Catalytic Membrane Reactors for SO₃ Decomposition in Iodine–Sulfur Thermochemical Cycle: A Simulation Study

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Abstract

The possibility of applying a catalytic membrane reactor (CMR) to SO_3 decomposition in a low-temperature range was theoretically evaluated with the purpose of producing CO_2 -free hydrogen in an Iodine–Sulfur thermochemical cycle. A one-dimensional, isothermal and plug-flow model was developed for a cocurrent membrane reactor with selective permeation from the reactant stream to the permeate stream. Simulation results have revealed that CMRs can greatly reduce the reaction temperature for SO_3 decomposition from the conventional 1,200–1,400 K to about 900 K. We predicted that porous inorganic membranes with a high O_2 permeability and with selectivities of more than 50 for O_2/SO_3 and less than 10 for O_2/SO_2 had the potential to effectively improve SO_3 conversion. CMRs were simulated to carry out SO_3 decomposition at different catalyst weights, reaction temperatures, and SO_3 feed flow rates as well as pressures in feed and permeate streams. SO_3 conversion at 900 K was increased to 0.93 beyond the equilibrium conversion of 0.28 due to a shift in thermodynamic equilibrium.

Keywords:

Catalytic membrane reactor, SO_3 decomposition, IS process, Simulation

1. Introduction

With the simultaneous growth of the demand of global energy and of urgent concerns for reduction of greenhouse gas emissions, hydrogen has become a promising energy carrier[1]. Currently, hydrogen is derived from nonrenewable natural gas and petroleum, but could in principle be generated from renewable resources such as biomass or water. Splitting water via a thermochemical cycle presents a viable option for large-scale hydrogen production[2]. Among the large number of thermochemical cycles that can be used to split a molecule of water, the Iodine-Sulfur thermochemical water-splitting cycle (IS process), which was initially proposed by General Atomics, is considered an efficient, massive and CO₂-free approach[3,4]. As indicated in Figure 1, the IS process primarily consists of three chemical reactions that involve the decomposition of sulfuric acid (H₂SO₄) and hydrogen iodide (HI), followed by the regeneration of these reagents using the Bunsen reaction[5]. High temperatures equal to, or greater than, 1,100 K are required to decompose H₂SO₄. The exothermic Bunsen reaction is performed at temperatures ranging from 300 to 400 K. Hydrogen is generated during the HI decomposition, using a heat source higher than 600 K.

Fig. 1 Schematic of the iodine-sulfur thermochemical water-splitting cycle.

The thermal decomposition of H_2SO_4 is actually divided into two sub-reactions:

Both of those reactions are highly endothermic and proceed smoothly without side reactions and with a high equilibrium conversion ratio at the temperature range indicated. Figure 2 shows the effect of temperature on computed equilibrium concentrations of components obtained from the decomposition of 1 mol of pure H_2SO_4 [6]. The above two processes (1 and 2) were compared for dependence on temperature: the decomposition of H_2SO_4 to H_2O and SO_3 was predominant between 400 and 700 K while the reduction of SO_3 to SO_2 reached high conversions at temperatures higher than 1,200 K [7]. Therefore, one key challenge for the IS process

is the extremely high temperatures that are required for the decomposition of SO_3 to SO_2 and O_2 , which requires a substantial expenditure of energy. Recent reports have cited great potential for nuclear heat to power hydrogen production plants that utilize the IS process without producing greenhouse gas emissions [8]. Under normal operating conditions, the output of a nuclear reactor can achieve temperatures of more than 1,100 K [9]. A laboratory-scale, fixed-bed reactor with supported Pt/Pd catalysts was constructed and experimentally evaluated for SO_3 decomposition. At 1,103 K, SO_3 conversions were equivalent to 0.60, which reached 80% of the equilibrium value [10]. Moreover, the development of catalysts with high catalytic activity and stability is also an important issue for the enhancement of SO_3 decomposition [11,12]. If SO_3 decomposition could attain a higher degree of conversion at medium temperatures (900–1,000 K), which extend the catalyst lifetime, this coupled system could result in hydrogen production that is both highly efficient and economic.

Fig. 2 Temperature dependence of equilibrium composition for the decomposition of 1 mol of pure

A catalytic membrane reactor (CMR) is a combination of a permselective membrane and heterogeneous catalysts. [13] CMRs have the inherent capability and advantage of combining both a reaction and a separation in a single unit. The membrane provides selective removal of products in parallel with a reversible reaction, which shifts the equilibrium towards the product side and thus results in a higher reaction conversion even at lower temperatures [14]. Because equilibrium-limited reactions usually take place at high temperatures, the membranes used for CMRs are either metal or ceramic: palladium [15], dense perovskite [16], zeolite [17], silica [18], and alumina [19]. Considerable research effort has been devoted to the utilization of CMRs for catalytic reactions such as methane steam reforming [20] and water-gas shift reactions [21]. Tsuru et al. [22] developed a bimodal catalytic membrane reactor for H_2 production via the steam reforming of methane. With H_2 extraction through the membrane, methane conversion was highly enhanced from 0.44 to 0.70 at 500 °C because of the equilibrium shift effect.

The modeling and simulation of CMRs has attracted increasing interest [23,24], with objectives that include modeling the flow as well as mixing and dispersion processes to develop appropriate guidelines for reactor design [25,26] and simulating the performance of an experimental reactor to validate a mathematical model [27,28]. Gallucci et al. [29] proposed a mathematical model for the simulation of

a CMR in methane steam reforming, and the effect of parameters, such as reaction pressure, temperature, reactor length, and membrane thickness on methane conversion were theoretically investigated. Recently, a one-dimensional, isothermal, and plug-flow model for catalytic membrane reactors operated under cocurrent flow conditions [30] was applied to simulate several catalytic reactions, which included methane steam reforming [31], NH_3 decomposition [32], and the dehydrogenation of methylcyclohexane [33]. With a given value for catalyst weight, which was the single fitting parameter, the simulation results obtained from the CMRs with/without membrane extraction were in good agreement with the experimental investigation, which verified that the mathematical model was effective in predicting the performance of the CMRs. This kind of simple model is beneficial to an understanding of the mechanism of CMRs and to the development of an optimal design, including membrane performance (e.g., permeance and selectivity) and operation conditions such as temperature, pressure and feed flow rate.

Previous theoretical studies [34,35] have confirmed that a dense O_2 removal membrane could significantly increase the O_2 yield in SO_3 decomposition from 62.3% to 90.1% at 1,000 K due to a shift in the equilibrium. In the present study, SO_3 decomposition in a cocurrent configuration CMR was evaluated via a one-dimensional, isothermal, plug-flow model. The aim was to find the key parameters controlling the catalytic performance in CMR-assisted SO_3 decomposition. The effects of membrane types (dense or porous) and membrane characteristics (permeation and selectivity) on SO_3 conversion were theoretically discussed. The

influence of operating conditions, such as catalyst weight, reaction temperature, SO_3 feed flow rate, and pressure in the feed and permeate streams on CMR performance, were also systematically investigated.

2. Simulation

The mathematical model of SO_3 decomposition in catalytic membrane reactors considers the following hypotheses: (1) steady-state operation; (2) plug flow in retentate and permeate streams; (3) isothermal reaction, which only occurs over the catalyst on the retentate side; (4) negligible pressure drop along the axial direction of the membrane reactor; and, (5) no concentration polarization effect for gas permeation through the membrane. A schematic model of the catalytic membrane reactor used in the simulations is shown in Figure 3.

Fig. 3 Schematic model for catalytic membrane reactor simulation

The molar flowrates for each species in the retentate and permeate streams are

given by Eqs. (3) and (4), respectively [30,32]:

Feed stream

$$\frac{dF_i}{dz} = r_d w_{cat} - s P_i (x_i p_R - y_i p_P) \quad (3)$$

Permeate stream

$$\frac{dQ_i}{dz} = s P_i (x_i p_R - y_i p_P) \quad (4)$$

where F_i and Q_i represent the flow rates of the i -th component in the feed and permeate streams, and the corresponding mole fractions are denoted as x_i and y_i , respectively; z indicates the axial direction along the membrane; w_{cat} is the weight of the catalysts; s represents the membrane area per membrane unit length; in this simulation, the total length and outer diameter of membrane were set to 0.30 m and 0.01 m, respectively; P_i is the permeance of the i -th component through the membrane; and, p_R and p_P indicate the pressure of the feed and permeate streams, respectively. For alumina-palladium catalyst, the reaction rate of SO_3 decomposition (r_d) can be described as follows [36]:

$$r_d = \frac{\left(k_s K_{SO_3} p_{SO_3} \left(1 - \frac{p_{SO_2} p_{O_2}^{0.5}}{p_{SO_3} K_e} \right) \right)}{\left(1 + K_{SO_3} p_{SO_3} + K_{SO_2} p_{SO_2} + K_{O_2}^{0.5} p_{O_2}^{0.5} \right)^2} \quad (5)$$

where p_{SO_3} , p_{SO_2} and p_{O_2} are the partial pressures of the components. K_e is the equilibrium constant for the SO_3 decomposition as calculated by thermodynamic analysis. The reaction rate constant k_s is expressed as follows:

$$k_s = 1.38 \times 10^{10} e^{\frac{-1.54 \times 10^5}{RT}} \quad (6)$$

K_{SO_3} , K_{SO_2} and K_{O_2} are the adsorption coefficients of the components, which can be represented by the Arrhenius equation [36]:

$$K_{SO_3} = 5.32 \times 10^8 e^{\frac{-2.3 \times 10^5}{RT}} \quad (7)$$

$$K_{SO_2} = 2.65 \times 10^{22} e^{\frac{-5.1 \times 10^5}{RT}} \quad (8)$$

$$K_{O_2} = 3.75 \times 10^{34} e^{\frac{-8.1 \times 10^5}{RT}} \quad (9)$$

The simulation of SO_3 decomposition was conducted in a cocurrent configuration CMR. The membrane permeability and selectivity, reaction temperature (T), pressure in the feed and permeate streams, catalyst weight and SO_3 feed flow rate ($F_{SO_3,0}$) were adopted as parameters to study the effect on CMR performance in terms of SO_3 conversion. The volume of the membranes was equated with the reactor volume to calculate the weight hourly space velocity (WHSV) and gas hourly space velocity (GHSV) since the catalysts were often loaded into the bore side of the tubular membranes in the catalytic membrane reactors.

SO_3 conversion (X) is defined as the percentage of reacted SO_3 ($F_{SO_3,0} - F_{SO_3,L} - Q_{SO_3,L}$) to the inlet ($F_{SO_3,0}$), and is expressed in the following equation:

$$X = \frac{F_{SO_3,0} - F_{SO_3,L} - Q_{SO_3,L}}{F_{SO_3,0}} \quad (10)$$

3. Results and discussion

3.1. Effect of catalyst weight

The performance of a catalytic reactor is strongly dependent on the activity of the catalysts, which accelerates the reaction rate. A theoretical analysis was carried out to investigate variations in catalyst weight and the effect on the conversion of SO_3 , and the results are shown in [Figure 4](#). The catalyst used in this study was a Pd/Al₂O₃ catalyst, APK-2 [36]. The simulation was carried out in a fixed-bed reactor

(FBR), which was accomplished by using a CMR without extraction. The reaction temperature ranged from 800 to 1,000 K and the feed flow rate of SO_3 was maintained at $1.5 \times 10^{-5} \text{ mol s}^{-1}$. The SO_3 conversion was increased with increases in the reaction temperature due to the endothermic nature of the SO_3 decomposition. The conversion of the decomposition reaction was relatively low when the w_{cat} that was used was less than 0.15 g. When a higher catalyst weight was employed, the reaction conversion reached equilibrium because of an increase in the surface area of the catalysts, which also increased the number of adsorption sites available for SO_3 molecules that could then react. The present simulation study mainly focused on the aspect of membrane separation in catalytic membrane reactors, thus relatively high ratios of the catalyst weight to the feed flow rate of SO_3 were used to ensure that the SO_3 conversion would reach equilibrium.

Fig. 4 Effect of catalyst weight on SO₃ conversion in a fixed-bed reactor ($F_{SO_3,0} =$

$$1.5 \times 10^{-5} \text{ mols}^{-1}, p_R = 100 \text{ kPa}).$$

It is noteworthy that another impact of the catalyst amount in a membrane reactor is the enhancement in driving force for gas permeation [33]. Figure 5 illustrates the SO₃ conversion profile in the fixed-bed reactor. With a catalyst weight of 1.0 g, the SO₃ decomposition reached equilibrium at 800 and 1,000 K. When a larger amount of catalyst was used ($w_{cat} = 1.5 \text{ g}$), the reaction quickly reached equilibrium at a position nearer the inlet of the reactor, which significantly increased the partial pressure difference of a given component between the feed and permeate streams. Thus, an obvious enhancement in conversion can be expected since the selective extraction of produced O₂ and SO₂ from the reaction stream to the permeate stream would lead to a shift in the thermodynamic equilibrium. Thus, 1.5 g, which corresponds to a WHSV of 2.88 h⁻¹ and a GHSV of 4980 h⁻¹, was considered a suitable catalyst weight in the present study.

Fig. 5 SO₃ conversion profile in a fixed-bed reactor at 800 and 1,000 K ($F_{SO_3,0} = 1.5 \times 10^{-5}$ mol

s⁻¹, $p_R = 100$ kPa).

3.2. Effect of membrane characteristics

SO₃ decomposition in a membrane reactor requires high temperatures that make the use of polymer membranes unfeasible. One option is the use of dense inorganic membranes (oxygen ion conducting dense membranes, for example), which at elevated temperatures allow only the transport of oxygen ions driven by an O₂ partial pressure gradient across the membrane [37,38]. Another alternative is porous inorganic membranes (mainly zeolite, silica and carbon) that can separate gas components based on molecular size. Figure 6 shows the axial profiles of SO₃ conversion and O₂ partial pressure normalized by total feed pressure in CMRs for different membrane types that would be maintained at 900 K. Without a

membrane-based extraction whereby the permeate stream is kept at atmospheric pressure, the SO_3 conversion was approximately equal to an equilibrium conversion of 0.28. When the CMR was equipped with a porous inorganic membrane that showed a Knudsen selectivity for permeating O_2 over SO_2 ($\alpha(\text{O}_2/\text{SO}_2) = 1.414$) and a high selectivity for O_2 over SO_3 ($\alpha(\text{O}_2/\text{SO}_3) = 70$), then O_2 , SO_2 and a small amount of SO_3 permeated the membrane, and resulted in a significant enhancement in the SO_3 conversion. With a SO_3 feed flow rate of $1.5 \times 10^{-5} \text{ mol s}^{-1}$, the simultaneous extraction increased the SO_3 conversion to 0.93, which was far beyond the equilibrium conversion of 0.28. As shown in Figure 6, the SO_3 conversion and O_2 partial pressure in the inlet zone of the reaction side ($z/L < 0.1$) was increased initially, with as a resultant catalytic decomposition of SO_3 in the reactor. For $z/L > 0.1$, the SO_3 conversion in a porous membrane reactor was increased in a linear fashion with z/L , which indicated that selective extraction highly facilitated the SO_3 conversion. Also, no obvious decrease was observed in the O_2 partial pressure along the axial direction, which significantly increased the driving force for permeation. A slight increase in SO_3 conversion, however, that was caused by the gradual decrease in the O_2 partial pressure difference between the reaction side and the permeate side occurred in the membrane reactor when membranes that only allow for oxygen permeation were used in the reactor simulation. The reason simultaneous extraction caused a significant increase in SO_3 conversion is probably because the reaction rate of SO_3 decomposition (r_d) had a linear dependence on the square root of the O_2 partial pressure but occurred in inverse proportion to the SO_2 partial pressure, according to Eq. (5). He et al.

[39] recently prepared oxygen ion conducting dense membranes and applied them to the separation of O_2 and SO_2 at high temperatures. Unfortunately, it was obvious that the membrane performance was degraded once the SO_2 was introduced into the feed stream. These results suggest that porous inorganic membranes with excellent chemical stability have the potential to improve SO_3 conversion for SO_3 decomposition in a membrane reactor.

Fig. 6 Axial profiles of SO₃ conversion and O₂ partial pressure normalized by feed pressure in a reactor by different membrane types ($T = 900$ K, $F_{SO_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}$, $P_{O_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$,

$$\alpha(O_2/SO_2) = 1.414, \alpha(O_2/SO_3) = 70, p_R = 100 \text{ kPa}, p_P = 5 \text{ kPa}, w_{cat} = 1.5 \text{ g}).$$

The membrane performance can be evaluated using permeance, which is the permeating mole of a component through a membrane relative to the transmembrane pressure and membrane area [31]. The effect of O₂ permeance on SO₃ conversion at different reaction temperatures is shown in Figure 7. The O₂ permeance for state-of-the-art microporous membranes reached $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at temperatures higher than 750 K [40]. Thus, O₂ permeance was varied between 10^{-10} and $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ in this simulation, while $\alpha(O_2/SO_2)$ and $\alpha(O_2/SO_3)$ were fixed at 1.414 and 70, respectively. These small values for O₂ permeation indicate the limited effect of selective permeation that O₂ had on SO₃ conversion. Conversions with O₂ permeance lower than $10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ were approximately equal to equilibrium conversions. An increase in O₂ permeance, which can be obtained by precise control of membrane structures, significantly affected the enhancement of SO₃ conversion, and, as a consequence, SO₃ conversion at 900 K was increased to 0.93 beyond the equilibrium conversion of 0.28 when $P_{O_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. It is evident that the SO₃ conversion was increased with an elevated P_{O_2} that was within the temperature range of the decomposition reaction, which indicates that porous inorganic membranes with high O₂ permeability may be good candidates for SO₃ decomposition in the CMR.

Fig. 7 Effect of O_2 permeance on SO_3 conversion as a function of reaction temperature ($\alpha(O_2/SO_2) =$

$$1.414, \alpha(O_2/SO_3) = 70, p_R = 100 \text{ kPa}, p_P = 5 \text{ kPa}, w_{cat} = 1.5 \text{ g}).$$

Another important membrane characteristic is membrane selectivity, which is defined by the permeance ratio between components. To date, an $\alpha(O_2/SO_3)$ for membranes with pore sizes of less than 1 nm has not yet been reported in the literature, but an ideal O_2/SO_2 selectivity of 491 has been reached for ZSM-5 zeolite membranes [41]. Given the components involved in SO_3 decomposition, O_2 , SO_2 and SO_3 , a microporous membrane with a pore size controlled within a narrow distribution was expected to enhance the extraction efficiency. The effect of $\alpha(O_2/SO_2)$ and $\alpha(O_2/SO_3)$ on SO_3 conversion was simulated in CMRs performed at 900 K with an O_2 permeance of $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, which is plotted in Figure 8. A maximum SO_3 conversion of 0.96 was achieved at the lowest $\alpha(O_2/SO_2)$ and at values

for $\alpha(\text{O}_2/\text{SO}_3)$ that were higher than 100. As $\alpha(\text{O}_2/\text{SO}_2)$ was increased, SO_3 conversion was decreased to 0.52, which equated to values for $\alpha(\text{O}_2/\text{SO}_2) = 8$ and $\alpha(\text{O}_2/\text{SO}_3) = 100$. With low values for $\alpha(\text{O}_2/\text{SO}_2)$, the increases in $\alpha(\text{O}_2/\text{SO}_3)$ generally contributed to an improvement in SO_3 conversion, which could be explained by the equilibrium shift that increases the reaction rate, because more SO_3 remains in the retentate stream and thus participates in the decomposition reaction. However, membranes with a high selectivity for O_2 over SO_2 (for example, $\alpha(\text{O}_2/\text{SO}_2) = 8$), which equates to allow SO_2 permeance, hinder the reaction reaching a higher equilibrium conversion despite a significant promotion in $\alpha(\text{O}_2/\text{SO}_3)$ due to the increased concentration of SO_2 on the feed side. In the present study, we concluded that the selectivities of porous inorganic membranes for use in CMRs for SO_3 decomposition should be higher than 50 for O_2/SO_3 and lower than 8 for O_2/SO_2 to effectively improve the reaction conversion. Forsberg et al. [42] reported that porous inorganic membranes with pore sizes on the order of 1 nm at 400 K showed selectivities for O_2 and SO_2 over SO_3 that were 2.3 and 2.2, respectively, suggesting that the separation requirements for SO_3 decomposition in the iodine–sulfur thermochemical cycle can be fulfilled by using porous inorganic membranes with high O_2 and SO_2 permeance and a low permeance for SO_3 .

Fig. 8 Effect of $\alpha(\text{O}_2/\text{SO}_2)$ on SO_3 conversion as a function of $\alpha(\text{O}_2/\text{SO}_3)$ ($T = 900 \text{ K}$, $F_{\text{SO}_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}$, $p_{\text{O}_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $p_R = 100 \text{ kPa}$, $p_P = 5 \text{ kPa}$, $w_{\text{cat}} = 1.5 \text{ g}$).

3.3. Effect of operation conditions

The reaction temperature plays an important role in the performance of a membrane reactor via thermodynamics and kinetics. Figure 9 shows SO_3 conversion profiles versus temperature for SO_3 decomposition in a fix-bed reactor (FBR) and a CMR. For both FBR and CMR, the SO_3 decomposition reaction was carried out using a SO_3 feed flow rate of $1.5 \times 10^{-5} \text{ mol s}^{-1}$ and a pressure of 100 kPa in the feed stream. In particular, in the CMR, the pressure in the permeate stream was kept at 5 kPa accompanied by an O_2 permeance of $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and the selectivities of O_2/SO_2 and O_2/SO_3 were 1.414 and 70, respectively. The SO_3 conversion for both the FBR and the CMR was strongly dependent on the reaction temperature. SO_3 conversion

for the CMR was always higher than that for the FBR: for example, at 850 K, SO_3 conversion for the CMR was 0.64 versus 0.19 for the FBR, which was a result of the selective permeation of O_2 and SO_2 through the membrane shifts in the equilibrium of the reaction towards the products. It is noteworthy that in order to obtain the same level of SO_3 conversion, the required temperature for SO_3 decomposition in the CMR was much lower compared than that in the FBR, which indicates that CMR offer the viability of a strong reduction in the reaction temperature for SO_3 decomposition from the conventional 1,200-1,400 K to about 900 K. Moreover, the SO_3 conversion in the CMR represents a linear growth, which was probably due to the increase in SO_3 conversion being limited by the degree of extraction efficiency.

Fig. 9 SO_3 conversion profiles for the CMR and the FBR as a function of reaction

temperature ($F_{\text{SO}_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}$, $P_{\text{O}_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $\alpha(\text{O}_2/\text{SO}_2) = 1.414$, $\alpha(\text{O}_2/\text{SO}_3) =$

$$70, p_R = 100 \text{ kPa}, p_P = 5 \text{ kPa}, w_{cat} = 1.5 \text{ g}).$$

The relationship between the SO₃ feed flow rate and the SO₃ conversion at 900 K in both the FBR and the CMR is shown in Figure 10. SO₃ conversion in a FBR without membrane permeation showed an approximately equilibrium conversion at the outlet of the reactor, indicating that the reaction rate was sufficiently high in the range of the SO₃ feed flow rate for the amount of catalysts, which corresponds to WHSV increases of from 1.92 to 19.2 h⁻¹. Compared with those reported studies [10], our work assumed a competitive range of WHSV, which was intended to highlight the feasibility of enhancing the reaction conversion with CMRs. For SO₃ decomposition performed in the CMR where the permeate stream was evacuated to 5 kPa, the simultaneous permeation of O₂ and SO₂ through the membrane resulted in an enhancement in the SO₃ conversion. When SO₃ was fed into the CMR at a flow rate of $1.5 \times 10^{-5} \text{ mol s}^{-1}$, the SO₃ conversion was significantly increased from 0.28 to 0.93 due to the shift in the reaction equilibrium. However, the SO₃ conversion was decreased when the SO₃ feed flow rate was raised due to an increase in the space velocity. Increasing the O₂ permeate flux that is restricted by the membrane characteristics such as O₂ permeance and membrane area, as well as by the operational conditions, could be an effective approach to improvements in the performance of a CMR during high space velocities in order to achieve a greater shift away from the equilibrium limitations and higher rates of production and separation [43].

Fig. 10 Effect of SO_3 feed flow rate on SO_3 conversions for CMRs and FBRs ($T = 900 \text{ K}$, $P_{\text{O}_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $\alpha(\text{O}_2/\text{SO}_2) = 1.414$, $\alpha(\text{O}_2/\text{SO}_3) = 70$, $p_R = 100 \text{ kPa}$, $p_P = 5 \text{ kPa}$, $w_{\text{cat}} = 1.5 \text{ g}$).

Theoretically, SO_3 decomposition operated in a pressurized reactor is unfavorable because the equilibrium conversion decreases due to increased moles of products when the reaction pressure is increased. For a membrane reactor, however, the increased pressure in the feed stream results in an enhanced driving force for the permeation of components from the reaction stream to the permeate stream, which may lead to an equilibrium shift that improves reaction conversion. Figure 11 shows the catalytic performance of a CMR for SO_3 decomposition at feed pressures that ranged from 100 to 200 kPa while the pressure in the permeate stream was fixed at 5 kPa. The feed flow rate of the SO_3 and the reaction temperature were kept at $1.5 \times 10^{-5} \text{ mol s}^{-1}$ and

900 K, respectively. In a CMR equipped with a membrane that possessed a $\alpha(\text{O}_2/\text{SO}_2) = 2$, the SO_3 conversion was kept at values higher than 0.80 when the feed pressure increased, while the equilibrium conversion of SO_3 was decreased by the pressure and was lowered to 0.25 at 200 kPa by a shift towards the SO_3 decomposition side that had more moles of gas. No further increase in SO_3 conversion was observed with a $\alpha(\text{O}_2/\text{SO}_2) = 2$ at higher feed pressures, because of the enhanced permeation of SO_3 from the feed side to the permeate side due to the raised partial pressure of SO_3 , which allowed for the permeation of unreacted SO_3 to the permeate stream. As the simulation in [Figure 8](#) shows, a lower $\alpha(\text{O}_2/\text{SO}_2)$ would be preferable to decompose more SO_3 . However, with an increase in the pressure of the feed stream, the SO_3 conversion was significantly increased even with a raised $\alpha(\text{O}_2/\text{SO}_2)$. Therefore, it is noteworthy that a pressurized CMR increased the partial pressure differences of O_2 and SO_2 between the retentate and the permeate sides, which effectively improved the SO_3 conversion.

Fig. 11 Effect of feed pressure and $\alpha(\text{O}_2/\text{SO}_2)$ on SO_3 conversion ($T = 900 \text{ K}$, $F_{\text{SO}_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}$, $P_{\text{O}_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $\alpha(\text{O}_2/\text{SO}_3) = 70$, $p_P = 5 \text{ kPa}$, $w_{\text{cat}} = 1.5 \text{ g}$).

In membrane separation, the permeation rate of a component was profoundly affected by the partial pressure on the permeate side, which could be reduced either by vacuum or by a sweep gas. Figure 12 shows the predicted influences on SO_3 conversion of the permeate pressure (p_P) and the sweep gas flow rate ratio (f) that is defined as the ratio of the sweep gas flow rate over the feed gas flow rate. Feed and sweep gas should enter a reactor co-currently at $T = 900 \text{ K}$, $F_{\text{SO}_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}$ and $p_R = 100 \text{ kPa}$. When the permeate pressure is fixed at 100 kPa and no sweep gas is fed ($f = 0$), a CMR should approach the behavior of a conventional FBR, at which point a SO_3 conversion of 0.28 should be observed. With a decrease in permeate pressure, SO_3 conversions should be increased due to a drop in the partial pressures of O_2 ,

SO₂ and SO₃ on the permeate side, leading to higher permeation fluxes through the membrane[44,45]. However, the production of a vacuum adds to the cost of energy, while the use of a sweep gas is a more economical alternative. As illustrated in Figure 12, with a higher sweep gas flow rate, SO₃ conversion is promoted as a result of decreases in the partial pressure of the component on the permeate side, which increases the driving force for permeation. When the SO₃ decomposition was carried out at $p_p = 100$ kPa with a sweep gas flow rate of $7.5 \times 10^{-5} \text{ mol s}^{-1}$ ($f = 5$), the SO₃ conversion was about 0.81, which was approximately equal to that of a CMR operated with the permeate stream evacuating to about 15 kPa and no sweep gas. It was clear that the improvement in membrane reactor performance increased as the permeate pressure decreased and/or the sweep gas flow rate increased.

Fig. 12 Effects of the permeate pressure and the sweep gas flow rate ratio on SO₃ conversion

$$(T = 900 \text{ K}, F_{SO_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}, P_{O_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}, \alpha(O_2/SO_2) = 1.414, \alpha(O_2/SO_3) = 70, p_R = 100 \text{ kPa}, w_{cat} = 1.5 \text{ g}).$$

Figure 13 summarizes the qualitative analysis of recent experimental results in terms of SO_3 conversion obtained from the literature [46–51] and draws comparisons with the predicted SO_3 conversion in a CMR in the present study. The SO_3 conversions that were obtained from FBRs were scattered because of different operation conditions such as WHSV and the partial pressure of SO_3 in a dilute gas mixture. As shown, achieving a high SO_3 conversion required operation at very high temperatures of between 1,100 and 1,200 K, and most of the SO_3 conversions lower than 0.40 are reported at temperatures that ranged from 850 to 950 K. For comparison, SO_3 decomposition was simulated in a CMR with a permeance of O_2 of $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and the selectivities of O_2/SO_2 and O_2/SO_3 were 1.414 and 70, respectively. It is evident that, at 900 K, SO_3 conversion in a CMR is significantly increased beyond the equilibrium conversion of 0.28 to 0.93 due to the selective extraction of produced O_2 and SO_2 from the reaction stream to the permeate stream, leading to a shift in the thermodynamic equilibrium. These results demonstrate that, with CMRs, SO_3 decomposition could be carried out at a lower reaction temperature, which would result in the benefit of energy savings with no need of high-temperature sources to supply heat. Another advantage would be great SO_3 conversions. To confirm the predictions in this simulation and to refine the mathematical models, experimental investigations with CMRs are necessary.

Fig. 13 SO_3 conversion as a function of temperature (points are experimental SO_3 conversions in a FBR taken from recent reports in the literatures [46–51]; the CMR predictions were calculated under $F_{\text{SO}_3,0} = 1.5 \times 10^{-5} \text{ mol s}^{-1}$, $P_{\text{O}_2} = 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $\alpha(\text{O}_2/\text{SO}_2) = 1.414$, $\alpha(\text{O}_2/\text{SO}_3) = 70$, $p_R = 100 \text{ kPa}$, $p_P = 5 \text{ kPa}$, $w_{\text{cat}} = 1.5 \text{ g}$).

4. Conclusions

Membrane reactor simulation, using a one-dimensional, isothermal and plug-flow model with selective permeation from the reactant stream to the permeate stream, demonstrated the possibility of applying CMRs to SO_3 decomposition in a low temperature range for the purpose of producing CO_2 -free hydrogen in an Iodine–Sulfur thermochemical cycle. In particular, porous inorganic membranes with a high O_2 permeability, as well as selectivities that were higher than 50 for O_2/SO_3 and lower

than 10 for O₂/SO₂, were predicted to have the potential to effectively improve SO₃ conversion in a CMR. Simulation results revealed that CMRs offer a strong reduction in the reaction temperature for SO₃ decomposition from the conventional 1,200–1,400 K to about 900 K. SO₃ conversion at 900 K was increased to 0.93 beyond the equilibrium conversion of 0.28 due to a shift in the thermodynamic equilibrium. SO₃ conversion was enhanced further with an increase in the feed pressure and/or by decreasing the permeate pressure.

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Nomenclature

F	Feed-side molar flow rate, mol s ⁻¹
f	Sweep gas flow rate ratio, dimensionless
k_s	Reaction rate constant, mol s ⁻¹ kg _{cat} ⁻¹
K_e	Equilibrium constant, Pa ^{0.5}
K_{SO_3}	Adsorption coefficients of SO ₃ , Pa ⁻¹
K_{SO_2}	Adsorption coefficients of SO ₂ , Pa ⁻¹
K_{O_2}	Adsorption coefficients of O ₂ , Pa ⁻¹

L	Reactor length, m
p	Pressure, Pa
p_R	Feed-side pressure, Pa
p_p	Permeate-side pressure, Pa
P	Gas permeance, $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$
Q	Permeate-side molar flow rate, mol s^{-1}
r_d	Reactionrate of SO_3 decomposition, $\text{mol s}^{-1} \text{kg}_{\text{cat}}^{-1}$
s	Membrane area per unit membrane axial length, $\text{m}^2 \text{m}^{-1}$
T	Absolute temperature, K
w_{cat}	Catalyst weight per unit membrane axial length, $\text{kg}_{\text{cat}} \text{m}^{-1}$
x	Feed-side mole fraction, dimensionless
X	SO_3 Conversion, dimensionless
y	Permeate-side mole fraction, dimensionless
z	Axial coordinate, m

Greek letter

α	Membrane selectivity, dimensionless
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Subscripts

i	Component i
0	Inlet of the membrane reactor
L	Outlet of the membrane reactor

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