a maximum.

Conclusions

The active carbon supported molybdenum carbide catalysts showed improved activity and alcohol selectivity compared to bulk carbides. Unpromoted Mo₂C/AC exhibited a high activity for CO conversion to Hydrocarbons as the dominant products with a trace amount of alcohols. The potassium carbonate promoter plays an essential role in obtaining alcohols rather than hydrocarbons. The optimum selective towards higher alcohols and to alcohols at a K/Mo molar ratio of 0.22. The effect of the molybdenum carbide loading on the selectivity could be related to the composition of the supported carbide clusters. The current work focuses on evaluating the composition of the carbide clusters of different samples by determining the Mo-C and Mo-Mo coordination numbers using *in-situ* XAS and XRD investigations.

Acknowledgements

The experimental work is financed by the Technical University of Denmark, Haldor Topsøe A/S, and the Danish Ministry for Science, Technology and Development under the "Catalysis for Sustainable Energy" initiative.

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