The methanol-higher alcohol synthesis over Cs-Cu/ZnO/Al2O3 and Cu/Co/ZnO/Al2O3 catalysts
Breman, Berthold Berend

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

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

Publication date:
1996

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Breman, B. B. (1996). The methanol-higher alcohol synthesis over Cs-Cu/ZnO/Al2O3 and Cu/Co/ZnO/Al2O3 catalysts. s.n.

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 12-02-2020
SUMMARY

Methanol is an important base chemical. Nowadays it is produced from synthesis gas (a mixture of CO, H₂ and CO₂) via a gas-solid process, characterized by passing synthesis gas through a reactor packed with Cu/ZnO-based catalyst particles at pressures from 50 - 100 bar and temperatures from 200 °C to 300 °C. A gas-slurry process, where the synthesis gas is passed through a suspension of small catalyst particles in an inert high-boiling liquid, may be an attractive alternative.

Methanol is increasingly more applied as an octane booster in gasoline in order to replace lead containing compounds to the benefit of the environment. Especially in Germany and the U.S.A. there is a strong belief that methanol can be also utilized as an economically competitive straight-run vehicle fuel, offering substantial strategic and environmental advantages. However, at least 15 volume % regular unleaded gasoline has to be added to methanol in order to avoid technical problems. Unfortunately, methanol-gasoline blends show phase separation at low temperatures, which is disastrous for its practical application. This poor low-temperature phase stability is improved by adding higher alcohols to the methanol-gasoline blends, where the higher alcohols act as a co-solvent for methanol.

Higher alcohols can be produced via classical petrochemical processes. However, it is probably much more attractive to produce higher alcohols and methanol simultaneously from synthesis gas by implementation of a suitable catalyst in a modified gas-solid (or gas-slurry) methanol process. Currently, two types of catalyst systems are mainly of potential industrial interest, i.e. alkali-promoted and cobalt-modified Cu/ZnO/Al₂O₃ methanol catalysts. Kinetic information is essential in designing a methanol-higher alcohol process and to study its feasibility. Therefore, the main objective of this thesis is to study the kinetics of the methanol-higher alcohol synthesis over both a Cs-promoted Cu/ZnO/Al₂O₃ - and a Cu/Co/ZnO/Al₂O₃ catalyst.

Reaction mechanisms relevant for the methanol-higher alcohol synthesis are reviewed in Chapter 2. Reaction mechanisms for the methanol synthesis and the water-gas-shift reaction over Cu/ZnO-based catalysts appear to be relatively well established. The higher alcohol synthesis over Cu/ZnO-based catalysts can proceed via an aldol condensation or a CO-insertion mechanism. No reaction mechanisms are available for the simultaneous formation of hydrocarbons. CH₂-insertion in metal-alkyl bonds is proposed as the mechanism for chain growth over Cu/Co/ZnO-based catalysts. Subsequent hydrogenation/dehydrogenation or CO₂ addition form higher alcohols.

Chapter 3 presents the methanol synthesis over a Cs-Cu/ZnO/Al₂O₃ product. Further, data on methyl esters, n-paraffins, CO₂, and higher alcohols, olefins and 1-octene is presented to predict the measurements and do not include the network, taking the predictions of all models with especially pressures and high temperatures. The higher alcohol formation increases with increasing temperatures for low H₂/CO ratios (approximately 0.2). Carbon conversion rates increases with increasing H₂/CO ratio. The Cu/Co/Cu/ZnO catalysts; however, have a slower higher alcohol:hydrocarbon ratio.

Chapter 4 deals with the methanol synthesis over a Cu/ZnO catalyst, whereas higher 1-alkanols, 1-alkenes, n-paraffins, CO₂ and co-products are presented. Literature models apply to predict the measurements and do not include the network, taking the predictions of all models with especially pressures and high temperatures. The resulting model proves to be superior to the existing model predictions of all measurements.

Carbon conversion rates increases with increasing temperature, as well as with increasing H₂/CO ratio. The Cu/Co/Cu/ZnO catalysts; however, have a slower higher alcohol:hydrocarbon ratio.

The kinetics of the methanol-higher alcohol synthesis over a Cs-Cu/ZnO/Al₂O₃ catalyst is presented in Chapter...
dehydrogenation or CO-insertion results in the formation of paraffins/olefins or higher alcohols, respectively.

Chapter 3 presents kinetic data for the gas-solid methanol-higher alcohol synthesis over a Cs-Cu/ZnO/Al$_2$O$_3$ catalyst. Methanol appears to be the main product. Further, dimethyl ether, higher 1-alcohols, 2-methyl-1-alcohols, methyl esters, n-paraffins, CO$_2$ and H$_2$O were formed. Literature models appear to predict the measured product distribution of the alcohols only moderately and do not include the simultaneous formation of hydrocarbons. A new reaction network, taking the latter into account, is proposed. The resulting model proves to be superior to all existing literature models and gives accurate predictions of all measured product distributions. Catalyst deactivation turns out to be especially serious for the production of higher alcohols. High pressures and high temperatures appear to result in high carbon conversion rates. The higher alcohol:methanol ratios in the product gas increase with increasing temperatures and decreasing space velocity, whereas high pressures, low H$_2$/CO ratios and low CO$_2$ concentrations favour high higher alcohol:hydrocarbon ratios.

Chapter 4 deals with the kinetics of the gas-solid methanol-higher alcohol synthesis over a Cu/Co/ZnO/Al$_2$O$_3$ catalyst. Methanol was the main product, whereas higher 1-alcohols, 2-methyl-1-alcohols, methyl esters, n-olefins, n-paraffins, CO$_2$ and H$_2$O were analyzed as secondary products. The available literature models appear to predict the measured product distributions of the alcohols, olefins and paraffins poorly, because of the assumption of a single growing carbon chain at the catalyst surface only. A new reaction network, based on the presence of three different growing carbon chains, is proposed. The resulting model is shown to predict the measured product distributions accurately. The catalyst turns out to be reasonably stable within 2500 hrs. Carbon conversion rates appear to increase with increasing pressure and increasing temperature. The higher alcohol:methanol ratios are hardly affected by the process conditions, whereas the higher alcohol:hydrocarbon ratio increases with increasing pressure, increasing temperature and decreasing H$_2$/CO ratio. The Cu/Co/ZnO/Al$_2$O$_3$ catalyst turns out to be less suitable for the methanol-higher alcohol synthesis than the Cs-Cu/ZnO/Al$_2$O$_3$ catalyst (see Chapter 3), because of relatively low carbon conversion rates and relatively low higher alcohol:hydrocarbon ratios.

The kinetics of the gas-slurry methanol-higher alcohol synthesis over a Cs-Cu/ZnO/Al$_2$O$_3$ catalyst, concluded in Chapter 4 to be the best catalyst, is presented in Chapter 5. The product distribution model proposed for the
gas-solid system in Chapter 3 also predicts the measured gas-slurry product distributions accurately. The presence of n-octacosane as a slurry liquid appears to affect the product distributions and the catalyst aging patterns substantially. However, the catalyst performs less in the slurry relative to the gas-solid system, because of lower carbon conversion rates, lower higher alcohol:methanol ratios and lower higher alcohol:hydrocarbon ratios.

From the above Chapters the gas-solid process, using a Cs-Cu/ZnO/Al₂O₃ catalyst, appears to be the most attractive for the methanol-higher alcohol synthesis. Its "long-term" performance in an integral fixed-bed reactor regime under constant, industrial attractive process conditions (300 °C, 70 bar, H₂/CO = 1) is the subject of Chapter 6. The catalyst showed a reasonable stability with a deactivation of about 15 % in 310 hrs. The selectivities were 0.49, 0.15, 0.094, 0.046 and 0.22 to methanol, higher alcohols, hydrocarbons, other oxygenates (mainly dimethyl ether + methyl esters) and CO₂, respectively, at a CO conversion of 25 %. The differential reactor regime model of Chapter 3 appears to give also reasonably accurate predictions for the integral reactor regime, despite the high CO conversions.

The possible impact of the results obtained in this thesis are qualitatively discussed in Chapter 7. For the time being, the gas-solid process, using a Cs-Cu/ZnO/Al₂O₃ catalyst in a (close to isothermal) multi-tube reactor at a temperature of ± 573 K, a pressure of ± 70 bar, a space velocity of ± 0.4×10⁻³ Nm³ kg⁻¹ s⁻¹ and a H₂/CO ratio of ± 1, is concluded to be close to optimal for the methanol-higher alcohol synthesis. Based on the carbon conversion rates, a methanol-higher alcohol reactor has to be about three times larger than a low-pressure methanol reactor at similar production capacity. A further modification needed in the synthesis loop relative to the methanol process is the removal of CO₂ from the recycled product gas. A preliminary estimate shows that a methanol-higher alcohol mixture can be produced for a price, which is about a factor 1.4 higher than the price of pure methanol (per kg). For comparison, this factor is 2.6 for methyl tertiar butyl ether (MTBE: applied as an octane booster in gasoline), and ranges from 3.5 - 7 for pure C₃+ alcohols produced via classical petrochemical processes. Hence, both the production of a methanol-higher alcohol mixture as well as the co-production of methanol and pure higher alcohols via a gas-solid process, using a Cs-Cu/ZnO/Al₂O₃ catalyst, seem to be economically feasible. Further improvement of both the catalyst stability and selectivity are key parameters in improving the feasibility of the methanol-higher alcohol production process.