

Catalytic membrane contactors for methanol conversion to dimethyl ether

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Highlights

- Methanol dehydration to dimethyl ether on zeolite and γ -Al₂O₃ catalytic membranes.
- Analysis of the effect of support of the zeolitic membranes, used as contactors.
- No irreversible drops in performance during long-term analysis.

1. Introduction

Dimethyl ether (DME) is considered one of the most promising alternative fuels of the future because it can be used as a clean high-efficiency compression ignition fuel with reduced emissions of NO_x, SO_x and particulate matter. So far, methanol dehydration is regarded as the most mature route for producing DME, by using different solid acid catalysts such as acid zeolites. Alumina-based catalysts have been widely studied at lab-scale for this reaction at a high temperature because of their high selectivity toward DME in addition to their low cost, thermal and mechanical stability and high selectivity to DME. However, γ -Al₂O₃ suffers the presence of water, owing to the blocking of the active sites [1]. In alternative, zeolites (mainly ZSM-5 and BEA) revealed better stability to water than γ -Al₂O₃ and good conversion and selectivity. Nevertheless, the zeolite catalysts promote other reactions above 250°C, among which also the coke formation [2]. On the light of this considerations, it is still a considerable challenge to develop new strategies to simultaneously enhance the reaction conversion and selectivity, limiting phenomena such as catalyst deactivation induced by water presence.

In this work, we used a catalytic zeolite membrane reactor as a contactor for DME production by MeOH dehydration. The membrane reactor was used in “through flow” configuration, thus letting pass the whole feed through the membrane and having only the permeate as outlet stream. This choice was done considering that the passage of a continuous flow through the catalytic membrane could promote the removal of water from catalytic sites, reducing the catalyst deactivation that is usually observed in traditional catalytic beds. The results were compared with that obtained using a γ -Al₂O₃ membrane in the same configuration, and traditional catalysts, aiming at investigating the effective advantages offered by the use of membranes in terms of MeOH conversion and yield, DME selectivity and stability in time.

2. Methods

The tubular ZSM-5 and γ -Al₂O₃ supported membranes were supplied by Fraunhofer – IKTS. The performance of each membrane contactor was analysed as a function of temperature (150-300° C), feed pressure (120-300 kPa), WHSV (0.4-13.3 g_{MeOH} g_{Catalyst}⁻¹ h⁻¹) and feed composition (25-100%mol MeOH).

3. Results and discussion

At all the investigated conditions, ZSM5-Al₂O₃ and ZSM5-TiO₂ membrane reactors exhibited full DME selectivity. ZSM5-Al₂O₃ membrane behaved better than ZSM5-TiO₂, reaching a conversion up to 1.5 times greater. The best performance was achieved at 200°C and 0.7 h⁻¹, obtaining a conversion of 86.6%, very close to equilibrium one (Figure 1). At 200 °C, despite the difference in acidity with TR, ZSM5-Al₂O₃ membrane leads to a higher conversion with respect to the other two reactors, whereas this effect seems to disappear at 220 °C as the performance of TR was slightly better than the catalytic membrane reactors. However, it needs to be considered that the measurements were carried out at a slightly different WHSV (Figure 2). Comparing the two membrane reactors, the conversion obtained with the ZSM5-Al₂O₃ membrane reactor was about 1.8 and 1.3 times greater than that achieved with the ZSM5-

TiO₂ membrane at 200 and 220 °C, respectively. This enhanced conversion can be ascribable to an additional catalytic activity exerted by the Al₂O₃ support, which further promoted the conversion with respect to the membrane supported by TiO₂. A full DME selectivity was obtained with both MRs, contrarily to what reported for TR which selectivity was 96-97%. Contrarily to what happens in a traditional reactor, the catalytic membrane configuration operated in through flow is such that the catalyst is continuously exposed to a permeating flux. This can limit the deactivation of the catalytic sites, promoting the continuous removal of reaction products (DME and water) and depleting the secondary reactions.

The conversion of methanol to DME in the membrane contactor equipped with γ -Al₂O₃ membrane reached a conversion of 85%, at 300°C and 0.4 h⁻¹, and a selectivity towards DME always higher than 90%. Stability measures on this membrane showed stable performance up to 15 hours and the possibility to fully restore the membrane under N₂ flux for 24 hours.

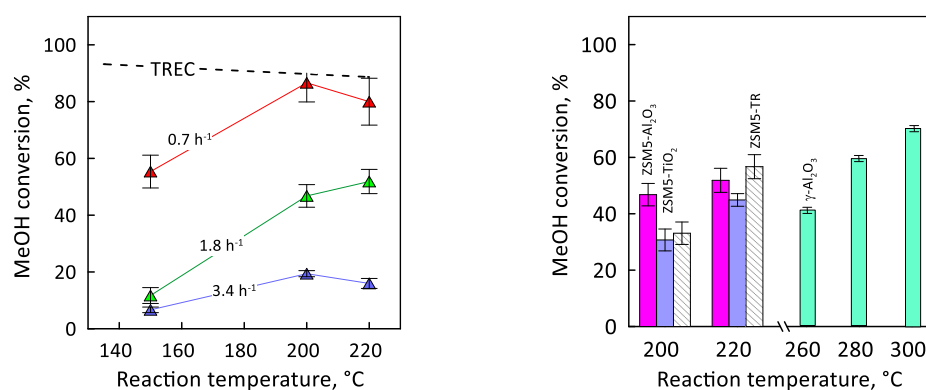


Figure 1. MeOH conversion as a function of the temperature in (left-side) ZSM-5/Al₂O₃ membrane reactor at different WHSVs and (right-side) for the three MRs and a TR (adapted from [1]). Feed pressure = 120 kPa. Feed MeOH, only.

4. Conclusions

Zeolite-based and γ -Al₂O₃ membranes showed good performance: high selectivity towards DME and methanol conversion, most likely as an effect of the continuous exposition of the catalytic layer to a gas flow, which favours the removal of species (i.e. water) from catalytic sites, thus limiting catalyst deactivation. The stability analysis of the different membranes investigated showed that overall membrane contactor configuration guarantees longer stability with respect to packed bed reactors, with the possibility to use the same membrane for months with periodic restoring without showing irreversible drops in performance.

References

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“Methanol dehydration, Catalytic membrane reactor, DME, Membrane contactor”.