Investigation of the catalytic activity under green methanol operating conditions

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Highlights

- Dynamic operations simulating fluctuating renewable energy were utilized to benchmark catalysts for green methanol synthesis
- 4 commercial catalysts were compared to assess the best performances in terms of methanol production, byproducts formation and catalyst deactivation
- Results showed how the CO_2 affects the catalyst life and performances under fluctuating conditions

1. Introduction

The exponential increase of CO_2 in the atmosphere is causing the increase of the average temperature of Earth [1]. This leads to several serious effects such as more frequent droughts. In view of this,, governments agreed to mitigate global warming by decreasing the net CO_2 emissions, with goal to achieve carbon neutrality [2]. A viable route to achieve this is the consumption of CO_2 to produce useful chemicals, such as Methanol. Methanol is a fundamental building block of the chemical industry, being the precursor of several industrial organic compounds and today is produced starting from syngas (CO+ CO_2+H_2). In this view, there is the need to study the performance of catalyst during green-methanol production, to allow the design and optimization of industrial converters and methanol refinement units [3]. The goal of this work is the assessment of the activity of 4 commercial catalysts under green MeOH conditions, to achieve a deep understanding of: 1) methanol productivity; 2) by-products formation; 3) operating conditions and catalyst deactivation; and 4) the operative costs of green MeOH converters.

2. Methods

A packed bed reactor, placed in an electric furnace was used. The catalytic bed's axial temperature profile was measured by a multipoint thermocouple. Bottles of pure CO_2, N_2 and H_2 (Purity Grade 4.5) were used as feedstock. H_2 and N_2 were further purified from water traces and together with CO2 from oxygen. Mass flow controllers were used to dose the gases to the inlet of the reactor.

An internally developed LabVIEW program was used to log and program the experimental conditions. Online micro-GC measurements were performed to detect and quantify CO_2, H_2, N_2, MeOH, CO, H_2O and by-products at the outlet of the reactor as a function of time. Since during this reaction the number of moles changes, N_2 was used as internal standard to perform mass balances.

Pure CO_2 is provided as a liquid with a pressure below 55barg since this pressure is the vapor liquid equilibrium one at ambient temperature. Catalytic tests were performed above 55barg. A dedicated setup was built to rise pure CO_2 up to more than 100barg. This allows to flexibly set the overall composition of the mixture in a wider range of pressure.

The investigated operating conditions are aligned to the possible industrial operating conditions of green Methanol (g-MeOH) converters. The performance and deactivation with time of catalysts suitable for this application were studied in different operating conditions. In particular, the dependence of the catalyst performance on i) the catalyst bed temperature, ii) Gas Hourly Space Velocity (GHSV), iii) inlet gas feed compositions were studied.

3. Results and discussion

4 catalysts were tested to compare their relative performance. The composition of the mixture, GHSV and catalytic inlet bed temperature were changed to understand the effect of each parameter on the performance of the catalysts. The performances of the catalysts are monitored considering not only the methanol productivity but considering all the byproducts with particular attention to by-products such as DME and ethanol that are fundamental for the sizing of the crude methanol refinement units.

Moreover, the activity of the catalysts was investigated by performing the same experimental campaign on all the catalysts and repeating several times the same operating condition (Figure 1). Catalyst C showed a superior stability over time compared to the other investigated catalysts.

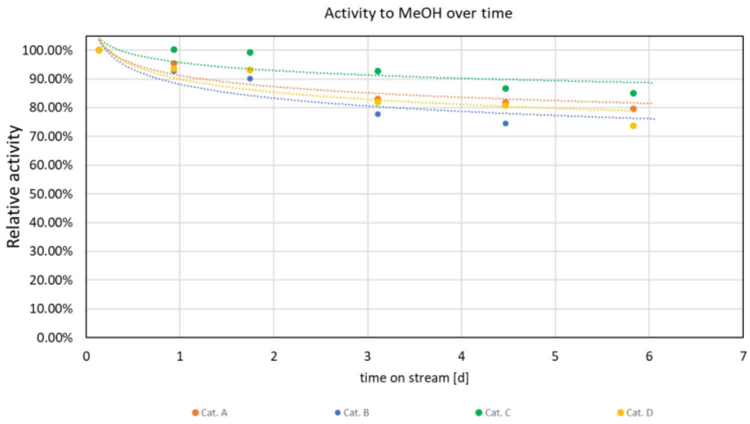

Figure 1. Relative activity, estimated in terms of MeOH concentration, is plotted against the time on stream for the 4 investigated catalysts.

Based on the results obtained it is possible to define the conditions and instrumentation to be used in the design of green MeOH plant. Moreover, experimental results can be used to develop procedures that may support troubleshooting and operations in green MeOH plants.

4. Conclusions

This study provided new insights in the behavior of Methanol synthesis catalyst under green operating conditions. The results obtained will support the improvement of the industrial operating conditions, allowing to identify problems in real plant and helping to act in a due time to preserve the catalyst and the production of methanol. This work paves the way towards the design and optimization of industrial scale reactors and plants for green Methanol production.

References

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Keywords

Methanol; Green Methanol; Catalyst deactivation