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COMMUNICATION

High Yield Direct Synthesis of Dimethyl Ether from CO_2 and H_2 in Dry Reaction Environment

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Direct dimethyl ether (DME) synthesis from CO_2 and H_2 is considered as a promising production route. However, this process is thermodynamically and kinetically restricted by byproduct water. In this study, the water-conduction membrane was incorporated to the direct DME synthesis reactor to generate a dry reaction environment. At the absence of water, the activities of CO_2 hydrogenation catalyst (CZA) and methanol dehydration catalyst (HZSM-5) were boosted 4 and 10 times, respectively, and the single-pass CO_2 conversion up to 73.4%, far beyond the equilibrium, and DME yield up to 54.5% were obtained. Moreover, well protected catalysts against fast deactivation were demonstrated.

Dimethyl Ether (DME) is the simplest ether and has been considered as a prospective “future fuel” for replacing diesel[1,2] or blending with liquefied petroleum gas (LPG) for automotive and cooking applications,[2,3] due to its desirable properties, including high cetane number of 55, low auto-ignition temperature,[4] high thermal efficiency of combustion, low emissions of NO_X and CO, and ease of transportation that is compatible to the existing infrastructure for LPG. Besides, DME can also be used to produce a variety of chemicals, such as diethyl sulphate, oxygenates, olefins and gasolines.[5,6] The global market size of DME was projected to be USD 9.7 Billion by 2020, and thus, the synthesis of DME gains increasingly academic and industrial attention in the past decades.[7–9]

DME can be produced in two routes, indirect synthesis from methanol (MeOH) dehydration and direct synthesis from syngas (CO and H_2) or CO_2 and H_2. Due to the increased concerns of CO_2 concentration raise in the atmosphere and demands for renewable fuels [10–12] and the higher intrinsic reaction rate of CO_2 hydrogenation than CO hydrogenation,[13,14] direct DME synthesis from CO_2 and H_2 is deemed as a promising synthesis route and one of the core technologies for CO_2 utilization.[15–18] Furthermore, as shown in the equations in Figure 1, the in-situ dehydration of MeOH to DME in the reactor leads to further conversion of CO_2 and eliminates the process of MeOH purification. Therefore, the direct synthesis route is thermodynamically and economically advantageous over the indirect synthesis route.

Currently, DME synthesis from CO_2 and H_2 is focused on optimizing the catalysts to enhance reaction rate and MeOH and DME selectivity while maintaining a good stability, and very promising results have been demonstrated.[2,19] However, the reported CO_2 conversion and DME yield were still low, for example, less than 30% CO_2 conversion (Table S1),[5,20,29–32,21–28] mainly due to the severe kinetic and thermodynamic restrictions imposed by the byproduct water. Furthermore, water also deactivates the catalysts by sintering the active sites of CO_2 hydrogenation catalysts and deteriorates the MeOH dehydration catalysts, for example, zeolite HZSM-5, at the high-temperature and high-pressure reaction conditions.[25] Therefore, it is crucial to create a dry reaction environment by fast and effective water removal from the reaction system. A

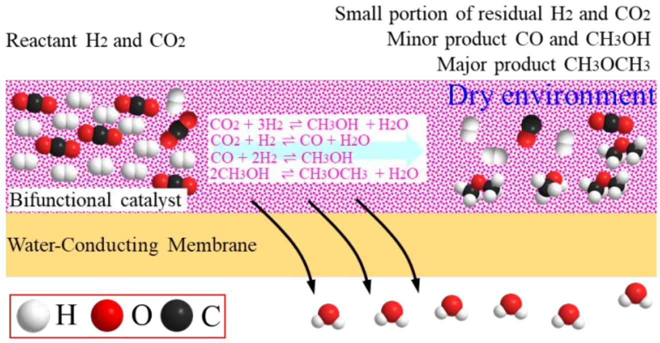

Figure 1. Schematics of high yield direct synthesis of renewable DME from CO_2 and H_2 in dehydration MR.

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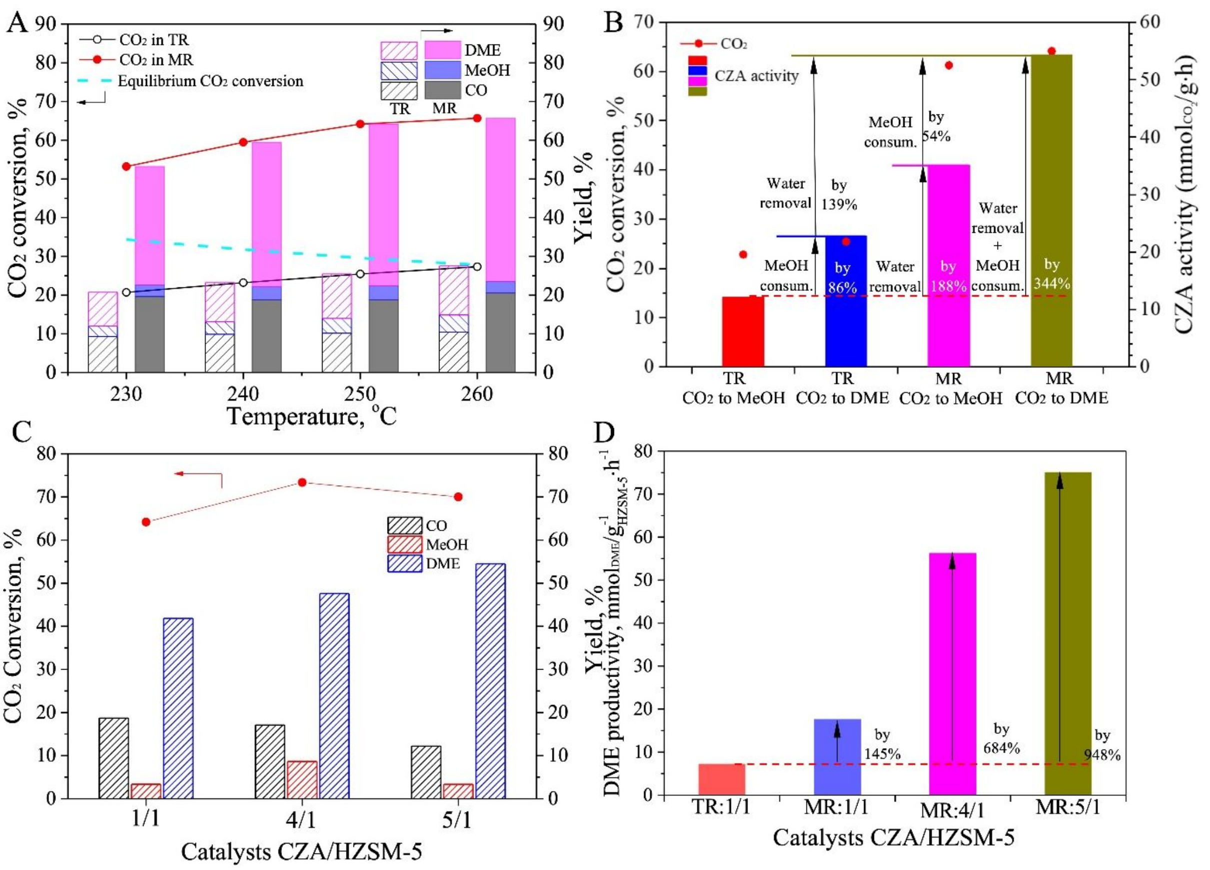

Figure 2. Catalytic performances of direct DME synthesis from CO_2 and H_2 in dehydration MR. A: Comparisons of catalytic results (CO_2 conversion: point; product yield: column) in TR and MR at 35 bar and different temperatures; CZA/HZSM-5=1/1. B: CO_2 conversions and CZA activity on converting CO_2 in 4 reactor configurations; mass ratio of CZA/HZSM-5=1/1. C: CO_2 conversions (point) and product yields (column) of DME synthesis on bifunctional catalysts in MR with different mass ratios of CZA/HZSM-5 at 250 °C and 35 bar. D: DME productivity on HZSM-5 in TR and MR with different bifunctional catalysts mass ratios at 250 °C and 35 bar. Membrane length: 45 mm; GHSV: 4,200 $L\cdot kg_{cat}^{-1}\cdot h^{-1}$.

dehydration membrane that can exclusively remove water in-situ from but retain other reaction components within the reaction system, therefore, is ideal for creating such a desired dry reaction environment to greatly enhance the efficiency of direct DME synthesis from CO_2 and H_2. A few simulation studies had investigated the merits of a membrane reactor (MR) on promoting the DME synthesis from CO_2 and H_2.[33,34] However, no experimental results have been reported because of the high requirements for such dehydration membranes and the harsh conditions of high-temperature and high-pressure.

Recently, Na^+-gated, water-conduction membrane (WCM), which allows the permeation of small, polar water molecules but impedes large, non-polar gas molecules, was developed for effectively removing water molecules at high temperature and pressure conditions.[35] By incorporating WCM into the reactor of MeOH synthesis from CO_2 hydrogenation, the water molecules permeated through the membrane layer hundreds of times faster than the reactant gases (H_2, CO_2) and products (CO, MeOH), dramatically boosting the reaction kinetics and shifting the thermodynamic equilibrium to MeOH. As a result, CO_2 conversion far surpassing the equilibrium conversion and very high MeOH yield were obtained. Moreover, the in-situ removal of water from the reaction system also resulted in high-purity liquid MeOH after condensation and well protected catalysts from deactivation.

In this study, as shown schematically in Figure 1, we applied the unique WCM for direct synthesis of DME from CO_2 and H_2, intending to achieve high yield DME synthesis by in-situ water removal. Physically mixed bifunctional Copper-Zinc-Aluminum (CZA)/HZSM-5 catalysts were loaded on the surface of WCM to convert CO_2 and H_2 efficiently to DME with CO_2 conversion up to 73.4% and DME yield up to 54.5% at 250 °C and 35 bar. It was also demonstrated that the in-situ water removal not only boosted the activity of CZA catalyst and HZSM-5 catalyst by 3.4 and 9.5 times, respectively, but also successfully protected these catalysts from fast deactivation.

WCM was prepared on ceramic hollow fiber with O.D. of 1.5 mm, I.D. of 0.75 mm, and length of 300 mm, following the previously reported procedure.[35] For direct DME synthesis in MR, WCM was cut into pieces with length of about 45 mm. Bifunctional catalysts with mass ratio of CZA/HZSM-5 = 1/1 were first loaded on the surface of WCM in MR. For the traditional reactor (TR), to keep similar packing of the catalysts, WCM was replaced by a non-permeable support with the same dimensions. After the catalysts were reduced by pure H_2 at 250 °C and atmospheric pressure for 10 h, a gas mixture of CO_2/H_2

with molar ratio of 1/3 was fed into the reactor to conduct the DME synthesis with gas hourly space velocity (GHSV) of 4,200 $L\cdot kg_{cat}^{-1}\cdot h^{-1}$ at 35 bar and temperature from 230 to 260 ^oC. After reaction, only water, MeOH, CO and DME were detected as the products by gas chromatography (GC). The catalytic results were shown in Figure 2A. For TR, the CO_2 conversion and DME yield increased with temperature, from 20.7% and 8.8% at 230 ^oC to 28.1% and 12.7% at 260 ^oC, respectively. All the CO_2 conversions were below the corresponding equilibrium conversions[36] and similar to those reported in the literature (Table S1). In strong contrast, after incorporation of WCM, both the CO_2 conversion and DME yield increased drastically and were well above the equilibrium CO_2 conversion, apparently because of the effective water removal. Similar to the trend in TR, the CO_2 conversion and DME yield also increased with temperature, from 53.2±0.1% and 30.6±0.1% at 230 ^oC to 65.7 ±0.1% and 42.2±0.3% at 260 ^oC, respectively.

The CZA catalyst was responsible for more challenging CO_2 activation and conversion to MeOH, whereas HZSM-5 for subsequent MeOH dehydration to produce DME. In our previous work for MeOH production from CO_2 hydrogenation using only CZA catalyst, it had been shown that in-situ water removal by WCM can significantly promote the activity of CZA, resulting in up to 61.4% CO_2 conversion and up to 40% MeOH yield.[35] In direct synthesis of DME from CO_2 and H_2 in MR, not only water will be removed by WCM, but also will the product MeOH be consumed. Both processes will favor further CO_2 conversion by the CZA catalyst. To understand the activity of CZA for CO_2 conversion upon consumption of MeOH and/or water removal, as shown in Figure 2B, the CO_2 conversion and CZA catalyst activity for CO_2 conversion in 4 reactor configurations were plotted. Note for CO_2 to MeOH, only CZA catalyst was used, and for CO_2 to DME, bifunctional catalysts (mass ratio of CZA/HZSM-5: 1/1) were loaded, with the CZA mass only 68% of that for MeOH synthesis. Compared with the CZA activity in MeOH synthesis (12.2 mmol $CO_2\cdot g_{CZA}^{-1}\cdot h^{-1}$) in TR, it increased by 86% to 22.7 mmol $CO_2\cdot g_{CZA}^{-1}\cdot h^{-1}$ in DME synthesis in TR, due to the MeOH consumption on HZSM-5 per the Le Chatelier's principle. For MeOH synthesis in MR, the CZA activity increased by 188% to 35.2 mmol $CO_2\cdot g_{CZA}^{-1}\cdot h^{-1}$, highlighting the advantage of in-situ water removal by WCM. Thanks to the synergistic effect of removing water by WCM and MeOH consumption on HZSM-5 in DME synthesis, the CZA activity was enhanced by 344% to 54.3 mmol $CO_2\cdot g_{CZA}^{-1}\cdot h^{-1}$ in MR. The CZA activity was maximized by simultaneously removing water and MeOH from the reaction system, and in-situ water removal contributed more than that of MeOH consumption; the in-situ water removal led to more than 139% of increasement in CZA activity, whereas MeOH consumption resulted in 54-86% of increasement.

It should be mentioned that MeOH dehydration to DME is also kinetically and thermodynamically inhibited by water,[37] and in-situ water removal is expected to facilitate the consumption of MeOH and thus contribute actually more on boosting the CZA activity. Furthermore, per Le Chatelier's principle, the facilitated MeOH consumption would shift the conversion of CO_2 towards more MeOH than CO. Indeed, compared with DME synthesis in TR, lower CO selectivity but higher MeOH plus DME selectivity were obtained in MR (Figure S1). Although much more CO_2 was converted to MeOH in MR, the yield and concentration of residual MeOH in MR were similar to those in TR and remained at very low levels, indicating that HZSM-5 was able to dehydrate MeOH very quickly and effectively.

To further improve the CO_2 conversion and DME yield, bifunctional catalysts with higher mass ratios of CZA/HZSM-5 (4/1 and 5/1) were then placed in MR to perform the DME synthesis from CO_2 and H_2. As expected and shown in Figure 2C, higher CO_2 conversion and DME yield were obtained; the highest CO_2 conversion was 73.4% obtained at mass ratio of CZA/HZSM-5 = 4/1, while the highest DME yield was 54.5% obtained at mass ratio of CZA/HZSM-5 = 5/1. The relatively lower CO_2 conversion at CZA/HZSM-5 = 5/1 was probably due to the relatively lower amount of HZSM-5 catalyst inside the reactor, which limits the consumption rate of abundant MeOH and thus the overall reaction rate. Similar results were also obtained in TR.[38] Due to the in-situ water removal by WCM, shifting the equilibrium of CO_2 hydrogenation towards MeOH formation and enhancing the activity of CZA catalyst, higher amounts of CZA catalyst converted more CO_2, and thus higher CO_2 conversion. At the same time, the excellent capability of HZSM-5 catalyst for dehydrating MeOH at the absence of water in the reactor enabled the fast dehydration of the produced large amount of MeOH to DME. In return, the enhanced MeOH dehydration kinetics shifted the selectivity of CO_2 conversion reactions, and thus more MeOH and less CO were formed, evidenced by the decrease of CO yield (Figure 2C) and selectivity (to less than 20%, Figure S2). Similar results were also obtained at lower temperatures (Figure S3).

Correspondingly, as shown in Figure 2D, the DME productivity of HZSM-5, namely the amount of DME in moles produced per gram of HZSM-5 catalyst per hour, was greatly enhanced. The in-situ water removal raised the DME productivity from 7.2 $mmol_{DME}\cdot g_{HZSM-5}^{-1}\cdot h^{-1}$ in TR to 17.6 $mmol_{DME}\cdot g_{HZSM-5}^{-1}\cdot h^{-1}$ in MR loaded with CZA/HZSM-5 = 1/1. Producing and dehydrating more MeOH to DME by increasing the CZA/HZSM-5 mass ratio under the dry condition in MR further boosted the DME productivity by 684%, to 56.2 $mmol_{DME}\cdot g_{HZSM-5}^{-1}\cdot h^{-1}$ using bifunctional catalysts CZA/HZSM-5 = 4/1 and by 948%, to 75.0 $mmol_{DME}\cdot g_{HZSM-5}^{-1}\cdot h^{-1}$ using CZA/HZSM-5 = 5/1. These results revealed the extraordinary inherent activity of current CZA for activating CO_2 and HZSM-5 catalysts for dehydrating MeOH and the severity of water inhibiting effect, implying the merits of removing water from the reaction system and maintaining the dry reaction environment during reaction.

GHSV is one of the critical operation parameters that determine the overall catalytic performance and efficiency of a reactor. Decreasing GHSV and extending the residence time of reactants inside the catalyst bed generally results in higher conversion and product yield, and thus improves the reactor efficiency. Influence of GHSV on DME synthesis over CZA/HZSM-5 = 5/1 catalysts in MR was investigated at 250 ^oC and 35 bar. GHSV varied from 3,500 to 4,900 $L\cdot kg_{cat}^{-1}\cdot h^{-1}$ by changing the feed flow rate from 20 to 28 sccm. As shown in Figure 3, with the decrease of GHSV, both the CO_2 conversion (black dots) and DME yield

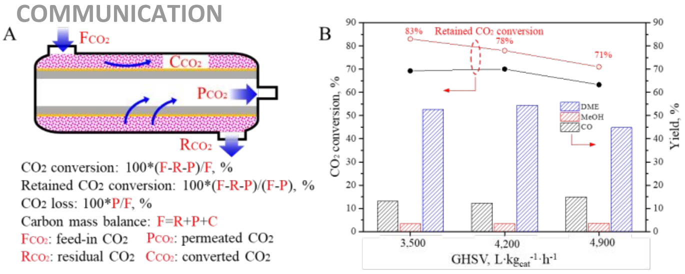

Figure 3. Catalytic performance of direct synthesis of DME from CO_2 and H_2 under different conditions in MR. A: Schematics showing CO_2 in feed, permeate and retentate and converted CO_2 in MR. B: DME synthesis performance at different gas hourly space velocities (GHSVs) at 250 °C and 35 bar. Mass ratio of bifunctional catalysts (CZA/HZSM-5): 5/1.

first increased and then slightly decreased. The initial performance increase with the decrease of GHSV was expected, whereas the slight decrease could be attributed to the permeation of small fraction (8-12%) of CO_2 through WCM. This portionof CO_2 did not participate in the reaction, but was taken into account for the calculation of CO_2 conversion (Figure 3A, Eq.S1). Therefore, the calculated CO_2 conversion did not represent the actual conversion of CO_2 or retained CO_2 conversion. Considering the actual CO_2 amount in catalyst bed, we found the retained CO_2 conversion (red dots in Figure 3B) increased with the decreasing GHSV. The highest retained CO_2 conversion reached 83% at GHSV of 3,500 $L{\cdot}kg_{cat}^{-1}{\cdot}h^{-1}$. In contrast, to achieve a similar CO_2 conversion in TR, the reactant gas with molar ratio of $CO_2/H_2=10/1$ was reported to be heated to 260 °C and pressurized to 360 bar,[39] which is more than 10 times higher than the pressure used in this study. Moreover, a stable DME synthesis in MR, much better than that observed in TR[25] (Figure S4), was obtained, suggesting the negligible deactivation of CZA and HZSM-5 catalysts, although a slight coking of HZSM-5 was detected (Figure S5) after the long-term stability testing. These results serve as extra direct experimental evidence of the importance of removing water from the DME synthesis reactor.

Finally, we compared our results for direct synthesis of DME from CO_2 and H_2 obtained in TR and MR with those reported in the literature in terms of CO_2 conversion and DME yield. As shown in Figure 4 and Table S1, the catalytic performance of bifunctional CZA/HZSM-5 catalysts in TR was moderate: the CO_2 conversion was below the equilibrium values, and DME yield was amid the literature results. After incorporating WCM and generating a dry reaction environment, both CO_2 conversion and DME yield were dramatically boosted, much higher than the reported results obtained under similar or even higher temperatures and pressures. To the best of our knowledge, these results represent the highest performance to date.

Conclusions

In conclusion, WCM was applied to create a dry reaction environment in MR for direct synthesis of DME from CO_2 and H_2 on CZA/HZSM-5 bifunctional catalysts. Thanks to the in-situ water removal by WCM, single-pass CO_2 conversion up to 73.4% (retained single-pass CO_2 conversions up to 83%) and DME yield up to 54.5% were obtained. The activity of CZA was boosted more than 4 times by simultaneously water removal and MeOH consumption, while the activity of HZSM-5 increased by up to 9.5 times over the combination of the in-situ water removal and increasing mass ratio of bifunctional catalysts. Such high activity and good stability at the absence of water would largely facilitate the deployment of direct DME synthesis from CO_2 and H_2. Furthermore, WCM is also expected to boost other reactions that are kinetically or thermodynamically inhibited by water, such as Fischer-Tropsch synthesis and dimethyl carbonate synthesis from CO_2 and MeOH.

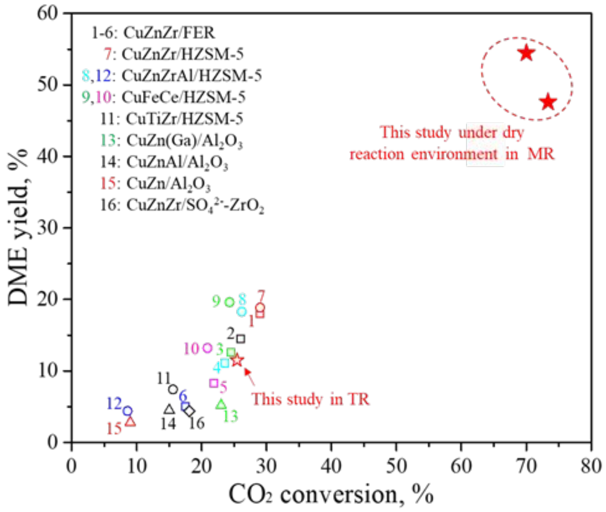

Figure 4. Comparisons of catalytic results in the MR using WCMs in this study with TR results from literature in terms of CO2 conversion and DME yield. Data points with corresponding references: 1[20], 2[21], 3[22], 4[23], 5[22], 6[24], 7[5], 8[25], 9[26], 10[27], 11[28], 12[29], 13[30], 14[16], 15[31], 16[32].

Conflicts of interest

There are no conflicts to declare.

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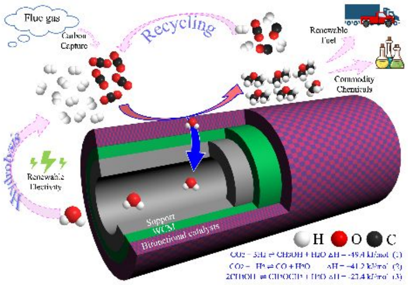

Highly efficient DME synthesis from CO_2 and H_2 was realized in a dry reaction environment by incorporating a water-conduction membrane.