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Separation enhanced methanol and dimethyl ether synthesis

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Separation enhanced reaction processes are promising process intensification strategies for carbon dioxide utilisation. In recent years, major improvements have been made in adsorption and membrane technology for the direct production of methanol and dimethyl ether from carbon dioxide rich feedstock and hydrogen. *In situ* water removal results in high single-pass conversions, thereby circumventing the disadvantages of conventional routes, such as the low carbon efficiency, energy intensive downstream separation and large recycles. *In situ* water removal by adsorption results in extremely high single-pass conversion and yield, especially in direct DME production. Membrane reactors allow for high single-pass conversion and yield, especially for methanol production. Here, we highlight recent advances in membrane and adsorption-enhanced synthesis of methanol and DME.

Methanol and dimethyl ether (DME), the simplest ether and the dehydrated form of methanol, are valuable platform chemicals and synthetic fuels. They are expected to play an important role in the energy transition, where fossil-based fuels and chemicals have to be replaced by products from renewable feedstock, including switching to bio-based feedstock and the chemical recycling of carbon dioxide.[1] However, the conventional production processes are limited starting from CO_2, and therefore considered unattractive.[2,3] As for many other industrial CO_2 utilisation processes a main hurdle is the production and efficient handling of steam.[1,4,5] Steam separation enhancement is shown to be a promising route for CO_2 conversion.[4] The concept of separation enhancement is based on Le Chatelier's principle, where an equilibrium limited reaction is shifted to enhance conversion by selectively removing reaction products, and is mainly utilised for various processes and products considering CO_2 separation.[6,7] The recent review and outlook by van Kampen *et al.* (2019) addressed the opportunities of adsorptive and membrane reactors for CO_2 utilisation processes, discussing the advantages and the future developments for both technologies. Crucial aspects discussed are the hydrothermal stability of the membranes and their permselectivity, whereas high temperature working capacities and heat management are crucial aspects for reactive steam adsorption processes.[4]

Thermal stability of polymer membranes limits their temperature of operation, requiring more active low temperature catalysis, a topic which also gained a lot of attention in the recent years. While zeolite membranes have been shown to outperform the other membrane types in steam permeance and selectivity at higher temperatures, their stability, mainly associated to defects, remains a point of attention. Recently Li *et al.* (2020) have created a defect-free zeolite (NaA) membrane and have shown its performance in a membrane reactor for CO_2 conversion to methanol.[8] Indeed, Fig. 1 illustrates the important progress made in membrane reactors for methanol synthesis from 2004 (zeolite), to 2015 (polymer), to 2020 (zeolite).[8–10] Gallucci *et al.* (2004) have shown good performance of a zeolite membrane reactor. The CO_2 conversion was higher than for a traditional reactor at similar conditions, but the improvement remained modest with a yield of 8.7%.[9] In the CARENA project (2011–2015) polymer membranes have been developed and tested for their eased production and lower costs

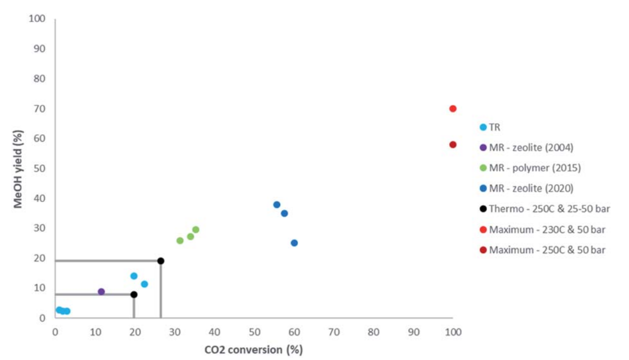

Fig. 1 Comparison of CO_2 conversion and methanol yield for membrane reactors (MR) with results for traditional reactors (TR). TR: light blue.[9,11] MR (2004): purple.[9] MR (2015): green.[10] MR (2020): dark blue.[8] Thermodynamic equilibrium at 250 °C and 25–50 bar: black. Theoretical maximum at 230–250 °C and 50 bar: red.

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compared to zeolite membranes. Although limited by lower operating temperatures and therefore reduced catalyst activity, thermodynamic equilibria for traditional methanol synthesis have been exceeded by measured yields up to 30%.[10] In Fig. 1 also the maximum single-pass methanol yield is shown. A fundamental limit exists in the maximum methanol yield that can be achieved using separation enhancement, because even though the synthesis of methanol from CO is also equilibrium limited, it does not produce water. Therefore, even by removing all water and achieving full CO_2 conversion, a mixture of methanol and CO will remain, of which the composition is dictated by thermodynamics. Ongoing research should lead to improving cost efficiency, focusing on the large scale production of defect-free zeolite membranes, improved selectivity and permeance of cheaper polymer membranes, and improved operation and system integration.

In the direct synthesis of DME a maximum single-pass yield of 100% could theoretically be achieved by removal of all by-product water (Fig. 2). The developed NaA zeolite membrane reactor was also demonstrated in the direct production of DME from CO_2, achieving a single-pass conversion up to 73% and a DME yield up to 54.5%.[11] In parallel, sorption enhanced technology for the production of DME has been developed and scaled up in recent years.[4,12–18] Interestingly, the most promising materials for high temperature steam adsorption are again LTA-type zeolites. LTA zeolites, and specifically 3A, are highly selective for water due to size exclusion by the limited pore size.[14] Whereas the preferential permeation of polar molecules (water and methanol) is observed for various zeolitic membranes (FAU and MFI) and can be explained by a preferential adsorption mechanism rather than a size exclusion mechanism.[4] The recent experimental validation of pressure swing regeneration in sorption enhanced DME synthesis (SEDMES), already demonstrating a factor four increase in productivity, has opened up further process optimisation by cycle design.[13,15] For sorption enhanced DME synthesis from CO_2, conversions up to 99% and DME yields of up to 82% have been reported.[4] Adsorption technologies are very well suited for steam level reductions as low as trace amounts, thereby maximising CO_2 conversion. The product distribution consists of DME and some remaining, unconverted CO. As illustrated by the methanol synthesis, an equilibrium between methanol and CO remains even at dry conditions and consequently for conversion of the remaining CO to DME even deeper drying is required. Although the concept of sorption enhanced methanol synthesis has been demonstrated by several authors, the performances are limited, obtaining more CO than methanol, and more research is required to assses the suitability of the process.[19,20] Ongoing research, ultimately improving the cost efficiency, focuses on cycle design, i.a. faster cycling, improved operating conditions, closely linked to the system integration.

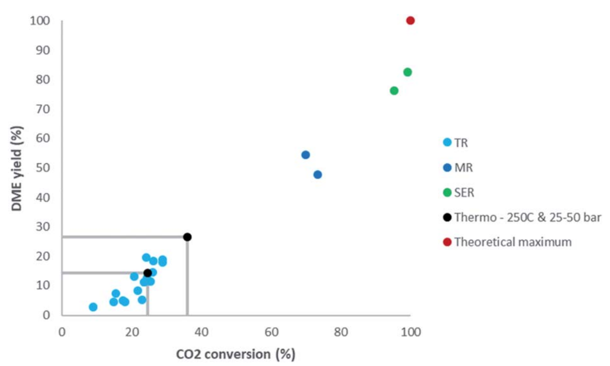

Fig. 2 Comparison of CO_2 conversion and DME yield for sorption enhanced reactors (SER) and membrane reactors (MR) with results for traditional reactors (TR). TR: light blue.[11] MR: dark blue.[11] SER: green.[4,15] Thermodynamic equilibrium at 250 °C and 25–50 bar: black. Theoretical maximum: red.

In conclusion, recent developments in separation enhanced reaction processes using membranes and adsorbents, have proven their potential for carbon dioxide conversion to methanol and DME. Both technologies outperform traditional reactor concepts, achieving single-pass conversions far beyond equilibrium. *In situ* water removal by adsorption allows deep drying and results in extremely high single-pass conversion and yield, especially in DME production. Membrane reactors allow for high single-pass conversion and yield, especially for methanol production. Techno-economic and life cycle analyses of the various, suitable process intensifications, such as adsorption and membranes processes, but also condensation and absorption processes for methanol synthesis,[21–24] would allow for the appropriate reactor selection for a specific case.

Conflicts of interest

There are no conflicts to declare.

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