



## Article

# Simultaneous Production of Aromatics and CO<sub>x</sub>-Free Hydrogen via Methane Dehydroaromatization in Membrane Reactors: A Simulation Study

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**Abstract:** As an alternative route for aromatics and hydrogen production, methane dehydroaromatization (MDA) is of significant academic and industrial interest due to the abundance of natural gas resources and the intensive demand for aromatics and CO<sub>x</sub>-free hydrogen. In the present work, a simulation study on MDA in membrane reactors (MRs) was performed with the aim of co-producing aromatics and CO<sub>x</sub>-free hydrogen with a highly improved efficiency. The effects of various parameters, including catalytic activity, membrane flux and selectivity, as well as the operating conditions on the MR performance were discussed with respect to methane conversion, hydrogen yield, and hydrogen purity. The results show that catalytic activity and membrane flux and selectivity have significant impacts on CH<sub>4</sub> conversion and H<sub>2</sub> yield, whereas H<sub>2</sub> purity is mainly dominated by membrane selectivity. A highly improved MDA is confirmed to be feasible at a relatively low temperature and a high feed pressure because of the hydrogen extraction effect. To further improve MDA in MRs by intensifying H<sub>2</sub> extraction, a simple configuration combining a fixed-bed reactor (FBR) and an MR together is proposed for MDA, which demonstrates good potential for the high-efficiency co-production of aromatics and CO<sub>x</sub>-free hydrogen.

**Keywords:** methane dehydroaromatization; membrane reactor; CO<sub>x</sub>-free hydrogen; aromatics; hydrogen separation



**Citation:** Ye, F.; Fan, S.; Li, W.; Wang, Y.; Lang, X.; Zhang, J.; Li, J.; Li, G. Simultaneous Production of Aromatics and CO<sub>x</sub>-Free Hydrogen via Methane Dehydroaromatization in Membrane Reactors: A Simulation Study. *Membranes* **2022**, *12*, 1175. <https://doi.org/10.3390/membranes12121175>

Academic Editors: Jie Shen, Zongyao Zhou and Sheng Zhou

Received: 8 November 2022

Accepted: 19 November 2022

Published: 22 November 2022

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## 1. Introduction

Natural gas is the most abundant and cleanest energy carrier among fossil resources; thus, the conversion of methane instead of petroleum and coal into liquid fuels and high-value-added chemicals has been highly desirable in the chemical industry [1–6], particularly with the recent boom in the exploitation of unconventional shale gas [7–11] and natural gas hydrate [12,13] resources and with increasing concerns over environmental issues worldwide. Currently, the catalytic conversion of methane to important products, for instance, methanol [14] and olefins [15], is technologically dominated by an indirect route, which involves multistep reactions, and the highly energy-intensive intermediate step for syngas production, either by reforming or by partial oxidation, is generally inevitable, which results in a complicated process with a high production cost and a poor atom economy [16]. Therefore, direct conversion of methane to liquid fuels and chemicals without the syngas production intermediate step is of significant importance for practical applications.

In particular, a direct route, i.e., methane dehydroaromatization (MDA) ( $\text{CH}_4 \rightleftharpoons \frac{1}{6}\text{C}_6\text{H}_6 + \frac{3}{2}\text{H}_2$ ) under nonoxidative conditions, has gained significant interest

for methane utilization after a pioneering study by Wang et al. [17]. Compared with the conventional aromatic production process using petroleum as the feedstock, the MDA process has been widely accepted as an attractive alternative to produce aromatics with a better sustainability. On the other hand, it is noteworthy that the MDA process can simultaneously generate substantial  $\text{CO}_x$ -free hydrogen, which can be directly used as the fuel for polymer electrolyte membrane fuel cells (PEMFCs) with neither the removal of CO, which is a poison to the Pt catalyst, nor the emission of  $\text{CO}_2$ , which is mainly responsible for the greenhouse effect. Therefore,  $\text{CO}_x$ -free hydrogen produced from MDA demonstrates significant advantages against the conventional methane steam reforming process, i.e., the main route for current hydrogen production with an intensive energy consumption and massive emissions [18,19], in PEMFC applications. Currently, one of the major obstacles to the industrial implementation of the MDA process is its relatively low conversion because MDA is significantly limited by thermodynamic equilibrium. To achieve an acceptable conversion, MDA must be conducted at very high temperatures ( $\geq 700^\circ\text{C}$ ) [20–24]; unfortunately, this results in very rapid catalyst deactivation due to the serious coking effect. Thus far, how to simultaneously maintain a high conversion and high catalytic stability for MDA remains a great challenge for industrial applications.

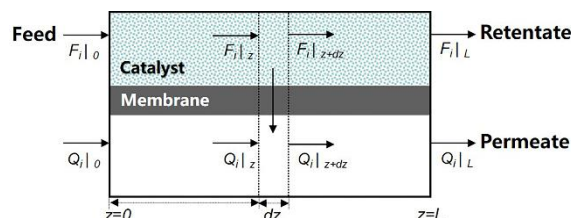
Membrane reactors (MRs), which integrate both separation and catalytic processes into a compact single unit, are promising for enhancing the conversion and/or enabling a lower reaction temperature for thermodynamically limited endothermic reactions because of the equilibrium shift effect. Considering the above advantages against conventional fixed-bed reactors (FBRs), MRs are extremely attractive for high-temperature MDA reactions, and various types of MRs have been successfully developed in an attempt to improve MDA performance [25–33]. Among them, most studies focus on Pd and its alloy MRs for MDA application because of its exclusive permeation for hydrogen; however, these Pd-based membranes are very expensive and prone to degradation at high temperatures [26]. Although highly hydrogen-permselective dense ceramic membranes with an excellent stability have been examined as an alternative for MDA application [30,31], the flux of these membranes is too low. On the other hand, in addition to hydrogen-permselective MRs, dense oxygen-permeable ceramic MRs, which allow for finely tuned oxygen distribution in the feed, were also employed for MDA [32,33], and an improved catalytic performance was observed due to the favorable thermodynamics of MDA under oxidative conditions. However, the addition of oxygen to the feed using oxygen-permeable ceramic membranes should be controlled very carefully; otherwise, overoxidation is prone to occur, which results in an extremely low selectivity for MDA. Furthermore, because the generation of CO under oxidative conditions is inevitable, hydrogen produced from oxygen-permeable MRs must be subjected to further purification before use in PEMFCs, which greatly impairs the economic and technical feasibility of the produced hydrogen for PEMFC applications because the separation of CO from hydrogen to an extremely low concentration is both costly and challenging.

Considering the high flux and high selectivity, as well as the excellent thermal stability, porous inorganic membranes, such as zeolite and amorphous silica, are good candidates for MDA applications. Unfortunately, to the best of our knowledge, no porous MRs have been reported for MDA, and details regarding how such factors as the catalytic activity, membrane performance and operating conditions affect the MR performance of MDA in terms of  $\text{CH}_4$  conversion,  $\text{H}_2$  yield and  $\text{H}_2$  purity are still not well understood. In this study, a simulation study of MDA in porous hydrogen-permselective MRs is conducted for the simultaneous production of aromatics and  $\text{CO}_x$ -free hydrogen, and insights into the above membrane intensification process would offer important inspiration for developing high-performance porous MRs for practical MDA applications.

## 2. Modeling

The mathematical model for MDA in concurrent configuration MRs was developed based on the following assumptions: (1) the reactor is isothermal and operates under a

steady state, (2) both the feed and permeate streams in the reactor are plug flows and a catalytic reaction only occurs in the feed stream, (3) concentration polarization effects are negligible, and (4) there are no pressure drops in the MR. A schematic model for the simulation study of MRs is shown in Figure 1.



**Figure 1.** Schematic model for the membrane reactor simulation.

The molar flow rate of component  $i$  in the MR can be expressed as follows [34,35]:

Feed side

$$\frac{dF_i}{dz} = v_i R w_{cat} - s P_i (x_i p_h - y_i p_l) \quad (1)$$

Permeate side

$$\frac{dQ_i}{dz} = s P_i (x_i p_h - y_i p_l) \quad (2)$$

where  $F_i$  and  $Q_i$  are molar flow rates of component  $i$  in the feed and permeate streams, and  $x_i$  and  $y_i$  are denoted as their corresponding molar fractions, respectively,  $p_h$  and  $p_l$  are the pressures of the feed and permeate streams, respectively,  $z$  is the axial position along the membrane,  $v_i$  is the stoichiometric number of component  $i$ ,  $P_i$  indicates the permeance of component  $i$  through the membrane,  $w_{cat}$  and  $s$  indicate the catalyst weight and membrane area per membrane unit length, respectively, and  $R$  is the reaction rate of MDA based on the following global reaction equation:



It is believed that a highly stable and selective catalyst for MDA can be expected by carefully tuning the properties of the support and metal species [36–38]. Therefore, side reactions in MDA are not considered in the present modeling for simplification in order to evaluate the potential of benzene production in MRs. With the assistance of the dimensionless parameters of the Damköhler number ( $Da$ ), permeation number ( $\theta$ ), reaction rate ( $R^*$ ), pressure ( $p_r$ ), permeance ( $\alpha_{H_2/i}$ ), and axial position ( $\zeta$ ) defined in Equations (4)–(9):

$$Da = R^{\max} W_{cat} / F_{CH_4,0} \quad (4)$$

$$\theta = P_{H_2} s L p_h / F_{CH_4,0} \quad (5)$$

$$R^* = R / R^{\max} \quad (6)$$

$$p_r = p_l / p_h \quad (7)$$

$$\alpha_{H_2/i} = P_{H_2} / P_i \quad (8)$$

$$\zeta = z / L \quad (9)$$

Equations (1) and (2) can be further expressed as dimensionless forms, as shown in Equations (10) and (11), respectively.

Feed side

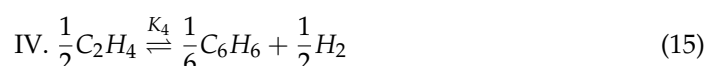
$$\frac{df_i}{d\zeta} = v_i R^* Da - \frac{\theta (x_i - y_i p_r)}{\alpha_{H_2/i}} \quad (10)$$

Permeate side

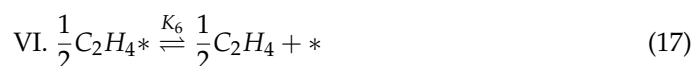
$$\frac{dq_i}{d\zeta} = \frac{\theta(x_i - y_i p_r)}{\alpha_{H_2/i}} \quad (11)$$

where  $f_i$  and  $q_i$  are the dimensionless flow rates normalized by the  $CH_4$  feed flow rate for component  $i$  in the feed and permeate streams, respectively,  $\zeta$  is the axial position of the MR normalized by the membrane length,  $\theta$  is defined as the permeation number that corresponds to  $H_2$  flux through the membrane normalized by the  $CH_4$  feed low rate,  $\alpha_{H_2/i}$  is the permeance ratio of  $H_2$  to component  $i$ ,  $p_r$  is the pressure ratio of the permeate stream to the feed stream,  $R^*$  is the ratio of the reaction rate  $R$  to the maximum reaction rate  $R^{max}$  based on the inlet feed composition,  $Da$  is the Damköhler number, which is defined as the ratio of the product of the maximum reaction rate  $R^{max}$  and the total catalyst weight of the membrane module  $W_{cat}$  to the  $CH_4$  feed flow rate, and  $Da$  indicates the effect of the catalyst and the feed flow rate on the catalytic performance, which can be used as a measure of the catalytic activity. The higher  $Da$  is, the closer the reaction is to equilibrium.

According to a simple single-site mechanism [39], the global reaction of MDA (Equation (3)) consists of the following series of elementary steps:



where  $*$  indicates the active site of the catalyst, and step III is obtained by merging the  $CH_2$  dimerization and  $C_2H_4$  desorption steps in Equations (16) and (17):



Step II is considered to be the rate-determining step in MDA, yielding a reaction rate expression for the global reaction in Equation (18) [39].

$$R = k_2 \frac{P_{CH_4} - \frac{1}{K_p} P_{C_6H_6}^{1/6} P_{H_2}^{3/2}}{1 + K_1 P_{CH_4} + \frac{K_3}{K_4} P_{C_6H_6}^{1/6} P_{H_2}^{1/2}} \quad (18)$$

where

$$K_4 = \exp\left(-\frac{\Delta G_4}{R_g T}\right) \left(p^\ominus\right)^{\frac{1}{6}} \quad (19)$$

$$K_p = \exp\left(-\frac{\Delta G}{R_g T}\right) \left(p^\ominus\right)^{\frac{2}{3}} \quad (20)$$

$p^\ominus$  is the standard pressure,  $P_{CH_4}$ ,  $P_{C_6H_6}$  and  $P_{H_2}$  are the partial pressures of  $CH_4$ ,  $C_6H_6$ , and  $H_2$ , respectively,  $\Delta G$  and  $\Delta G_4$  are the Gibbs free energies of the global (Equation (1)) and step IV (Equation (15)) reactions, respectively,  $k_2$  is the reaction rate constant of step II, and  $K_1$ ,  $K_3$ ,  $K_4$  and  $K_p$  are equilibrium constants for steps I, III, IV and the global reaction, respectively. For a 0.5%Ru-3%Mo/ZSM-5 catalyst, the reaction rate and equilibrium constants ( $K_1$ ,  $K_3$ ,  $k_2$ ) are shown in Table 1 according to Iliuta et al. [39], which were adopted in the present work for the simulation study.

**Table 1.** Reaction rate and equilibrium constants used in the present simulation.

Temperature (K)	$k_2$ (mol g <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup> bar <sup>−1</sup> )	$K_1$ (bar <sup>−1</sup> )	$K_3$ (bar <sup>−1/2</sup> )
873	0.00717	2.877	2.359
898	0.0102	2.197	2.870
923	0.014	1.675	3.020
948	0.019	1.280	3.185
973	0.025	1.029	3.300

The simulation study of MDA in concurrent MRs was performed at temperatures of 873–973 K, with porous H<sub>2</sub>-permselective membranes, showing H<sub>2</sub>/CH<sub>4</sub> selectivities in the range of 10–∞, under feed and permeate pressures of 100–1000 and 5 kPa, respectively. Because both CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> are much larger than H<sub>2</sub> in terms of molecular size, they are assumed to permeate through the defects of H<sub>2</sub>-permselective membranes based on a Knudsen diffusion mechanism; therefore, the selectivity of CH<sub>4</sub> to C<sub>6</sub>H<sub>6</sub> in the MR is fixed to the Knudsen selectivity in the simulation. Because benzene is a condensable product that is easily separated and collected on both retentate and permeate sides of the MR, the yield of benzene in the MR is defined based on the product obtained in both retentate and permeate streams, and the effect of the presence of benzene on the final H<sub>2</sub> purity can be negligible. On the other hand, both H<sub>2</sub> yield and H<sub>2</sub> purity is defined based on only the permeate side, because purified H<sub>2</sub> is highly desirable. Therefore, the CH<sub>4</sub> conversion ( $X_{CH_4}$ ), benzene yield ( $Y_{C_6H_6}$ ), H<sub>2</sub> yield ( $Y_{H_2}$ ), and H<sub>2</sub> purity ( $C_{H_2}$ ) obtained in the MRs are defined as follows:

$$X_{CH_4} = \frac{F_{CH_4,0} - F_{CH_4,L} - Q_{CH_4,L}}{F_{CH_4,0}} \quad (21)$$

$$Y_{C_6H_6} = \frac{6F_{C_6H_6,L} + 6Q_{C_6H_6,L}}{F_{CH_4,0}} \quad (22)$$

$$Y_{H_2} = \frac{2Q_{H_2,L}}{3F_{CH_4,0}} \quad (23)$$

$$C_{H_2} = \frac{Q_{H_2,L}}{Q_{CH_4,L} + Q_{H_2,L}} \quad (24)$$

For FBRs, the CH<sub>4</sub> conversion, benzene yield, H<sub>2</sub> yield and H<sub>2</sub> purity are defined in Equations (25)–(28):

$$X_{CH_4} = \frac{F_{CH_4,0} - F_{CH_4,L}}{F_{CH_4,0}} \quad (25)$$

$$Y_{C_6H_6} = \frac{6F_{C_6H_6,L}}{F_{CH_4,0}} \quad (26)$$

$$Y_{H_2} = \frac{2F_{H_2,L}}{3F_{CH_4,0}} \quad (27)$$

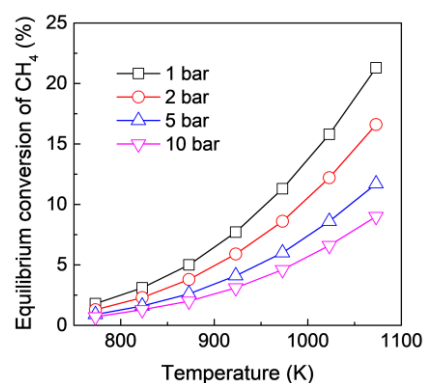
$$C_{H_2} = \frac{F_{H_2,L}}{F_{CH_4,L} + F_{H_2,L}} \quad (28)$$

### 3. Results and Discussion

#### 3.1. Thermodynamic Analysis and Model Validation

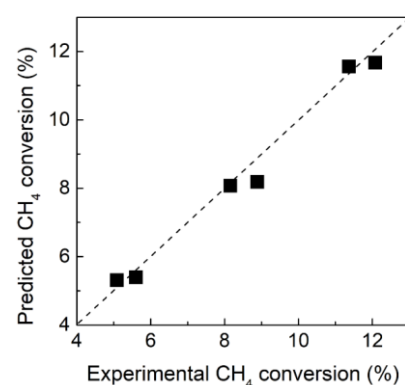
Figure 2 shows the equilibrium conversion of CH<sub>4</sub> in MDA under different temperatures and feed pressures. The equilibrium conversion of CH<sub>4</sub> is quite low, particularly under a low temperature and a high pressure. The above calculation confirms that MDA is significantly thermodynamically unfavorable. Although CH<sub>4</sub> conversion in MDA can be improved by increasing the reaction temperature, catalyst deactivation is reportedly even faster due to the more serious coking effect at a higher temperature [40]. Therefore,

to strike a balance between  $\text{CH}_4$  conversion and catalytic stability, MDA is generally conducted at 700 °C and at atmospheric pressure [21–23], which corresponds to an equilibrium conversion of approximately 12% due to the significant thermodynamic limitation. The above results demonstrate that there is significant potential to use  $\text{H}_2$ -permselective MRs for highly enhanced MDA because the equilibrium of MDA can be efficiently shifted to the product side after selective  $\text{H}_2$  extraction.



**Figure 2.** Equilibrium conversion of  $\text{CH}_4$  in MDA under different temperatures and pressures.

To validate the proposed model for the simulation study of MDA in MRs, we first calculated the  $\text{CH}_4$  conversion based on the present model and previously reported experimental parameters [39] using the same cylindrical reactor without  $\text{H}_2$  extraction under various operating conditions. As shown in Figure 3, both the theoretically predicted and experimentally obtained  $\text{CH}_4$  conversions showed an excellent agreement, which verifies the feasibility of the proposed model for the simulation study of MDA. Unfortunately, further verification cannot be conducted by applying  $\text{H}_2$  extraction to MRs because Pd-based membranes are prone to poison in the presence of hydrocarbons at high temperatures, and the actual  $\text{H}_2$  permeation performance of the membrane reactor, which is reportedly significantly different compared with that obtained during the  $\text{H}_2$  permeation test [28], is currently not yet available during MDA.



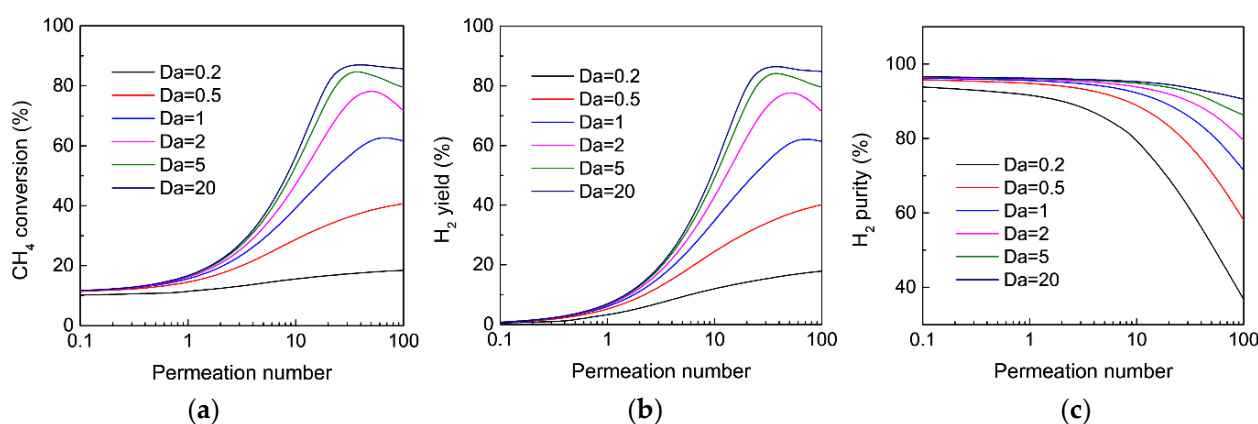
**Figure 3.** Comparison of experimentally obtained and theoretically predicted  $\text{CH}_4$  conversions in the MR without  $\text{H}_2$  extraction.

### 3.2. Effect of Catalysts on the MR Performance

Figure 4 shows the effect of the Damköhler number on  $\text{CH}_4$  conversion,  $\text{H}_2$  yield, and  $\text{H}_2$  purity as a function of the permeation number for MDA in the MR. When the catalytic activity of the MR is relatively low, for instance,  $Da = 0.2$  and  $0.5$ , both  $\text{CH}_4$  conversion and  $\text{H}_2$  yield obtained in the MR gradually increased with an increasing permeation number, which could be ascribed to the improved equilibrium shift effect, since  $\text{H}_2$  extraction from the MR is enhanced. For MR with a relatively active catalyst ( $Da \geq 1$ ), the improvement in the  $\text{CH}_4$  conversion and  $\text{H}_2$  yield is more remarkable due to the enhanced driving force



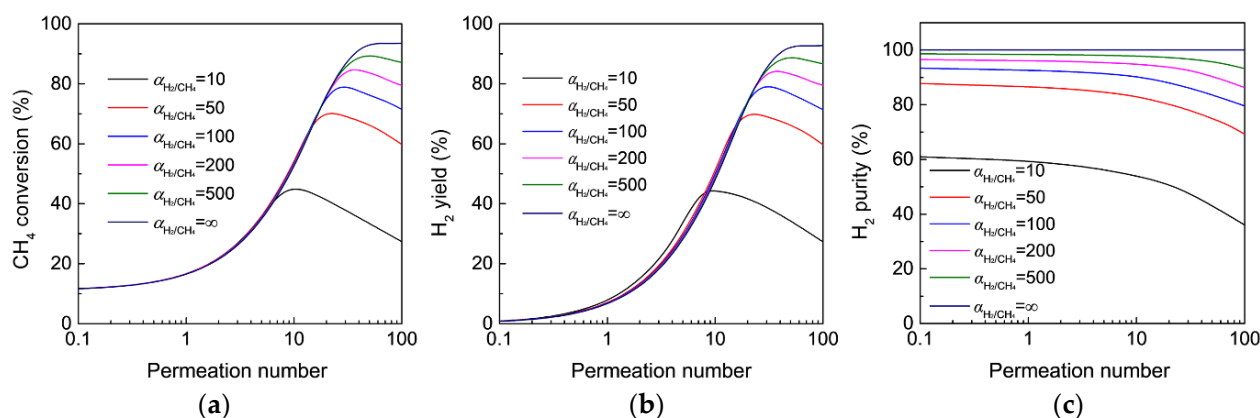
for  $H_2$  extraction. However, both the  $CH_4$  conversion and  $H_2$  yield show a maximum as the permeation number increases, which could be mainly attributed to the adverse effect of  $CH_4$  permeation through the membrane because the amount of  $CH_4$  permeation through the membrane becomes remarkable at high  $Da$  values and permeation numbers. Similar trends were also previously observed for various dehydrogenation reactions in  $H_2$ -permselective MRs [34,35]. On the other hand, the  $H_2$  purity in the permeate stream always decreases with an increasing permeation number, regardless of the values of  $Da$ , which mainly results from the enhanced  $CH_4$  permeation through the membrane at a high permeation number. However, for a given permeation number,  $H_2$  purity increases as  $Da$  increases because  $CH_4$  conversion is improved and the permeation of  $CH_4$  through the membrane becomes slower. The above results demonstrate that an active catalyst is necessary for the effective enhancement of MDA in an MR with respect to  $CH_4$  conversion,  $H_2$  yield and  $H_2$  purity.



**Figure 4.** Effect of the Damköhler number on (a)  $CH_4$  conversion, (b)  $H_2$  yield, and (c)  $H_2$  purity as a function of permeation number for MDA in the MR. (Simulation conditions:  $T = 973$  K,  $\alpha_{H_2/CH_4} = 200$ ,  $\alpha_{CH_4/C_6H_6}$  = Knudsen selectivity,  $p_h = 1$  bar,  $p_l = 0.05$  bar).

### 3.3. Effect of Membranes on the MR Performance

Figure 5 shows the effect of  $H_2/CH_4$  selectivity of the membrane on  $CH_4$  conversion,  $H_2$  yield, and  $H_2$  purity as a function of permeation number for MDA in the MR. As the permeation number increases from 0.1 to 100, both the  $CH_4$  conversion and  $H_2$  yield in porous MRs with a given  $H_2/CH_4$  selectivity initially increase and then subsequently decrease, resulting in a maximum. This is because the equilibrium shift effect after  $H_2$  extraction that contributes to the improved  $CH_4$  conversion and yield is dominative at a relatively low permeation number, whereas the effect of  $CH_4$  permeation from the feed to the permeate side that lowers the  $CH_4$  conversion and yield becomes very important at a high permeation number. The maximal  $CH_4$  conversion and  $H_2$  yield are effectively enhanced as the  $H_2/CH_4$  selectivity of the MR is increased from 10 to 500 because the leakage of  $CH_4$  from the feed to permeate sides can be significantly reduced with a highly  $H_2$ -selective membrane. Note that the MR shows a low degree of improvement in  $CH_4$  conversion and  $H_2$  yield at a low permeation number, even though the membrane selectivity is extremely high. This is because only a very limited amount of  $H_2$  is extracted from the reactor at a relatively low permeation number. Therefore, a remarkable improvement is achieved only for MR with both an acceptable  $H_2$  flux and selectivity.



**Figure 5.** Effect of  $H_2/CH_4$  selectivity on (a)  $CH_4$  conversion, (b)  $H_2$  yield, and (c)  $H_2$  purity as a function of permeation number for MDA in the membrane reactor. (Simulation conditions:  $T = 973$  K,  $Da = 5$ ,  $\alpha_{CH_4/C_6H_6}$  = Knudsen selectivity,  $p_h = 1$  bar,  $p_l = 0.05$  bar).

Considering the excellent  $H_2$  separation performance of Pd-based membranes, MDA in MRs should be effectively improved after  $H_2$  extraction according to the present and previously reported theoretical simulations [41,42]. However, experimental investigations [25,26,28] have demonstrated that Pd-based MRs show only a very limited enhancement for MDA compared with FBRs under the same operating conditions. We believe that the remarkable difference between the theoretical prediction and the experimental results is most likely attributed to the significantly decreased  $H_2$  permeation flux of Pd-based membranes during MDA because Pd-based membranes are reportedly poisoned in the presence of hydrocarbons at high temperatures [43], which significantly hinder  $H_2$  permeation by blocking Pd sites on the membrane surface from adsorbing and dissociating  $H_2$  molecules. Recently, Natesakhawat et al. [28] compared the  $H_2$  permeation performance of a tubular Pd membrane in 10%  $H_2/N_2$  and 10%  $H_2/CH_4$  mixtures at 700 °C to study the effect of  $CH_4$  on the Pd membrane performance. The Pd membrane in a later system lost up to 75% of its  $H_2$  permeability, which confirms the occurrence of serious  $CH_4$  poisoning for the Pd membrane. Moreover, the reduction of  $H_2$  permeability of Pd membranes was reportedly even much more noticeable during MDA [28]. The above simulation results confirm that the poor catalytic performance of Pd-based MRs in experimental investigations most likely results from the severe degradation of  $H_2$  permeation flux during MDA.

Importantly, it is worth noting that the porous MR with a  $H_2/CH_4$  selectivity of 200 shows almost the same MDA performance in terms of the  $CH_4$  conversion and  $H_2$  yield compared with those of the dense Pd-based MR with an infinite  $H_2/CH_4$  selectivity under the same permeation number ranging from 0.1 to 30, and both the maximal  $CH_4$  conversion and  $H_2$  yield exceed 80%, which demonstrates a significant potential for highly enhanced MDA in the porous MRs. Although dense Pd membranes show an exclusive permeation for  $H_2$ , taking their relatively lower flux during MDA and the high cost into consideration, porous MRs with an acceptable cost and  $H_2/CH_4$  selectivity ( $>200$ ) but a much higher  $H_2$  permeance ( $>10^{-6}$  mol  $Pa^{-1}$   $m^{-2}$   $s^{-1}$ ) free of  $CH_4$  poisoning, such as amorphous silica membranes [44–46], would be preferable for MDA in practical applications in terms of the  $CH_4$  conversion and  $H_2$  yield.

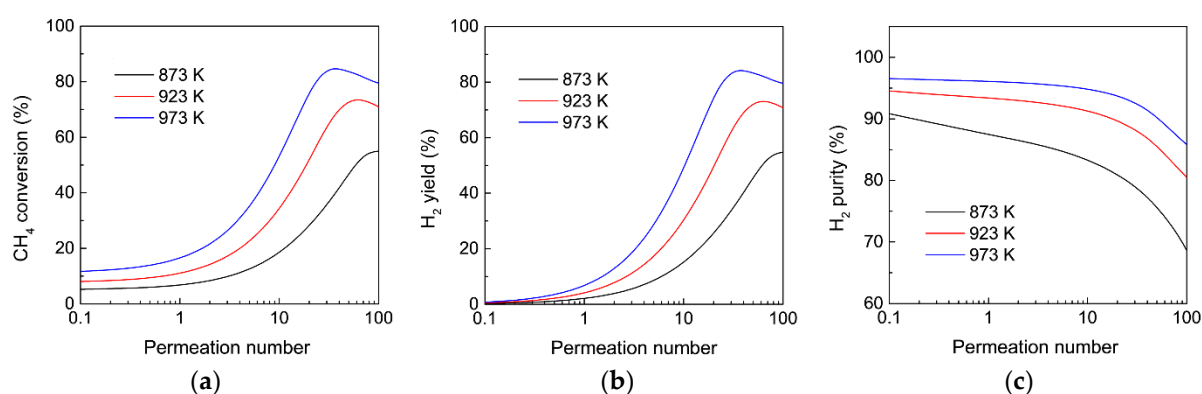
The  $H_2$  purity obtained in the MR can be significantly enhanced as the membrane selectivity increases, and the effect of the permeation number seems to have much less of an impact on the  $H_2$  purity, particularly for the MR with a  $H_2$  selectivity over 200. The above results demonstrate that both the  $CH_4$  conversion and  $H_2$  yield obtained in the MR are greatly affected by both the catalytic activity and membrane performance, while the  $H_2$  purity is mainly dominated by the membrane selectivity. In this regard, dense Pd membranes with exclusive  $H_2$  permeation are preferable when the  $H_2$  purity is a priority for MDA in the MR. Therefore, the selection of membrane materials should be carefully



considered according to the objective MR performance in terms of the  $\text{CH}_4$  conversion,  $\text{H}_2$  yield, and  $\text{H}_2$  purity.

### 3.4. Effect of Operating Conditions on the MR Performance

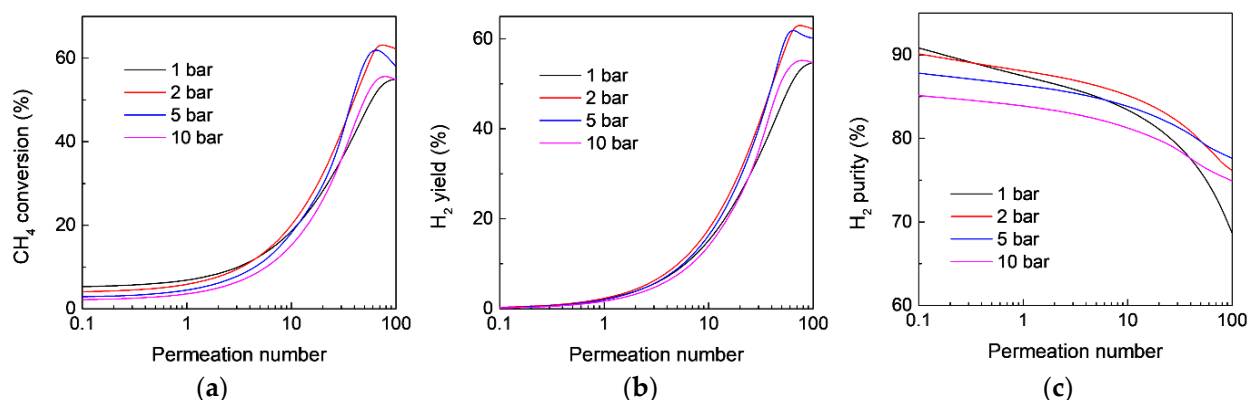
Thermodynamically, the coking reaction is much more favorable than MDA at a high temperature and leads to catalyst deactivation during MDA. To reduce the effect of coking on the catalytic stability, it is preferable to perform MDA under a relatively low temperature, which would impair the  $\text{CH}_4$  conversion for MDA in the conventional FBR. However, MR allows for the possibility that MDA is conducted at a lower temperature, whereas the  $\text{CH}_4$  conversion remains high because of the equilibrium shift effect after  $\text{H}_2$  extraction. Figure 6 shows the effect of the reaction temperature on the  $\text{CH}_4$  conversion,  $\text{H}_2$  yield, and  $\text{H}_2$  purity as a function of the permeation number for MDA in the MR. As expected, for a given permeation number, although  $\text{CH}_4$  conversion,  $\text{H}_2$  yield, and  $\text{H}_2$  purity all decrease with a decreasing reaction temperature because MDA is thermodynamically unfavorable at a low temperature, the MR performance greatly surpasses that obtained in the conventional FBR under the same reaction temperature, and the improvement is still extremely remarkable, even under 873 K if the MR is highly permeable. The above results demonstrate the significant importance of intensifying the MR performance for MDA by improving  $\text{H}_2$  permeance via reducing the membrane thickness. This is particularly important for MDA operated under a lower reaction temperature because the  $\text{H}_2$  partial pressure difference across the membrane is lower for  $\text{H}_2$  permeation. Recent progress has demonstrated that emerging two-dimensional-material membranes [47] constructed by 2D nanosheets with few atomic thickness layers show both a high flux and high selectivity, which would be a future candidate for the development of high-performance MRs for MDA.



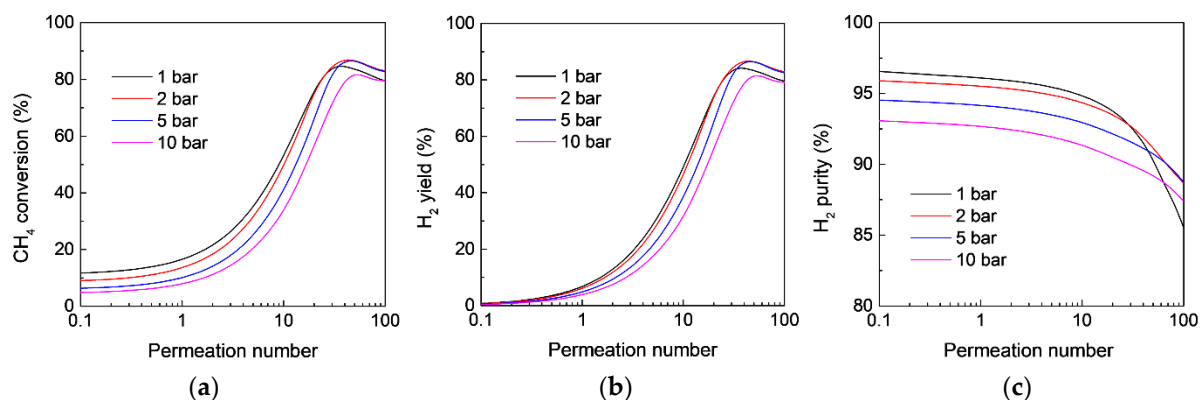
**Figure 6.** Effect of the reaction temperature on (a)  $\text{CH}_4$  conversion, (b)  $\text{H}_2$  yield, and (c)  $\text{H}_2$  purity as a function of the permeation number for MDA in the membrane reactor. (Simulation conditions:  $Da = 5$ ,  $\alpha_{\text{H}_2/\text{CH}_4} = 200$ ,  $\alpha_{\text{CH}_4/\text{C}_6\text{H}_6}$  = Knudsen selectivity,  $p_h = 1$  bar,  $p_l = 0.05$  bar).

On the other hand, although a high feed pressure is not favorable for MDA in an FBR according to the equilibrium shift by Le Chatelier's principle, as also confirmed in the aforementioned calculation (Figure 2), the effect of the feed pressure on MDA in the MR is more complicated because a high pressure also favors  $\text{H}_2$  permeation through the membrane, which is believed to boost MDA in MRs from the viewpoint of an equilibrium shift due to the enhancing  $\text{H}_2$  extraction. Therefore, whether a high feed pressure benefits MDA in MRs depends on the equilibrium shift effect caused by both  $\text{H}_2$  extraction and the feed pressure. However, how the feed pressure affects MDA in MRs remains unclear. Figures 7 and 8 show the effect of the feed pressure on  $\text{CH}_4$  conversion,  $\text{H}_2$  yield, and  $\text{H}_2$  purity as a function of permeation number for MDA in the MR at 873 and 973 K, respectively. For the same permeation number with a relatively low value, the MR shows a decreased  $\text{CH}_4$  conversion with an increasing feed pressure, regardless of the reaction temperature, because the final  $\text{CH}_4$  conversion is largely affected by the equilibrium shift effect by high feed pressures. However, when the permeation number is larger than 10,

compared with MDA in the MR under atmospheric pressure, the MR shows an enhanced  $\text{CH}_4$  conversion along with an improved  $\text{H}_2$  yield and purity in a pressurized system, although the high pressure is unfavorable for MDA in FBRs, which could be ascribed to the significant contribution of the equilibrium shift effect by enhanced  $\text{H}_2$  extraction at high feed pressures. It should be noted that the MR performance could again deteriorate at much higher pressures because the effect of feed pressure on the MR performance becomes more remarkable. For instance, the  $\text{CH}_4$  conversion at a feed pressure of 10 bar is lower than that obtained at atmospheric pressure at 873 K, even though the MR is highly permeable (Figure 8). Therefore, there is an optimal feed pressure to maximize the MDA performance in MRs, and the value highly depends on the specific reaction conditions used, such as temperature and catalyst.



**Figure 7.** Effect of the feed pressure on (a)  $\text{CH}_4$  conversion, (b)  $\text{H}_2$  yield, and (c)  $\text{H}_2$  purity as a function of the permeation number for MDA in the membrane reactor. (Simulation conditions:  $T = 873 \text{ K}$ ,  $Da = 5$ ,  $\alpha_{\text{H}_2/\text{CH}_4} = 200$ ,  $\alpha_{\text{CH}_4/\text{C}_6\text{H}_6} = \text{Knudsen selectivity}$ ,  $p_l = 0.05 \text{ bar}$ ).

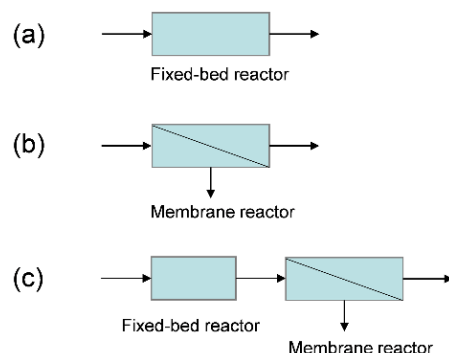


**Figure 8.** Effect of  $\text{CH}_4$  feed pressure on (a)  $\text{CH}_4$  conversion, (b)  $\text{H}_2$  yield, and (c)  $\text{H}_2$  purity as a function of the permeation number for MDA in the membrane reactor. (Simulation conditions:  $T = 973 \text{ K}$ ,  $Da = 5$ ;  $\alpha_{\text{H}_2/\text{CH}_4} = 200$ ,  $\alpha_{\text{CH}_4/\text{C}_6\text{H}_6} = \text{Knudsen selectivity}$ ,  $p_l = 0.05 \text{ bar}$ ).

### 3.5. Integration of an FBR and an MR for Enhanced MDA

The enhancement of the MR performance is significantly affected by the amount of extracted  $\text{H}_2$  during the reaction, and thus a high membrane packing density is highly desirable for practical MDA applications. Hollow fiber MRs are generally preferable when taking the very high packing density into account [48]. However, one of the major obstacles to the practical use of hollow fiber MRs is the relatively low catalyst loading capacity, which generally results in a poor performance of MRs due to the relatively low catalytic activity, as confirmed in Figure 4. This is because the  $\text{H}_2$  partial pressure across the membrane, which is the driving force for  $\text{H}_2$  permeation, is too low to extract sufficient  $\text{H}_2$  from the MR. Consequently,  $\text{H}_2$  permeation in hollow fiber MRs should be further intensified to

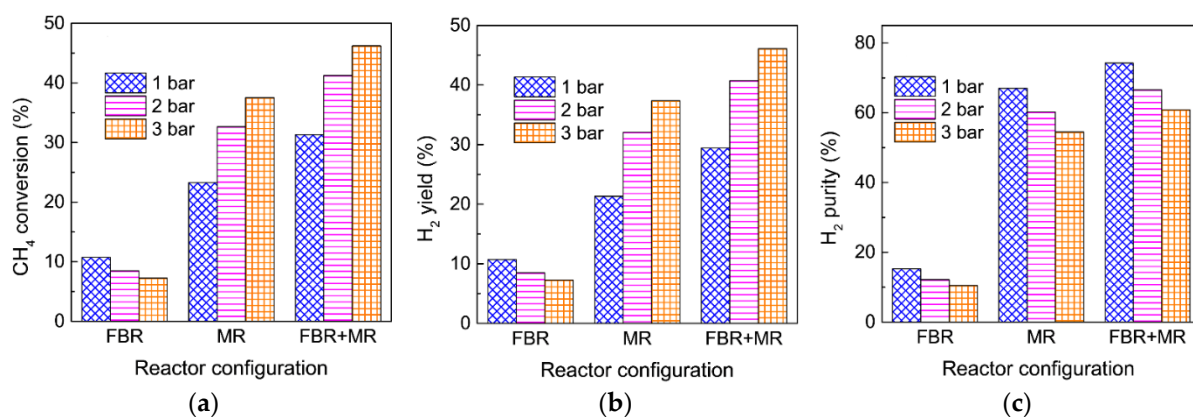
more efficiently promote the MDA performance. To achieve a higher MDA performance, a facile configuration that integrates a fixed-bed reactor (FBR) and an MR is suggested for MDA in which the FBR functions as a pre-reactor. For comparison, the performance of MDA in a single conventional FBR and a single MR are studied under identical operating conditions. The schematic reactor configurations are shown in Figure 9.



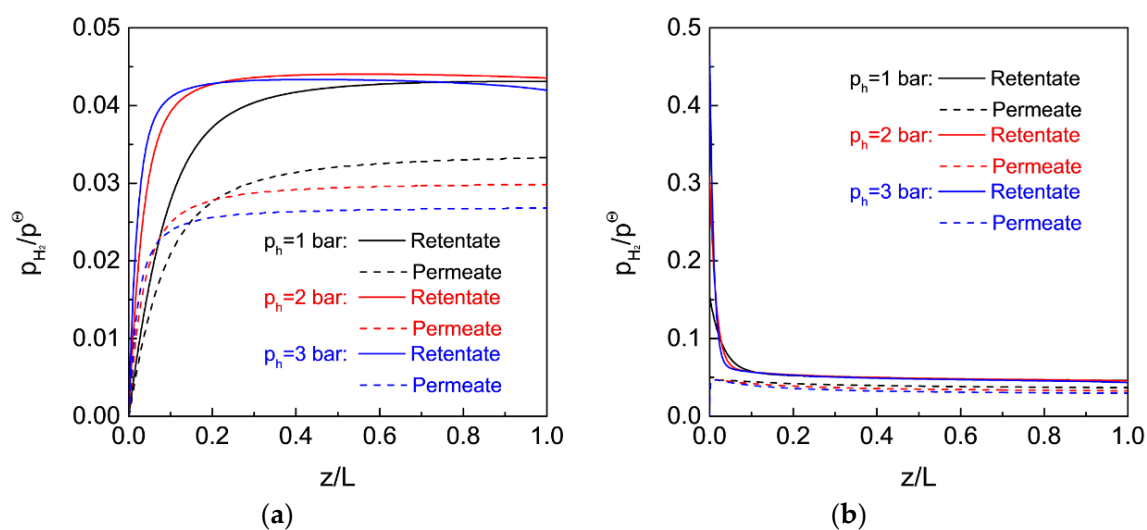
**Figure 9.** Different reactor configurations used for MDA. (a) Fixed-bed reactor; (b) membrane reactor; (c) integration of a fixed-bed reactor and a membrane reactor.

Figure 10 shows the effect of reactor configurations on the  $\text{CH}_4$  conversion,  $\text{H}_2$  yield, and  $\text{H}_2$  purity for MDA in the MR under different feed pressures. For a comparison, catalyst loading in the FBR (Figure 9a) and MRs (Figure 9b,c) are fixed at the same amount, while the  $\text{CH}_4$  conversion in the FBR (Figure 9c) is assumed to achieve equilibrium under atmospheric pressure because a high catalyst loading in the FBR is practically feasible. For the single conventional FBR (Figure 9a), the  $\text{CH}_4$  conversion,  $\text{H}_2$  yield and  $\text{H}_2$  purity are 10.7, 10.7 and 10.5%, respectively, at a feed pressure of 1 bar, and all of these values decrease with an increasing feed pressure, which can be ascribed to the equilibrium shift of MDA to the backward side at high feed pressures. However, the MDA performance is much enhanced in the single MR, particularly under a high feed pressure, although a pressurized system is unfavorable for MDA in an FBR. As the feed pressure increases from 1 to 2 and 3 bar, the  $\text{CH}_4$  conversion gradually increases from 23.3 to 32.7 and 37.6%, with the  $\text{H}_2$  yield increasing from 21.3 to 32.1 and 37.3%, and the  $\text{H}_2$  purity decreasing from 74.3 to 66.6 and 60.1%, respectively. This remarkable improvement in the MDA can be ascribed to the equilibrium shift effect of the MR after  $\text{H}_2$  extraction, where a higher feed pressure effectively promotes  $\text{H}_2$  extraction due to the higher  $\text{H}_2$  partial pressure difference across the membrane, as evidenced by the axial profiles of the normalized  $\text{H}_2$  partial pressure in the MR under different feed pressures in Figure 11a. The above result demonstrates that the MR performance under present pressurized conditions is largely affected by the equilibrium shift effect caused by  $\text{H}_2$  extraction, rather than by a high pressure. When an FBR is coupled with the MR (Figure 9c), after completion of the reaction in the FBR, the  $\text{H}_2$  partial pressure is quite high at the inlet of the MR, which would facilitate  $\text{H}_2$  extraction during the subsequent MR due to the increased driving force for  $\text{H}_2$  permeation. As expected,  $\text{CH}_4$  conversion in the MR is further improved to 31.3% at a feed pressure of 1 bar with the assistance of an FBR, and a higher feed pressure in the MR even improves the  $\text{CH}_4$  conversion to a higher degree (41.2 and 46.2% at 2 and 3 bar, respectively). The corresponding  $\text{H}_2$  yield also increases from 29.4 to 40.7 and 46.1%, whereas the  $\text{H}_2$  purity decreases from 74.3 to 66.6 and 60.1 at 1, 2 and 3 bar, respectively. Previously, an improved conversion was also observed for methylcyclohexane dehydrogenation in an MR when a FBR was coupled [49]. With the assistance of FBR as a pre-reactor, the exceptional MDA performance in the MR was primarily ascribed to the enhanced  $\text{H}_2$  extraction. As confirmed by the axial profiles of the normalized  $\text{H}_2$  partial pressure for MDA in the MR in Figure 11b, the employment of a pre-reactor indeed increases the  $\text{H}_2$  partial pressure difference across the membrane, particularly near the inlet zone of the MR. This effect is even more effective under pressurized systems, which further promotes the equilibrium shift of MDA to the

forward side and results in a much higher CH<sub>4</sub> conversion and H<sub>2</sub> yield and purity than those obtained in the single FBR and the single MR.



**Figure 10.** Effect of reactor configurations on (a) CH<sub>4</sub> conversion, (b) H<sub>2</sub> yield, and (c) H<sub>2</sub> purity for MDA in the membrane reactor with different CH<sub>4</sub> feed pressures. (Simulation conditions: Temperature = 973 K, catalyst amount = 0.15 g, CH<sub>4</sub> feed =  $6.59 \times 10^{-3}$  mol h<sup>-1</sup>, H<sub>2</sub> permeance = 72 mol m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, membrane length = 0.4 m, membrane diameter =  $2.5 \times 10^{-3}$  m,  $\alpha_{H_2/CH_4} = 200$ ,  $\alpha_{CH_4/C_6H_6}$  = Knudsen selectivity,  $p_l = 0.05$  bar, and  $p_h = 1, 2$  and 3 bar).



**Figure 11.** Axial profiles of H<sub>2</sub> partial pressure normalized by the standard pressure for MDA in the membrane reactor under different feed pressures (a) with and (b) without the assistance of a pre-reactor. (Simulation conditions: Temperature = 973 K, catalyst amount = 0.15 g, CH<sub>4</sub> feed =  $6.59 \times 10^{-3}$  mol h<sup>-1</sup>, H<sub>2</sub> permeance = 72 mol m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, membrane length = 0.4 m, membrane diameter =  $2.5 \times 10^{-3}$  m,  $\alpha_{H_2/CH_4} = 200$ ,  $\alpha_{CH_4/C_6H_6}$  = Knudsen selectivity,  $p_l = 0.05$  bar, and  $p_h = 1, 2$  and 3 bar).

Considering the effectively enhanced H<sub>2</sub> extraction, the proposed simple reactor configuration that combines an FBR and an MR is superior to both the conventional single FBR and the single MR in terms of the CH<sub>4</sub> conversion, H<sub>2</sub> yield and H<sub>2</sub> purity. In addition, it should be noted that MDA is endothermic; therefore, heat transfer to the catalyst bed must be fast enough to maintain a constant temperature in the reactor. The new reactor configuration consisting of two parts allows for sectional heating for MDA, which again benefits MDA for simultaneous large-scale production of aromatics and CO<sub>x</sub>-free H<sub>2</sub> in industrial applications under isothermal conditions.

#### 4. Conclusions

A dimensionless mathematical model was formulated and verified for a simulation study on methane dehydroaromatization in H<sub>2</sub>-permselective MRs for the simultaneous production of aromatics and CO<sub>x</sub>-free H<sub>2</sub>. The simulation results showed that the improvement in the CH<sub>4</sub> conversion and H<sub>2</sub> yield in the MR is strongly influenced by the catalytic activity and membrane flux and selectivity, whereas H<sub>2</sub> purity is mainly determined by the membrane selectivity. Compared with dense Pd-based membranes, porous membranes, such as amorphous silica, with a H<sub>2</sub>/CH<sub>4</sub> selectivity of several hundred are highly preferable for MDA with respect to the both CH<sub>4</sub> conversion and H<sub>2</sub> yield due to the high H<sub>2</sub> permeance and the absence of CH<sub>4</sub> poisoning. Operating conditions, including the reaction temperature and pressure, also exert important impacts on the MR performance. A low temperature generally results in a decrease in the MDA performance due to unfavorable thermodynamics, but a significantly higher performance, compared with that of conventional FBRs, can still be achieved in MRs due to the equilibrium shift effect after H<sub>2</sub> extraction. Therefore, MRs have great potential to lower the reaction temperature and thus reduce the coking on the catalyst for MDA. A pressurized system is confirmed to further improve MDA in the MR under certain conditions due to the enhanced H<sub>2</sub> extraction, although a pressurized system is unfavorable for MDA in FBRs. Finally, a simple configuration that combines an FBR and an MR is proposed for MDA, which demonstrates a much better performance in terms of the CH<sub>4</sub> conversion, H<sub>2</sub> yield, and H<sub>2</sub> purity compared with both the single FBR and single MR due to the intensified H<sub>2</sub> extraction. This simple and effective configuration shows a great potential for the simultaneous production of aromatics and CO<sub>x</sub>-free H<sub>2</sub> with a high efficiency for practical applications.

**Author Contributions:** Conceptualization, G.L.; investigation, F.Y.; writing—original draft preparation, F.Y.; writing—review and editing, S.F., W.L., Y.W., X.L., J.Z. and G.L.; project administration, J.Z.; funding acquisition, J.L. and G.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the National Natural Science Foundation of China, grant number U1662137; the Zhuhai Industry-University-Research Cooperation and Basic & Applied Basic Research Project, grant number ZH22017003210078PWC; and the Foundation of State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, grant number 2021-K40.

**Institutional Review Board Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### Nomenclature

$Da$	Damköhler number, dimensionless
$f$	dimensionless feed-side flow rate, dimensionless
$F$	feed-side molar flow rate, mol h <sup>−1</sup>
$C$	purity of hydrogen, dimensionless
$k$	reaction rate constant, mol g <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup> bar <sup>−1</sup>
$k_2$	reaction rate constant, mol g <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup> bar <sup>−1</sup>
$K_1$	equilibrium constant, bar <sup>−1</sup>
$K_3$	equilibrium constant, bar <sup>−1/2</sup>
$K_4$	equilibrium constant, bar <sup>1/6</sup>
$K_p$	equilibrium constant, bar <sup>2/3</sup>
$L$	membrane reactor length, m
$p$	partial pressure, bar
$p^\ominus$	standard pressure, bar
$p_h$	feed-side pressure, bar
$p_l$	permeate-side pressure, bar
$p_r$	pressure ratio, dimensionless

$P$	gas permeance, $\text{mol m}^{-2} \text{h}^{-1} \text{bar}^{-1}$
$q$	dimensionless permeate-side flow rate, dimensionless
$Q$	permeate-side molar flow rate, $\text{mol h}^{-1}$
$R$	reaction rate, $\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$
$R_g$	ideal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
$R_{\text{max}}$	maximum reaction rate, $\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$
$R^*$	dimensionless reaction rate, dimensionless
$s$	membrane area per unit membrane axial length, $\text{m}^2 \text{m}^{-1}$
$T$	absolute temperature, K
$w_{\text{cat}}$	catalyst weight per unit membrane axial length, $\text{g}_{\text{cat}} \text{m}^{-1}$
$W_{\text{cat}}$	catalyst weigh of the membrane module, g
$x$	feed-side mole fraction, dimensionless
$X$	conversion, dimensionless
$y$	permeate-side mole fraction, dimensionless
$Y$	yield, dimensionless
$z$	axial coordinate, m
Greek letters	
$\alpha$	permeance ratio, dimensionless
$\theta$	permeation number, dimensionless
$\nu$	stoichiometric coefficient, dimensionless
$\zeta$	dimensionless axial coordinate, dimensionless
$\Delta G$	Gibbs free energy, $\text{J mol}^{-1}$
$\Delta G_4$	Gibbs free energy, $\text{J mol}^{-1}$
Subscripts	
0	inlet of the membrane reactor
$i$	component
$L$	outlet of the membrane reactor

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