Dual-Role Membrane as NH$_3$ Permselective Reactor and Azeotrope Separator in Urea Alcoholysis

Gaofeng Zeng,*,† Yue Wang,‡‡ Dian Gong,†‡ Yanfeng Zhang,†⊥ Ping Wu,⊥⊥ and Yuhan Sun*†⊥

1CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, 100 Haike Road, Shanghai 201210, China
2School of Chemical Sciences, University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China
3School of Physical Science and Technology, ShanghaiTech University, 393 Mid Huaxia Road, Shanghai 201210, China

Supporting Information

ABSTRACT: Urea methanolysis is a green alternative to synthesize dimethyl carbonate (UM-to-DMC). However, it is strongly challenged by the generated NH$_3$ induced thermodynamic equilibrium limitation and the azeotropic products’ separation. Herein, these predicaments are well-relieved by introducing membranes in both reaction and product separation. An NH$_3$ permselective membrane reactor (MR) based on modified SAPO-34 membrane is successfully realized for UM-to-DMC. The permselectivity and acidity of the SAPO-34 membrane are significantly adjusted to cater the strict molecular sieving of NH$_3$/methanol and chemical inertness upon the reaction. The MR exhibits excellent reactant conversion and DMC selectivity, resulting in >139% higher DMC yield than that of the nonmembrane reactor, due to in situ removal of NH$_3$ by the membrane. The MR also demonstrates reliable chemical, thermal, and mechanical stability during >200 h. Moreover, the regular SAPO-34 membrane with controlled thickness presents remarkable separation performance for the methanol–DMC azeotrope, in which the methanol–DMC separation factors and the methanol permeance are 1–2 orders of magnitude higher than those of the polymeric membranes. This study suggests the great potential that integration of such membranes offers for process intensification, energy savings, and efficiency improvement in a series of urea alcoholysis and even other NH$_3$ releasing reactions.

1. INTRODUCTION

Dimethyl carbonate (DMC) is a versatile green chemical widely used as a solvent and intermediate and is also considered as a promising fuel additive.1–3 Among these nonphosgene routes for DMC synthesis, catalytic urea methanolysis (UM) is an environmentally friendly alternative, which totally avoids the poisonous, corrosive, and explosive reagents used in the competing routes like alcohol (oxy-) carbonylation and transesterification.4–7 Moreover, this strategy of urea alcoholysis possesses a flexibility to synthesize a series of organic carbonates by using different alcohols/phenols.8 In UM-to-DMC, the amino groups of urea are replaced by the methoxyl groups of methanol sequentially to form DMC with ammonia (NH$_3$) releasing.9 The byproduct NH$_3$ can be recycled back to urea synthesis with CO$_2$ in principle, turning it into a sustainable process with CO$_2$ utilization. With NH$_3$ generation, however, the reaction is strongly limited by the thermodynamic equilibrium, leading to a low single-pass conversion of urea. Meanwhile, it is unfeasible for NH$_3$ to be recovered from regular reactors in practice, which is far away from the original intention of NH$_3$ cycling. In sequence, it is easy for the product mixture to form the methanol–DMC azeotrope, resulting in an energy-intensive and complex purification process. Membrane technology is a highly potential approach to uncage these barriers.10–15 The product permselective membrane reactor (MR), integrating reaction and separation in a single unit, is an effective, facile, and green solution to in situ remove and collect one or more products. It offers several benefits compared to the nonmembrane reactors.14,16,17 These include the possibility of surpassing thermodynamic equilibrium limitations, reducing undesired side/sequential reactions, and lowering the separation efforts of the final product mixture with increased concentrations of target products by the selective removal of a product.18 Recently, the concept of product permselective MR has been successfully demonstrated for the hydrogen or water generated reactions through selectively removing H$_2$ or H$_2$O.12,14,16,17,19–21 Kim et al. developed the H$_2$ permselective zeolite MR to improve the propane dehydrogenation.14 Zhou et al. demonstrated a highly efficient methanol dehydration through a water selective MR.12 If the generated NH$_3$ can be selectively separated in situ in an MR, the UM-to-DMC reaction can be driven further, and NH$_3$ would be easily reused. Similarly, such an NH$_3$ permselective MR is also desired in various thermodynamic equilibrium limited reactions with NH$_3$ releasing like urea oligomerizations and alcoholysis of urea or its derivatives. Apart from high NH$_3$ permselectivity, the MR developed for UM-to-DMC should possess chemical inertness and thermal/mechanical stability.
upon the real reaction conditions. However, the NH₃ permselective membranes were infrequently investigated because NH₃-containing gas mixtures can be easily separated by nonmembrane methods like liquid washing in practice. Only poly(thiocyanate), molten LiNO₃ and ZnCl₂, silica, and MFI membranes were attempted for the NH₃ enrichment from the recycle gases mixture (NH₃ + N₂ + H₂) of NH₃ synthesis. However, they are not suitable for UM-to-DMC due to their low selectivity and/or unproven thermal/chemical tolerance. Therefore, NH₃ permselective MRs have not been developed so far. On the other hand, the azeotrope separation through the membrane is an efficient and energy-saving process. The membrane with the superior properties of chemical/thermal stability, high methanol–DMC selectivity, and high methanol flux is desired in the UM-to-DMC product separation. In the scope of membrane materials, small-pore zeolite membranes are promising to cater the requirements of the UM-to-DMC reaction and product separation due to the molecular sieving capacity and high stability.

In this work, SAPO-34-based membranes were successfully developed as an NH₃ permselective reactor and azeotrope separator to settle the two main issues of the UM-to-DMC reaction. We tailored NH₃–Zn–SAPO-34 membranes for in situ removal of NH₃ from UM-to-DMC. The impacts of reagents/products on the membrane permeance were investigated. The behaviors of the NH₃ permselective MR and nonmembrane fixed-bed reactor (FR) were comparatively studied, in which the MR exhibits significantly enhanced reactant conversion and DMC selectivity as well as a reliable long-term durability. Moreover, highly efficient separation of the MeOH–DMC mixture was demonstrated on the regular SAPO-34 membranes using the pervaporation method.

2. RESULTS AND DISCUSSION

2.1. Structure and Texture of NH₃ Permselective Membranes. In UM-to-DMC, the kinetic diameters (K.D.’s) of molecules are in the order of NH₃ (0.29 nm) < methanol (0.36 nm) < urea (0.42 nm) < methyl carbamate (MC, 0.52 nm) < DMC (0.60 nm). To remove NH₃ but reject other chemicals, the cutoff point of the membrane should be located between the size of NH₃ and methanol (Figure 1a). In addition, the membrane needs to be chemically stable to avoid forming additional byproducts. To obtain a methanol-tight and chemically inert membrane, therefore, the as-prepared SAPO-34 (pore aperture ~0.38 nm) membranes were post-treated with zinc ion-exchange and thermal NH₃–methanol solution in sequence, denoted as Zn–SAPO-34 and NH₃–Zn–SAPO-34, respectively. The SAPO-34 selective layers were deposited on the inner side of a porous ceramic tube (Figure 1b). The scanning electron microscope (SEM) surface view of NH₃–Zn–SAPO-34 exhibits a highly crystalline structure with
The cross-sectional SEM view of the membrane displays a dense and continuous morphology with a uniform thickness of ca. 8 μm (Figure 1d). The effects of post-treatments on the morphology of SAPO-34 crystals were observed by SEM, in which the smooth surface and regular cubic morphology of SAPO-34 crystals were observed by SEM, in comparison with the spectra of SAPO-34 and Zn−SAPO-34 matched well with the SAPO-34 reference, indicating that SAPO-34 crystals are stable in the post-treatments without degradation of crystallinity (Figure 1e). The original structure of SAPO-34 was well-remained even in the 5 wt % NH3 methanol solution (Figure S2). Moreover, the ion-exchange decreased the surface area and pore volume of SAPO-34 by ~30%, while the NH3 thermal treatment has a negligible effect on them (Figure S3). This suggests that the exchanged Zn2+ may enter the cages of SAPO-34 and decrease the pore size.32

Energy-dispersive spectrometry (EDS) analysis of the NH3−Zn−SAPO-34 membrane reveals that the Zn distribution is uniform on the membrane surface with a Si/Zn = 3.1 but gradually decreased from the top surface to support interface (Figure 1d, Figures S4 and S5). The near-surface and overall Si/Zn determined individually by X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence (XRF) were 3.0 and 3.7 (Table S1), respectively, confirming the distribution gradient of Zn from the surface into the bulk membrane. The IR spectrum of the NH3−Zn−SAPO-34 exhibits new bands at 3180 cm−1 (N−H stretching vibrations), 1470 cm−1 (N−C−N stretching), and 1410 cm−1 (rocking of −NH2) in comparison with the spectra of SAPO-34 and Zn−SAPO-34, indicating that NH3 strongly interacted with the zeolite (Figure 1f). The N 1s XPS band proves that new Si−O−NH bonds were formed between NH3 and SAPO-34 (Figure S6).

The impact of post-treatments on the acidity of SAPO-34 were measured by NH3 temperature-programmed desorption (NH3−TPD) (Figure 1g). The parent SAPO-34 exhibits both weak acid and medium−strong acid signals at 170 and 490 °C, respectively. In contrast, the medium−strong acidity of NH3−Zn−SAPO-34 was significantly diminished, which could be ascribed to the replacement of H protons on SAPO-34 by the Zn ions.32,37 The acidity decline is important to avoid undesired acid catalysis of methanol, like methanol dehydration to dimethyl ether, in the MR of UM-to-DMC.

2.2. Molecular Sieving of NH3 Perme selective Membranes. The effects of post-treatments on the CO2−CH4 (1:1) mixture separation through the SAPO-34 membrane (M1) were investigated as a control test. As shown in Figure 2a, the permeability of CO2 decreased by half after the treatments, while CH4 was significantly declined from 9.3 × 10−9 mol m−2 s−1 Pa−1 of the parent SAPO-34 membrane to 1.7 × 10−9 mol m−2 s−1 Pa−1 for NH3−Zn−SAPO-34, resulting in an increased CO2−CH4 selectivity from 51 of the parent membrane to 123 of the NH3−Zn−SAPO-34 membrane. This suggests that the post-treatments increased the permeation resistance for CH4, and the cutoff point of the NH3−Zn−SAPO-34 membrane was located between K.D. 0.33 nm of CO2 and K.D. 0.38 nm of CH4.

Since the MR for UM-to-DMC demands high rejection for all molecules except for NH3, the permeation properties of the SAPO-34 membrane (M2) before and after treatments for NH3 and the second-smallest molecule (methanol) were measured using a single gas method at the temperature close to the UM-to-DMC reaction (160 °C). As shown in Figure 2b, the NH3 permeability of M2 was slightly decreased from 9.2 × 10−7 mol m−2 s−1 Pa−1 of NH3−Zn−SAPO-34. In comparison, the methanol vapor...
permeability was 2 orders of magnitude declined from $1.5 \times 10^{-7}$ of the parent membrane to $6.7 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ of the NH$_3$–Zn–SAPO-34 membrane. Accordingly, the ideal selectivity of NH$_3$ to methanol over the NH$_3$–Zn–SAPO-34 membrane was notably improved from 6 of the parent membrane to 105. This demonstrates that NH$_3$ can pass easily, but most of the methanol was excluded by the NH$_3$–Zn–SAPO-34 membrane.

The effects of the post-treatments on the permeation behaviors of the SAPO-34 membrane upon the simulated UM-to-DMC conditions were further investigated in pure methanol and a mixture solution of 90 wt % MeOH–10 wt % DMC, respectively, at 160 °C and ΔP = 8 bar via vapor separation method. Without treatment, methanol could permeate easily through the parent membrane due to the larger pore size of SAPO-34 (~0.38 nm). After Zn ion-exchange, the methanol flux ($J_{\text{MeOH}}$) of the Zn–SAPO-34 membrane (M3) decreased 64% from ~2.77 kg m$^{-2}$ h$^{-1}$ of the parent membrane to ~1.03 kg m$^{-2}$ h$^{-1}$ in the single feeding of methanol (Figure 2c), confirming that the Zn-ion treatment markedly improved the rejection of methanol. $J_{\text{MeOH}}$ of M3 remained stable at ~1.08 kg m$^{-2}$ h$^{-1}$ during 80 h, indicating the chemical stability of the membrane in methanol at 160 °C. This was also supported by the XRD measurements, in which a nonvisible change of the crystal dimensions of the methanol-treated Zn–SAPO-34 sample was observed (Figure S7). In the 90% MeOH–10% DMC mixture feed, $J_{\text{MeOH}}$ decreased slightly from 0.78 to 0.65 kg m$^{-2}$ h$^{-1}$ during the first 100 h but then was stable (Figure 2c). The XPS analysis displayed that the DMC-treated sample has a higher surface carbon content than the untreated sample due to the slight adsorption of DMC (Table S2). Switching the feed to MeOH again, $J_{\text{MeOH}}$ of M3 recovered to 79% of the initial value (Figure 2c). Compared with its parent SAPO-34 membrane, $J_{\text{MeOH}}$ of Zn–SAPO-34 had been lowered by 72% in the mixture of MeOH–DMC. As the rejection of methanol is the key property of the MR to remove NH$_3$ but hold back other reagents, the higher or even complete rejections of methanol are highly desired. Therefore, $J_{\text{MeOH}}$ (0.65 kg m$^{-2}$ h$^{-1}$) of the Zn$^{2+}$-treated membrane is still too high to cater the methanol-tight demand of the MR.

Figure 3. Time dependence of MC conversion (a) and product selectivity (b) in the MR and FR (feed, 10 wt % MC–90 wt % methanol, $T = 180 ^\circ$C, WHSV = 0.6 h$^{-1}$). Effects of reaction temperature (160–220 °C) on the MC conversion (c) and DMC selectivity (d) in the MR and FR (feed, 10 wt % MC–90 wt % methanol, WHSV = 0.6 h$^{-1}$).

The effect of NH$_3$ treatment on the permeation of the Zn–SAPO-34 membrane (M4) was measured with the feeding of 1 wt % NH$_3$–89 wt % MeOH–10 wt % DMC at 160 °C (Figure 2d). Similar to M3, $J_{\text{MeOH}}$ of M4 was stable at 0.82 kg m$^{-2}$ h$^{-1}$ with the pure methanol feed. In the feed of the NH$_3$–MeOH–DMC mixture, however, $J_{\text{MeOH}}$ of M4 decreased significantly from 0.65 to 0.09 kg m$^{-2}$ h$^{-1}$ within 90 h, dropping to only 4% of its parent SAPO-34 membrane (i.e., 2.48 kg m$^{-2}$ h$^{-1}$). Back to pure methanol again, $J_{\text{MeOH}}$ of M4 recovered only slightly to ~0.13 kg m$^{-2}$ h$^{-1}$. Thus, M4 was almost methanol-tight under the simulated UM-to-DMC conditions. This suggests that the small amount of NH$_3$ in the feed mixture strongly impacted the permeation of methanol. The linked amino groups impede the methanol transport by increasing the steric hindrance. Therefore, Zn ion-exchange and particularly NH$_3$ thermal treatment together enhance the methanol rejection of SAPO-34 membranes a lot. As an example, the NH$_3$ permselective membrane reactor (M4) was prepared by treating a SAPO-34 membrane in zinc ions at 120 °C for 4 h and 1 wt % NH$_3$ methanol solution at 160 °C for 48 h in sequence, yielded small methanol permeances of ~1.2 × 10$^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and relatively high permeances of NH$_3$ ~3.2 × 10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, confirming that the NH$_3$–Zn–SAPO-34 membrane is NH$_3$ permselective under the simulated UM-to-DMC conditions (Figure S8).

2.3. Ammonia Permselective Membrane Reactor. In the UM-to-DMC, the −NH$_2$ groups of urea are replaced by the CH$_3$O− groups of methanol sequentially to form MC (eq 1) and then DMC (eq 2) with the releasing of an equal amount of NH$_3$ in each step, in which the later MC methanolysis to DMC in eq 2 is a rate-determining step.$^4$ N-Methyl methyl carbamate (NMMC), formed from the reaction

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of DMC and MC, can be detected as a byproduct in UM-to-DMC. Thus, MC methanolysis was investigated first in a nonmembrane fixed-bed reactor (FR) and fixed-bed NH₃-Zn–SAPO-34 MR to examine the effects of the NH₃ permeselective membrane on the thermodynamic equilibrium limited reaction under simplified conditions.

$$\text{H}_2\text{NCONH}_2 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCONH}_2 + \text{NH}_3$$  \hspace{1cm} (1)

$$\text{CH}_3\text{OCONH}_2 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCOOCCH}_3 + \text{NH}_3$$  \hspace{1cm} (2)

Figure 3a shows the MC conversions ($\alpha_{\text{MC}}$) in the MR and FR. During Stage I, only the condensed liquid products were collected periodically while the gaseous products were retained in the reactor, as depicted in Figure S9. This operation is used to simulate the closed batch reactor and named as “closed” mode. In Stage II, both liquid and gaseous products were liberated during sampling to simulate the common continuous flow reactor, denoted as “open” mode. In Stage I, the $\alpha_{\text{MC}}$ first located in 58–64% in the FR during the initial 40 h and then rapidly dropped to 15% within 70 h before slowly approaching 10%. In contrast, $\alpha_{\text{MC}}$ was highly stable at 87 ± 2% in the MR during Stage I, which is 8-fold higher than the stable state of the FR. The fast decline of $\alpha_{\text{MC}}$ in the FR suggests that the $\alpha_{\text{MC}}$ depends on the NH₃ content in the reactor: $\alpha_{\text{MC}}$ reached a high value at low NH₃ concentration and declined due to accumulation of NH₃. Contrarily, in the MR, $\alpha_{\text{MC}}$ was stably high owing to the continuous NH₃ removal keeping its concentration low. This shows already that the MR has a remarkably positive impact on the MC methanolysis. On the other hand, even the highest $\alpha_{\text{MC}}$ of FR (64%), obtained at low NH₃ content in the initial, is much smaller than that of the MR (87%), suggesting that the distinction between MR and FR is more than the apparent NH₃ accumulation. Thus, the reaction was compared in the “open” mode in Stage II to avoid the high concentration of NH₃ in either MR or FR. The $\alpha_{\text{MC}}$ of FR averaged at 63% close to the maximum in Stage I but without visible decline. This corroborates that the high concentration of NH₃ caused the $\alpha_{\text{MC}}$ decrease during Stage I in the FR. For the MR, the Stage II $\alpha_{\text{MC}}$ was practically the same as that of Stage I. At the microlevel, the reactant concentrations around the active sites of catalysts directly impact the reaction driving force. The newly generated NH₃ before desorption and diffusion make high NH₃ content around the active sites, which limits the further conversion in FR, whereas the produced NH₃ could diffuse and pass through membrane quickly because the membrane is compactly surrounding the catalyst bed (Figure 1a), lowering the NH₃ content in the catalyst bed and promoting the reaction. The reaction equilibrium constant of MC methanolysis ($K_{eq}$) can be expressed as $\ln K_{eq} = -1576.9/T - 0.92$, where $T$ ($K$) is the reaction temperature (Figures S10 and S11 and Tables S3 and S4, and see the equilibrium constant calculation details in the SI). Therefore, the corresponding equilibrium conversion of MC amounts to 39.8% at 180 °C (Figure 3a). The real $\alpha_{\text{MC}}$ values in the “closed” mode FR are much lower than the equilibrium conversion due to the limitation of released NH₃.

As the generated NH₃ was removed duly, in contrast, the equilibrium conversion of MC was significantly surpassed by ∼120% in the MR.

The product selectivity ($X_{\text{fi}}, \text{i} = \text{DMC or NMMC}$) of MC methanolysis on the MR and FR is shown in Figure 3b. During Stage I, the $X_{\text{DMC}}$ increased from 77% to 84% in the FR during the initial 60 h and then slightly dropped to 74%. Accordingly, the undesired $X_{\text{NMMC}}$ reached 26% in the FR. In comparison, the $X_{\text{DMC}}$ increased from 87% to 94% in 80 h and then slightly fluctuated around 93% in the MR. Hence, the relative $X_{\text{DMC}}$ was 26% higher in the MR than the FR. As DMC reacts with MC to form NMMC, the driving force for this reaction depends on their concentration ($C_{\text{f}}, \text{i} = \text{MC or DMC}$) around the catalyst. The $C_{\text{MC}}$ was always ∼0.5% in the MR because the
initial content (mol %) of MC in the feed mixture is 4.5%, and $a_{MC}$ is near 90%. However, $a_{MC}$ is much lower in the FR (i.e., 10–60%), resulting in a high $C_{MC}$ of 1.8–4.0%. Thus, it is easier to form NMMC in the FR than the MR.

During Stages III–VI, MC methanolysis was investigated with "open" mode between 160 and 220 °C in a 20 °C step-size. As shown in Figure 3c, the $a_{MC}$ improved with temperature in both reactors. In detail, $a_{MC}$ increased from 70% at 160 °C to 95% at 220 °C in the MR and from 56% to 90% in the FR. This is expected since the reaction is endothermic. However, higher temperatures also favor MC decomposition. In comparison with the FR, therefore, the MR allows not only NH$_3$ removal but also lower reaction temperatures with higher conversion, limiting undesired byproducts. Figure 3d shows the corresponding $X_{DMC}$ in the MR and FR. $X_{DMC}$ significantly declined in the FR from 91% at 160 °C to 63% at 220 °C. Clearly high temperatures are conducive to formation of NMMC. However, in the MR, $X_{DMC}$ slightly increased from 91% to 95% in the range 160–200 °C and then dropped to 88% at 220 °C. As explained before, the in situ removal of NH$_3$ promotes the formation of DMC, and the lower MC concentration in the MR will suppress the formation of NMMC. Thus, a higher $X_{DMC}$ can be obtained at elevated temperatures in the MR. This suggests that the MR could be operated at an even higher temperature for the purpose of a higher DMC yield.

As the MC methanolysis is the rate-controlling step of UM-to-DMC, it has been widely studied by different nonmembrane reactors (e.g., continuous stirred tank reactor and fixed bed reactor) on various catalysts. Our reaction performance in the nonmembrane FR is comparable with the literature results under the similar conditions, as summarized in Table S5. Obviously, both MC conversion and DMC selectivity in the MR were much higher than the reported results from the nonmembrane reactors even though the reactivity of the commercial catalyst here is not the best. This reveals that development of an eligible reactor is equally or even more important as/than the catalyst in this reaction.

The MR was further extended to operate for the full reaction of urea methanolysis, i.e., UM-to-DMC with "closed" (Stage VII) and "open" (Stage VIII) modes in sequence, as shown in Figure 4a,b. In Stage VII, the urea conversion ($a_{urea}$) first located at ~$87$% in the FR and then declined to ~$70$% in 130 h (Figure 4a). It is expectable that $a_{urea}$ would drop in the "closed" mode FR because the generated NH$_3$ restricts the shift of reaction equilibrium. For the "open" mode in Stage VIII, the $a_{urea}$ in FR fluctuated around 88% due to the periodical evacuation of NH$_3$. In comparison, the $a_{urea}$ remains stably high in the MR in both Stages VII and VIII, which is nearly complete conversion with an average of 98.7% owing to the removal of NH$_3$ in time. Crucially, the product distributions were significantly different between FR and MR (Figure 4b). The MR exhibited high $X_{DMC}$ averaged at 75% with ~21% of $X_{DMC}$ and ~4% of $X_{NMMC}$ resulting in a high $Y_{DMC}$ of 74%. In contrast, the main product in FR was the intermediate, MC, weighting 57% of all products, while the average $X_{DMC}$ was only 35%. This translated to much lower $Y_{DMC}$ in the range 25–31% in the FR. Therefore, the $Y_{DMC}$ values were >139% higher in the MR than in the FR. This further proves that the accumulated NH$_3$ limits the reactant/intermediate conversion. Since more NH$_3$ is generated in UM-to-DMC, the difference between MR and FR was larger compared with the MC methanolysis.

The reactivity behaviors in the MR demonstrate the membrane efficiency in the byproduct removal, while the mass balance (MB) of the MR would imply the effectiveness of the membrane in the protection of other reactants. Thus, MB is a key property for the MR, representing the practicability and economy. The MB in Stages I–VIII was calculated in Figure 4c. The real MB was derived from the weight ratio of liquid products to reactants, while the ideal MB was calculated from the feed amount, conversion, and selectivity with assuming that NH$_3$ was the only gaseous product. The real MBs of the FR were only slightly lower than the ideal values, indicating that the reactor was well-sealed, and other gaseous byproducts, e.g., CO$_2$, were very little. By comparison, the ideal/real MB gaps were slightly larger for the MR, implying a mild mass loss of liquid reagents in the MR. On average, the real MB of the MR was ~4% lower than the ideal values, in line with the small methanol permeance of the NH$_3$–Zn–SAPO-34 membrane in Figure S8. For zeolite membranes it is unprecedented to achieve infinite selectivity for the separation of a similar size gas mixture due to the inevitable defects of membranes. The slight mass loss in the MR is reasonable and acceptable relative to the technical and economic performance of the MR. Thus, the MB of the MR proved that the membrane has high permselectivity, which can protect most of the reactants except NH$_3$. At the same time, the real MB of the MR was slightly increased over 2100 h. This reflects that no new defects of the membrane were generated during long-term reaction, proving the chemical/mechanical stability of the membrane. After the reaction, the used membrane was still almost methanol-tight (Table S6) and retained a dense crystallinity without visible degradation (Figure S12).

As the control, the MC methanolysis was also tested in an MR using a regular SAPO-34 membrane without post-treatments. The MB was as low as 45% in the beginning due to methanol being able to pass through the membrane easily, and then, it was gradually increased to 79% in 500 h (Figure S13). This suggests that the leakage of methanol through the membrane was reduced by the interaction of generated NH$_3$ and the membrane, which is consistent with the effects of thermal NH$_3$ treatment on the methanol permeability. However, the related low MB reveals that considerable methanol still can leak from the MR, which proves that both Zn ion-exchange and NH$_3$ treatment are necessary to obtain a high MB.

2.4. Membrane Separation of Azeotrope Product of UMTOMDC. Although the ternary azeotrope of methanol–water–DMC in the competing routes of alcohol (oxy-) carbonylation and transesterification to DMC can be avoided in UM-to-DMC, the product mixture of UM-to-DMC still leads to a binary azeotropic mixture at 70 MeOH:30 DMC wt % and normal pressure. Gratifyingly, the untreated SAPO-34 membranes can separate this kind of azeotrope owing to its pore aperture ~0.38 nm being ideal for the separation of methanol (0.36 nm) and DMC (0.60 nm). Since UM-to-DMC is operated at >160 °C, moreover, the separation of UM-to-DMC product over the SAPO-34 membrane could be integrated with the reactor by the pervaporation method for the rational use of residual heat, as depicted in Figure 1a.

The impacts of membrane thickness, feedstock composition, and temperature on the methanol–DMC separation were investigated. A SAPO-34 membrane with ~8 μm thickness exhibited a $J_{MOH}$ of 1.7 kg m$^{-2}$ h$^{-1}$ with >99.99% methanol purity in the permeate side for the separation of the 90 wt %
Figure 5. Effects of (a) membrane thickness (140 °C, ΔP = 4 bar, 90 wt % methanol–10 wt % DMC), (b) methanol–DMC composition (140 °C, ΔP = 4 bar), (c) temperature (90 wt % methanol–10 wt % DMC, ΔP = 3 bar), and (d) operation time (90 wt % methanol–10 wt % DMC mixture, 150 °C and ΔP = 6 bar) on the separation performance of untreated SAPO-34 membranes for the pervaporation of the methanol–DMC mixture.

MeOH–10 wt % DMC mixture at 140 °C and ΔP = 4 bar, resulting in a high separation factor (SF MeOH–DMC) of 7780 (Figure 5a). As the permeation depends on the membrane thickness, SAPO-34 membranes with various thicknesses from ~2 to ~11 μm were prepared (Figure S14). As shown in Figure 5a, the J MeOH was significantly improved by using thinner SAPO-34 membranes. For example, J MeOH even reached 14.1 kg m⁻² h⁻¹ over a SAPO-34 membrane with ~2 μm thickness. As the defects increase, correspondingly, the SF MeOH–DMC declined gradually with the thinner membrane. However, the purity of the permeate side was still higher than 99.9% even for the thinnest membrane (Figure 5a).

For the real separation of UM-to-DMC products, DMC would be gradually concentrated with the selective removal of methanol. Therefore, the effect of feed composition on the separation performance of a ~4 μm thick SAPO-34 membrane was measured from 10 to 90 wt % methanol under ΔP = 4 bar and 140 °C (Figure 5b). As the partial pressure of methanol increased with its concentration, the methanol flux correspondingly increased from 2.8 to 9.9 kg m⁻² h⁻¹ with increasing methanol content from 10 to 90 wt % in the feedstock. Moreover, the methanol purity in the permeate side increased from 99.2% for 10% MeOH–90% DMC feeding to >99.99% for 90% MeOH–10% DMC feeding, leading to increased SF MeOH–DMC from 1025 to 2800. This reveals that DMC was well-rejected by the membrane, and the loss rate of DMC is ultralow even for the DMC-rich mixture. Additionally, the limit of the 70 wt % MeOH:30 wt % DMC azeotropic mixture can be easily broken away.

In pervaporation, the permeation is driven by the temperature difference between the feed side and permeate side of the membrane. Higher temperature translates into higher driving force and flux. As depicted in Figure 5c, the J MeOH over the 4 μm SAPO-34 membrane increased substantially with temperature, growing from 3.8 kg m⁻² h⁻¹ at 100 °C to 11.9 kg m⁻² h⁻¹ at 160 °C. This is expectable as the diffusivity of vapor molecules increased exponentially with temperature. Correspondingly, the SF MeOH–DMC decreased from 3930 to 2640 with the elevated temperature. This could be ascribed to the weaker competitive adsorption of methanol at higher temperature, which leads to slightly more permeation of DMC over the defects. As UM-to-DMC is >160 °C, highly efficient methanol separation would be achieved through such a membrane in the tight integration of upstream reaction and downstream separation.

To couple the UM-to-DMC reaction and separation, the long-term stability of the SAPO-34 membrane was carried out under the conditions close to the UM-to-DMC outlet (150 °C, ΔP = 6 bar, and 90 wt % methanol–10 wt % DMC). As shown in Figure 5d, the J MeOH remained stable and fluctuated around 12.6 kg m⁻² h⁻¹. The SF MeOH–DMC slightly increased from 2820 to 3700 during 300 h of testing, which may be ascribed to the adsorption of DMC on the defects, and then increased the diffusion resistance of DMC pass through defects.

For the separation of MeOH–DMC, many efforts have also been made using the polymer-based membranes like poly(vinyl alcohol) (PVA), chitosan, and polymer–inorganic fillers. However, the separation performance is mediocre with low J MeOH (~1 kg m⁻² h⁻¹) and/or SF MeOH–DMC (<50). Moreover, the membrane stability is also highly challenged by the swelling, plasticization, and fouling in the MeOH–DMC mixture. In contrast, the SAPO-34 membranes with moderate thickness demonstrated 1–2 orders of magnitude higher J MeOH and SF MeOH–DMC as well as reliable chemical/thermal/mechanical stability. Thus, the SAPO-34 membrane is highly promising for the UM-to-DMC product separation, which combined with the membrane reactor is expected to greatly simplify the UM-to-DMC process, save energy, and improve its efficiency.

3. CONCLUSION

In summary, the NH₃ permselective membrane reactor based on the modified SAPO-34 membranes was successfully realized for the UM-to-DMC reaction for the first time. The effective
pore size and acidity of SAPO-34 membranes were significantly reduced by zinc ion-exchange and thermal NH$_3$–methanol treatments. Compared with the nonmembrane reactor, the membrane reactor exhibits a surpassing of the thermodynamic equilibrium limitations doubly, excellent MC/urea conversion, and DMC selectivity due to in situ removal of the generated NH$_3$ by the membrane. The membrane reactor also shows reliable chemical, thermal, and mechanical stability during more than 2000 h of testing. As the modified membrane can separate NH$_3$ and methanol, it is highly promising to apply this kind of membrane in other ammonia generating reactions including urea alcoholysis with larger alcohols. At the same time, the thin SAPO-34 membranes display remarkable separation performance for the methanol–DMC azetrope. All in all, this study demonstrates the great potential that integration of such membranes offers for process intensification, energy savings, and efficiency improvement in urea alcoholysis.

4. METHODS

4.1. Membrane Preparation. Porous α-Al$_2$O$_3$ tubes (OD = 10 mm, ID = 7 mm) with the nominal pore size of 100 nm were used as membrane supports (Inopor). Leaving ~6.5 cm$^2$ for membrane deposition, both ends of the 6 cm long supports were glazed to provide a sealing surface (Figure 1b). The SAPO-34 membranes were prepared on the inner surface with a seeding method. The seeds were synthesized by a gel with the molar ratio of 1.0 Al$_2$O$_3$:2.0 P$_2$O$_5$:0.6 SiO$_2$:4.0 tetra-ethylammonium hydroxide:75 H$_2$O.31 The membrane synthesis gel had a molar ratio of 1.0 Al$_2$O$_3$:1.0 P$_2$O$_5$:0.3 SiO$_2$:1.0 tetra-ethylammonium hydroxide:1.6 dipropylamine:150 H$_2$O. Hydrothermal synthesis was carried out at 220 °C for 6 h. For different membrane thicknesses, the synthesis time was controlled in 3–7 h. To obtain a thinner thickness, the membranes were prepared by a two-step method combining 2 h of hydrothermal and 5 h of dry-gel synthesis.41 After washing and drying, the as-prepared membranes were calcined in air at 400 °C for 4 h to remove the templates. For ion-exchange, the calcined SAPO-34 membrane and the zinc acetate ethanol solution (0.1 mol L$^{-1}$) were placed on an autoclave and then heated to 120 °C and kept for 4 h. After ion-exchange, the membrane was washed with deionized (DI) water and dried at 200 °C. For the NH$_3$ treatment, the membrane was placed into an autoclave, which was filled with 1 wt % NH$_3$–methanol solution, and then heated to 160 °C and kept for 48 h. After treatment, the membrane was dried in vacuum at 70 °C overnight.

4.2. Membrane Performance Test. The membranes were sealed in a stainless-steel module with silicone O-rings. The feed pressure was controlled with a back-pressure regulator, and the permeate pressure was kept at ambient pressure. No sweep gas was used. The SAPO-34 membranes were first checked by gas permeation of the CO$_2$–CH$_4$ (50/50) mixture. Permeate fluxes were measured with a bubble flowmeter, and the permeate and retentate compositions were analyzed by a GC with a TCD detector and a HayeSep D column. The methanol permeance was measured by a pervaporation method. The membrane module was put into an oven at a desired temperature. The feed was injected into the upstream side of the membrane by a high-pressure constant pump. The permeate side was connected to a vacuum line. The permeates were collected in a liquid nitrogen trap and weighted to calculate the permeate flux. The composition of collected permeate was determined by GC. For NH$_3$ permeance, a buffer bottle with water was connected to the permeate side. The NH$_3$ amount was then decided by an acid–base titration using methyl red as indicator. The separation factor was defined as SF = ($Y_a/Y_b$)/($X_a/X_b$), where $X$ and $Y$ represent the fraction in the feed and permeate, respectively; $a$ and $b$ refer to the more permeable component and the less permeable component, respectively.

4.3. Membrane Reaction. The commercial Zn–Al mixed oxide catalyst was supplied by Zhongke Materials Co. (Kaifeng, China). The catalyst was ground to 20–40 mesh, and ca. 1.5 g of catalyst was loaded into the lumen side of membrane. The membrane with the catalyst bed was mounted to the reactor shell and sealed with O-rings (DuPont Kalrez). The feedstock was injected by a high-pressure constant pump with a desired speed. Sweep gas nitrogen was introduced to the permeate side of membrane with a flow rate of 20 mL min$^{-1}$. The products and reactants mixture passed through the retentate line to a container. The line and container were kept at 120 °C. The reaction temperature was controlled in the range 160–220 °C. The feed rate of the feedstock was measured by the weight difference, and the product amount was also determined by weight. The operation for the nonmembrane fixed-bed reactor is the same as that for the membrane reactor except that the surface of the porous tube was sealed gastight with glaze.

4.4. Characterization. The morphology of membranes was measured by an SEM (Zeiss SUPRA 55 SAPHIRE) equipped with an EDS (Oxford X-max). The crystal structure of samples was analyzed with an XRD (Rigaku, Ultima IV) using Cu Kα (0.1504 nm) radiation under 40 mA and 40 kV. The surface area and pore size distribution of the samples was determined by the NH$_3$–TPD (Tianjin Xianquan TP-5080) with TCD. FTIR (Thermo Scientific, Nicolet 6700) was used to detect the functional groups of SAPO-34. The near-surface chemical information was analyzed by XPS (K-Alpha, Al Kα radiation, 1486.6 eV, 12 kV, 3 mA). The composition of samples was analyzed by XRF (Bruker S4 PIONEER).

4.5. Safety Statement. No unexpected or unusually high safety hazards were encountered.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00812.

Experimental details, calculations of equilibrium constant, and the results of SEM, XRD, XPS, and BET (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: zenggf@sari.ac.cn.
*E-mail: sunyh@sari.ac.cn.

**ORCID**

Gaofeng Zeng: 0000-0002-0034-1871
Yanfeng Zhang: 0000-0002-5389-7769
Ping Wu: 0000-0001-5339-6211
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