

The influence of the process conditions in the synthesis of higher alcohols from syngas over a $K_2CO_3/Co/MoS_2/C$ catalyst

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Introduction

High octane numbers make alcohols well suited as additives to or substitutes for oil derived gasoline. However the lower alcohols and particularly methanol suffer from a limited miscibility with gasoline. These miscibility problems can largely be avoided by including higher alcohols in the mixture, since the higher species act as co-solvents and stabilize the alcohol/gasoline blend [1]. Such a mixture of methanol and higher alcohols can be produced directly from syngas, and this process is considered as a possibility for converting biomass and/or coal into fuel chemicals via gasification. The alcohol synthesis can be conducted over various types of modified methanol [2] or Fischer-Tropsch synthesis catalysts [3]. Another interesting alcohol synthesis catalyst, which is the subject of the present study, is alkali promoted molybdenum sulfide – perhaps additionally promoted with Co or Ni [4]. The sulfide catalyst can potentially produce a significant amount of higher alcohols, while the main limitation for this catalyst is the alcohol selectivity, since there is a non-negligible side production of short-chained hydrocarbons. In the context of selectivity optimization the process conditions are of the utmost importance, and this is the subject of the present work.

This work investigates the influence of the process conditions upon the alcohol synthesis over a carbon supported $K_2CO_3/Co/MoS_2$ catalyst. As part of the investigation we have also evaluated the potential conversion of lower alcohols (methanol and ethanol) co-fed to the reactor along with the syngas feed. This could emulate a work-up of products from external sources (e.g. bioethanol) or a recirculation of part of the alcohol product. Also investigated is the effects of the water content in the syngas feed.

Materials and Methods

The experimental work is conducted using a $K_2CO_3/Co/MoS_2/C$ catalyst (2.71 wt% Co; 13.60 wt% Mo, 9.0 wt% K; BET area 526 m²/g; $d_{p,avg}$ = 1.4 mm) provided by Haldor Topsøe A/S. The catalyst is prepared in the oxide form, and prior to use the catalyst is sulfided in a flow of 2 vol% H₂S in H₂ at atmospheric pressure. The sulfidation is initiated at 100 °C, and the temperature is then raised to 300 °C at a rate of 3 °C/min. The sulfidation is sustained until no further sulfur uptake can be detected. The bed of catalyst is placed in a quartz tube contained inside a stainless steel pressure shell. As the inside of the quartz tube is pressurized, nitrogen is dosed to the pressure shell to ensure an equal pressure on both sides of the quartz tube wall. Gases are supplied from pressurized cylinders, while components, which are normally in liquid form, are pressurized by means of an HPLC pump, evaporated and mixed with the syngas feed. Product characterisation downstream of the reactor is conducted using a GC-FID/TCD detection system. Typical operating conditions are: P = 100 bar; T = 325 °C; GHSV = 5000 h⁻¹; Feed: 50 mol% H₂, 50 mol% CO.

Results and Discussion

The selectivity to alcohols is enhanced by increasing pressure and decreasing temperature. In the temperature range 275-350 °C an increasing temperature is also observed to promote chain growth. Presumably this is mainly due to the fact that conversion of already formed alcohols into higher species becomes increasingly important at higher temperature. Lower alcohols co-fed along with the syngas are certainly observed to be converted into higher species. This is illustrated in figure 1, which shows the production of various higher alcohols as a function of the ethanol concentration in the syngas feed.

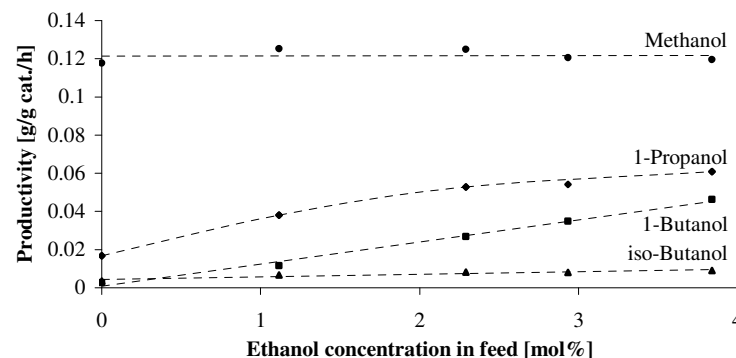


Figure 1. Production rates for different higher alcohols as functions of the ethanol concentration in the syngas feed. The experimental conditions are: T = 325.3 °C, P = 100 bar, GHSV = 5508 h⁻¹, Feed before ethanol addition: 49.1 vol % H₂, 50.9 vol% CO. Time on stream is +30 h.

Figure 1 shows that ethanol addition improves the production of higher alcohols, and an interesting point is that the effect upon 1-butanol is more pronounced than the effect upon 1-propanol. This might indicate that an important route to 1-butanol is coupling of C₂-species, which can be derived from ethanol. Figure 1 also shows that compared to the production of 1-butanol the production of iso-butanol is much less affected by the ethanol concentration.

Significance

This work is significant in relation to a potential industrial utilization of the process. Additionally some fundamental insight into the nature of the catalyst and the reaction mechanism may be inferred from the presented results.

References

1. Keller, J.L., *Hydrocarbon Process.* 58, 127 (1979).
2. Herman, R.G., *Catal. Today* 55, 233 (2000).
3. Courty, P., Durand, D., Freund, E. and Sugier, A., *J. Mol. Catal.* 17, 241 (1982).
4. Murchison, C.B., Conway, M.M., Stevens R.R. and Quarderer, G.J. in "Proceedings of the 9th International Congress of Catalysis" (Phillips, M.J. and Ternan, M. Ed.) Vol. 2 p. 626. Chemical Institute of Canada, Canada, 1988.