Kinetic study of methanol by-products formation on an industrial catalyst under real reaction conditions.

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Highlights

- 1660 experimental conditions were tested under a wide set of industrial relevant reaction conditions using different feedstocks.
- All conditions were fitted in one model customizing literature models.
- The main reagents and products fitting error is <15%.
- The main byproducts (CH_3CH_2OH, CH_4, DME, MF) fitting error is <30%.

1. Introduction

Methanol is an important feedstock for the production of many chemicals such as formaldehyde, acetic acid, methyl tert-butyl ether, and chloromethane. For this reason, methanol synthesis has an important industrial relevance and the study of the kinetic of this reaction is an important tool in the design and optimization of the process. Methanol is mainly produced at high temperature and pressure using copper-zinc based catalyst. Carbon monoxide, carbon dioxide, and hydrogen are the mixture feed used for this reaction, which may result from different production processes such as CH_4 steam reforming, carbon gasification or renewable sources. For this reason, the efficiency of the process and the formation of by-products are strongly dependent on all the parameters mentioned above. Therefore, the development of a kinetic model to understand the phenomena that regulate the methanol synthesis and to predict by-product formation is of crucial importance.

2. Methods

In this study, the goal was to achieve a kinetic model that could be adaptable at a wide range of operative conditions: 1660 experimental test were performed under a wide range of industrial relevant experimental conditions. Four coal gasification, four natural gas steam reforming, four green MeOH and one ATR feed were tested with temperatures from 190 to 310°C, pressures from 70 to 85 bar and space velocity in the range 6600-60000 1/h. To study the kinetics at the catalyst half-life, a high temperature pretreatment of the catalyst was done. To account for catalyst deactivation the catalyst activity was followed overtime at fixed conditions to scale the reaction rates accordingly for each experimental condition. The reactor used for this study was a Rotoberty CSTR reactor, that allowed to study the kinetics using full pellets and minimizing the mass transport limitation. All species (H_2, CO, CO_2, N_2, CH_3OH, H_2O, CH_3CH_2OH, CH_4, DME, MF, acetone, higher alcohols, etc) were monitored by Gas Chromatography. The experimental results were fitted iteratively with literature models [1-3] that were adapted to achieve a better fitting.

3. Results and discussion

Figure 1 reports the fitting of the experimental campaign with the kinetic model developed during this study. In figure are reported the main products and by-products of the methanol synthesis reaction, the

reactants, here not reported had a fitting error below 5%. The main products (methanol and water) achieved a fitting error below 15%.
In the case of the main by-products as ethanol, dimethyl ether and methyl formiate, the model shows a better agreement at low concentration, while at higher concentration it needs to be further defined.

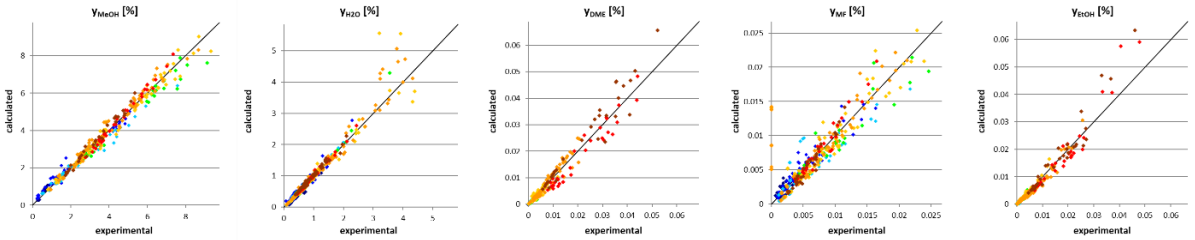

Figure 1 Fitting of CO, CO_2, MeOH, DME, EtOH and MF yield with the developed kinetic model

All conditions were fitted in one model customizing literature models, The main reagents and products fitting error is <15%; the main byproducts (CH_3CH_2OH, CH_4, DME, MF) fitting error is <30%.

4. Conclusions

The study presented in this work has considerable industrial importance since it can allow the implementation of a reactor design basis and it can guarantee precisely the byproducts formation. Therefore, it gives a new tool to improve industrial operative conditions and optimize the design of the synloop and the purification section in a wide set of industrial conditions.

References

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Keywords
Methanol; Kinetics; Byproducts