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SiC mesoporous membranes for sulfuric acid decomposition at high temperatures in the iodine–sulfur process†

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Inorganic microporous materials have shown promise for the fabrication of membranes with chemical stability and resistance to high temperatures. Silicon-carbide (SiC) has been widely studied due to its outstanding mechanical stability under high temperatures and its resistance to corrosion and oxidation. This study is the first to prepare mesoporous SiC membranes for use in sulphuric acid decomposition to achieve thermochemical water splitting in the iodine–sulfur process. Single-gas permeation was carried out to confirm the stability of this mesoporous membrane under exposure to steam and H₂SO₄ vapor. Benefiting from the excellent chemical stability of the α -Al₂O₃ membrane support and the SiC particle layer, the SiC membrane exhibited stable gas permeance without significant degradation under H₂SO₄ vapor treatment at 600 °C. Additionally, with extraction, the membrane reactor exhibited an increased conversion from 25 to 41% for H₂SO₄ decomposition at 600 °C. The high performance combined with outstanding stability under acidic conditions suggests the developed SiC membrane is a promising candidate for H₂SO₄ decomposition in a catalytic membrane reactor.

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1. Introduction

Over the past twenty years, the water-splitting iodine–sulfur (IS) process has been extensively investigated as a sustainable technology with a net production of H₂ and O₂, at much lower temperatures compared with the direct thermal decomposition of water.^{1–6} The IS process involves cyclic reactions such as the Bunsen reaction and the thermal decompositions of sulfuric acid at 850–950 °C and hydroiodic acid at 450 °C. In these cycles, the decomposition of sulfuric acid requires temperatures so high that the heat of solar or nuclear energy must be utilized.^{3,5–7}

Net reaction:

Bunsen reaction:

H₂ production:

O₂ production:

H₂SO₄ decomposes to produce O₂ in the following two steps: H₂SO₄ dissociates into H₂O at 300 °C (eqn (3)) and sulfur trioxide (SO₃), which further decomposes into sulfur dioxide (SO₂) and oxygen (eqn (4)) *via* catalysis around 850 to 950 °C. O₂ production from H₂SO₄ requires separation from co-produced SO₂, SO₃ and H₂O gaseous mixtures, while H₂ requires separation from HI and I₂. H₂ and O₂ are collected *via* the separation process for further applications. The high temperature of SO₃ decomposition (>850 °C) can be lowered *via* equilibrium shift by extracting O₂ from the reaction systems. Membrane-based separation methods such as microfiltration,⁸ ultrafiltration,⁹ nanofiltration,¹⁰ reverse osmosis,¹¹ and gas separation¹² consume the least amount of energy compared with other separation techniques.¹³ Membrane processes also provide a significant, convenient, and sustainable solution for H₂ and O₂ separation.^{14–18}

In recent years, several types of membranes have been developed for the iodine–sulfur cycle.^{4,19–28} Myagmarjav *et al.* reported that a hexyltrimethoxysilane (HTMOS) derived silica membrane achieved H₂ permeance on the order of 10^{–7} mol

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$\text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ with H_2/HI selectivity of more than 175.⁴ In addition, their silica-based ceramic membrane reactor achieved HI conversion of 0.70 and H_2 extraction of 0.98 at 400 °C.²⁷ However, it was also reported that silica membranes can't survive under humid environments at high temperatures,²⁹ and challenges remain for the use of silica membranes when using water in Bunsen reaction and H_2SO_4 decomposition reaction. Nomura *et al.* proposed a cation exchange membrane (CEM) constructed from polymerized divinylbenzene on Nafion for Bunsen reaction.¹⁹ HI and H_2SO_4 were obtained separately from CEM-divided cells by feeding SO_2 , I_2 and H_2O . He *et al.* discovered two Pt/carbon catalyst coated membranes (CCMs) that showed a reduced charge transfer resistance for the Bunsen reaction at room temperature.²⁴ The electrolytic voltage was reduced by 62.7% with cathode current efficiency that reached 97.41%. However, water permeated the cation exchange membrane to form H_2SO_4 , and resistance to H_2SO_4 remains unsolved. Several recent results have also shown promising membrane performances under H_2SO_4 for the IS process. PTFE-based materials were reportedly stable even after exposure to highly concentrated H_2SO_4 solutions at 80–120 °C.³⁰ Non-fluorinated membranes (*e.g.*, polybenzimidazole, non-fluorinated poly(arylene ether sulfone)) have also shown excellent stability against 30 and 60 wt% H_2SO_4 at 80 °C.³¹ However, for O_2 separation in integrated H_2SO_4 decomposition systems, stability under high temperatures (600–900 °C) for the second reaction, which is expressed as eqn (4), and for corrosion under strongly acidic conditions remains a challenge.

Generally, inorganic membranes are prepared with the strength to withstand high temperatures as well as oxidative and chemical conditions, which makes them promising candidates for O_2 separation from SO_3 decomposition, as mentioned in eqn (4). Notably, we reported several classes of inorganic membrane materials/metal oxides employed in membrane reactors for O_2/SO_3 separation.^{3,5} SiO_2 membranes, due to their excellent thermal stability and high gas selectivity,^{17,32} were first used by our team for O_2/SO_2 separation in 2015.³ Bis(triethoxysilyl)ethane (BTESE)-derived membranes, particularly those fabricated under high temperatures, have demonstrated high oxidation resistance and exhibited an O_2/SO_3 selectivity of 10 with an O_2 permeance of $2.5 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.³³ Despite a decrease in permeance after exposure to SO_3 , the BTESE membrane exhibited a very high level of SO_3 stability. On the other hand, highly water stable BTESE membranes have also been studied,^{17,34} and these have served as selective filters for $\text{H}_2\text{O}/\text{O}_2/\text{SO}_3$ separation. In addition, the membrane materials with high SO_3 (10% in O_2) resistance at 550 °C, such as SiO_2 , $\text{SiO}_2\text{-ZrO}_2$ (high Si/Zr ratio), and $\alpha\text{-Al}_2\text{O}_3$ powders were fundamentally studied.⁵

To the best of our knowledge, however, no study has yet reported the chemical stability of membrane materials against sulfuric acid at high temperatures (>400 °C), and as yet no effective strategy has been developed to fabricate an O_2 -selective membrane structure. Moreover, there has been no report of an attempt to apply a membrane reactor to H_2SO_4 decomposition. However, the use of high temperatures is essential for the separation of O_2 through membrane and catalytic

decomposition of H_2SO_4 . The present study expands our previous work on the stability of various types of metal oxides under SO_3 exposure,⁵ and provides insight from evaluating the characteristics of SiO_2 , ZrO_2 , SiC, homemade Al_2O_3 , $\text{SiO}_2\text{-ZrO}_2$, and $\alpha\text{-Al}_2\text{O}_3$ under H_2SO_4 vapor at high temperatures. After clarifying the chemical stability, the H_2SO_4 decomposition conversion of the membrane fabricated by SiC was further studied.

2. Experiments

2.1 Preparation of sol, gel and powders

$\text{SiO}_2\text{-ZrO}_2$ sols with sol concentrations of 2.0 wt% were synthesized from tetraethoxysilane (TEOS) and zirconium butoxide solutions (ZrBT, 80% in 1-butanol) in Si/Zr molar ratios of 5/5, 7/3 and 10/0 by hydrolysis and condensation reactions in H_2O with HCl (35 wt%) as the catalyst. The details can be found in our previous reports.^{5,35} Al_2O_3 gels were prepared *via* hydrolysis and condensation by mixing aluminium tri-*sec*-butoxide (AlTBT, 97%) with water, and HCl in molar ratios of AlTBT/ H_2O /HCl = 1/10/0.1. ZrO_2 sol was prepared *via* hydrolysis and condensation by mixing ZrBT, H_2O , and HCl in molar ratios of ZrBT/ H_2O /HCl = 1/1/0.1. Ethanol (99.5%) was added to adjust the concentration of AlTBT or ZrBT sols at 5 wt%. Al_2O_3 , SiO_2 , ZrO_2 , and $\text{SiO}_2\text{-ZrO}_2$ powders were prepared by drying Al_2O_3 , SiO_2 , ZrO_2 , and $\text{SiO}_2\text{-ZrO}_2$ (Si/Zr ratio = 7/3) gels at 50 °C and subsequently calcined at 600 °C under air for 24 h.

2.2 Characterizations

After drying SiO_2 , ZrO_2 , homemade Al_2O_3 , $\text{SiO}_2\text{-ZrO}_2$ (Si/Zr ratio of 7/3), and SiC powders at 600 °C under air, the exposure experiment was carried out in a quartz cell in which these powders were exposed to either H_2O or H_2SO_4 (98%) vapor under an absolute pressure of 1 bar at 600 °C for 24 h. Then, 2 ml of liquid (H_2O or H_2SO_4) was added into the quartz tube before heating, and after heating at 600 °C, and the vaporized liquid was refluxed in the tube as schematically shown in the diagram in the Fig. S1.† Powders were also exposed with an SO_3 of 10 kPa at 600 °C under sweep conditions similar to our previous report.⁵ Subsequently, those powders were followed by drying at 500 °C under air to remove the adsorbed gas on the surface. Then, characterizations of powders were carried out using Energy Dispersive X-ray Spectroscopy (EDS) Scanning Electron Microscopy (SEM, JCM-5700, JEOL Ltd.), X-ray diffraction (XRD, Bruker AXS, Japan), and N_2 adsorption under liquid nitrogen at 77 K (BELMAX, BEL Japan Inc.).

2.3 Preparation of mesoporous membranes

Fabrication of membranes for H_2SO_4 separation, $\alpha\text{-Al}_2\text{O}_3$ membrane support (cylindrical porous tubes with average pore size 2 μm ; outer diameter 1 cm; length 10 cm, Nikkato. Corp.) were used as substrates. 5 types membranes were fabricated as shown in Table 1. The outer surfaces of the tube were coated with α -alumina (2.0 and 0.2 μm , Sumitomo Chemical Co., Ltd) or silicon carbide (2.3 and 0.5 μm , Pacific Rundum Co., Ltd.) particles mixed with the sols ($\text{SiO}_2\text{-ZrO}_2$ at Si/Zr ratio of 5/5, 7/3

Table 1 Conditions of the membrane fabrication by using various particles and binder sols

No.	Particles	Binder sols
M1	—	—
M2	α -Al ₂ O ₃	SiO ₂ -ZrO ₂ (5/5)
M3	α -Al ₂ O ₃	SiO ₂ -ZrO ₂ (7/3)
M4	SiC	SiO ₂ -ZrO ₂ (7/3)
M5	SiC	SiO ₂ -ZrO ₂ (10/0)

or 10/0) as the binder to create a smooth and homogeneous surface, followed by firing at 600 °C for 15 min then cooling to room temperature. This procedure of coating particle layers was repeated several times to reduce the pore sizes of the membranes to approximately 20 nm. The schematic membrane structure is shown in Fig. 1.

2.4 Gas permeance of membranes and H₂SO₄ conversion

The gas permeation of membranes during H₂SO₄ and H₂O exposure was tested in membrane module shown schematically in Fig. 2. Distilled H₂O (0.48 ml h⁻¹) or H₂SO₄ (1.0 ml h⁻¹) was introduced into the membrane *via* a syringe pump, and helium was supplied as a carrier gas (flow rate of 90 ml min⁻¹) to control the molar ratio of H₂O or H₂SO₄ at 0.1 bar. Membranes of different types, M1–M5, were placed in an electric furnace with a controlled inner-side temperature of 600 °C for evaporation and reaction. Once H₂SO₄ was injected inside the heated zone, liquid H₂SO₄ was evaporated, and then thermally decomposed into sulfur trioxide and water vapor. After exposure tests for several hours, membranes were dried with N₂ flow in the furnace at 600 °C, followed by cooling to room temperature. Then, the membrane module and gas lines were carefully cleaned by water to wash out the remaining H₂SO₄ and dried in an 80 °C oven. Pure gas permeance was measured under the transmembrane pressure difference from 0.01 to 1 bar by feeding gas to the outside of the membrane.

An M4 membrane was used for the membrane reactor to investigate the effect of O₂ extraction on H₂SO₄ decomposition conversion. At 600 °C, the liquid sulphuric acid changes to a gas phase, and the decomposition reaction can be split into two

endothermic sub-reactions. The first sub-reaction is the dissociation of sulphuric acid into sulphur trioxide and water (reaction (3)), and the second is the decomposition of sulphur trioxide into sulphur dioxide and oxygen (reaction (4)). Here, SO₃ was decomposed to SO₂ with the Pt/Al₂O₃ catalyst (1.5 g, Shimadzu Corporation), which was packed inside the membrane. Outlet gases from the membrane reactor, consisting of mixtures of carrier gas He, and H₂O, SO₃, SO₂, and O₂, as produced from H₂SO₄ decomposition, subsequently passed through two bottles filled with 120 ml sodium hydroxide aqueous solution (20 wt%), where H₂O was condensed and SO₃ or SO₂ was trapped by the neutralization reaction. So the outlet gas consisted of He and O₂ and was measured using a soap film bubble flowmeter. NaOH was chosen for acidic gas absorption because it had high efficiency (nearly 100%) with SO₂ removal.³⁶ For safety, a SO₂ alarm (ToxiRAE II, PGM-1130) was set nearby the equipment to signal SO₂ leakage, and the outlet gas in the NaOH trap was monitored by the SO₂ alarm and the SO₂ content was found to be lower than 1 ppm.

H₂SO₄ conversion (*w*) can be quantified by the ratio of produced O₂ over theoretical O₂ since 1 mol of H₂SO₄ can produce 0.5 mol of O₂ after complete conversion. Therefore, the conversion can be expressed in the following equation:

$$w = \frac{F_r + F_p - F_c}{0.5F_h} \times 100\%$$

In that equation, *F_r* and *F_p* are the gas molar rate (mol s⁻¹) of retentate and permeate side of the membrane, *F_c* is the molar rate of carried gas He. *F_h* (mol s⁻¹) is the feed rate of liquid H₂SO₄. It is of note that H₂SO₄ was 100% decomposed to H₂O and SO₃ at 450 °C, hence, from this perspective, the H₂SO₄ conversion to SO₂ was dominated by SO₃ decomposition.

3. Results and discussion

3.1 Stability of membrane materials under H₂SO₄ exposure

It has been pointed out that the α -Al₂O₃, SiO₂ and lower-Zr-content SiO₂-ZrO₂ powders had good chemical stability against SO₂ and SO₃ even at 550 °C for O₂/SO₂ or O₂/SO₃ separation.^{5,37} The H₂SO₄ decomposition generates water vapor at temperatures higher than 300 °C, and, hence, the stability and corrosion under steam/acid still needs to be addressed. Therefore, Fig. 3 depicts the XRD patterns of the samples after being treated in SO₃ or H₂SO₄ vapor at 600 °C for 24 h. The XRD patterns of SiO₂ (Fig. 3A) showed a broad single peak centered at 23°, which was assigned to an amorphous SiO₂ phase, and no other peaks were observed in the XRD patterns. Additionally, Nadar *et al.* also reported that TG-DTA and XRD patterns of SiO₂ after H₂SO₄ exposure were similar to those before H₂SO₄,³⁸ indicating the high acid resistance of SiO₂. Table 2 shows the BET area of SiO₂ powders was largely decreased after being treated in steam and in H₂SO₄ vapor. The reason for this decrease in the BET area could have centered around the reaction of Si–O–Si and H₂O to form Si–OH, which could have led to large non-selective pores and resultant particles that became dense.^{34,39} XRD analyses of α -Al₂O₃ (Fig. 3B) powders revealed that the S in Al₂(SO₄)₃ and the percentage of sulfur/aluminum

Fig. 1 The schematic structure of α -Al₂O₃ or SiC particle membranes.

Fig. 2 (A) Schematic diagram of the experiment for steam and sulphuric acid treatment and gas permeance measurement. (B) Schematic illustration of the SiC membrane used as membrane reactor for H_2SO_4 decomposition.

detected by EDS had increased from 0.87 to 26%, as shown in Table 2. Also, the FT-IR spectra confirmed that an SO_4 peak was formed in $\alpha-Al_2O_3$ (ESI-2[†]), which was attributed to the reaction of alumina with the H_2SO_4 vapor at 600 °C. Furthermore, BET analyses revealed how the surface area of $\alpha-Al_2O_3$ had decreased from 8.8 to 1.9 $m^2 g^{-1}$ following exposure to H_2SO_4 , presumably due to the formation of $Al_2(SO_4)_3$ on the surface, which reduced the size of the pores. Regarding the homemade Al_2O_3 powder, which had a high surface area of 226 $m^2 g^{-1}$ compared with that

of crystalline $\alpha-Al_2O_3$ at 8.8 $m^2 g^{-1}$, the BET area was drastically decreased after exposure to SO_3 and H_2SO_4 , but the reactivity was significantly greater under H_2SO_4 vapor than under SO_3 . Fig. 3C shows the XRD of ZrO_2 , which exhibited an increased crystalline monoclinic (m) ZrO_2 from the tetragonal (t) phase⁴⁰ due to the temperature swings of the membrane furnace and the dryer oven. XRD analysis did not detect the sulfate phase for ZrO_2 and SiO_2-ZrO_2 (Si/Zr = 7/3) powders after SO_3 exposure, as shown in Fig. 3C and D, and corresponded to low S ratios of 2.7

Fig. 3 XRD of different powders after SO_3 or H_2SO_4 exposure at 600 °C under one-atmosphere pressure. S: zirconium sulfate or aluminum sulfate, t/m: tetragonal/monoclinic ZrO_2 . (A) Home-made SiO_2 . (B) $\alpha-Al_2O_3$. (C) ZrO_2 . (D) SiO_2-ZrO_2 (Si/Zr = 7/3). (E) SiC. (F) $\alpha-Al_2O_3$ membrane support.

Table 2 BET area and S ratio of powders after H₂O or H₂SO₄ exposure

Powders	Air-fired temperature (°C)	BET area (m ² g ⁻¹)			S/Al or S/(Si + Zr) mole ratio (%)
		Fresh	After H ₂ O	After H ₂ SO ₄	
SiO ₂	600	650	600	390	<0.1
Home-made Al ₂ O ₃	600	226	18	6.4	86
α -Al ₂ O ₃	>1200	8.8	11	1.9	26
Membrane support	>1200	0.21	0.14	0.57	17
SiO ₂ -ZrO ₂	600	115	25	14.9	4.0
ZrO ₂	600	21	20	3.2	100
SiC	>1800	10.0	10.5	9.0	<0.1

and 2.2%,⁵ respectively. On the contrary, after exposure to H₂SO₄ vapor at the same temperature of 600 °C, the S ratio was quite different between ZrO₂ and SiO₂-ZrO₂ powders. The XRD spectra in Fig. 3C shows the formation of Zr(SO₄)₂ from ZrO₂ after H₂SO₄ exposure, with only a small amount of crystalline Zr(SO₄)₂ (S peak)⁴¹ detected for SiO₂-ZrO₂ (Fig. 3D). In addition, Table 2 shows the S content measured by EDS was almost 100 and 4.0% for ZrO₂ and SiO₂-ZrO₂ powders, respectively. Probable reasons for the high sulfur composition in ZrO₂ powders after exposure to H₂SO₄ vapor could be primarily that H₂O activated ZrO₂ and formed ZrO(OH)₂ or Zr(OH)₄ at high temperature.⁴² Another explanation could be that either ZrO(OH)₂ or Zr(OH)₄ was more active in the reaction with SO₃ to form Zr(SO₄)₂. Fig. 3E shows the XRD spectra of silicon-carbide powders before and after H₂SO₄ exposure. No change in peaks was observed, probably because SiC is generally known for its ultrahigh chemical and thermal stability.^{43–45} Additionally, the α -Al₂O₃ membrane supports used in this study were proven to be chemically stable under H₂SO₄, which was confirmed by XRD analysis to have a lesser amount of aluminum sulfate (Fig. 3F) compared with that of α -Al₂O₃ powders (Fig. 3B). This was probably because SiO₂ was added to the Al₂O₃ membrane supports since Si was detected in the Al₂O₃ membrane supports, although the exact content was not available. Although the S content was 17% for α -Al₂O₃ membrane supports after H₂SO₄ exposure, the change in the element composition of the substrates had less of an effect on gas permeation (Fig. 5). To benefit the stability of these materials against H₂SO₄ in the IS

process, the use of α -Al₂O₃ membrane supports, SiC and SiO₂-ZrO₂ were proposed for the preparation of SiC membranes.

Fig. 4 features the SEM micrographs of SiO₂, α -Al₂O₃ and ZrO₂ before and after exposure to H₂SO₄. As shown in the images of Fig. 4A1 and A2, the surface of SiO₂ powders were smooth after H₂SO₄ exposure, which demonstrated morphological differences between the fresh state and after SO₃ exposure⁵ while maintaining approximately the same particle size. This could be explained by the densification of SiO₂ fine particles induced by the reaction between Si-O-Si and H₂O. Fig. 4B1 and B2 shows that α -Al₂O₃ particles had a relatively uniform morphology even after H₂SO₄ exposure while the size of the Al₂O₃ particles grew larger due to the formation of low-melting Al₂(SO₄)₃ on the surface, with which each of the primary particles seemed to be connected and aggregated that differed from the α -Al₂O₃ particles with SO₃ exposure.⁵ Given that α -Al₂O₃ particles after exposure were deposited with, and covered by, the Al₂(SO₄)₃, these SEM photos confirm the compositions obtained by EDS. The SEM images in Fig. 4C1 and C2 also show that the fine ZrO₂ particles had reacted with the H₂SO₄ vapor and increased in size, which is similar to the growth of α -Al₂O₃ powder under H₂SO₄ exposure, probably due to the effect of dissolution under the H₂O vapor and to the reaction with SO₃.

3.2 Permeance of the SiC membrane reactor for H₂SO₄ decomposition

Porous inorganic membranes were first explored under an extreme condition, *i.e.*, H₂SO₄ decomposition at 600 °C. Fig. 5

Fig. 4 SEM of fresh SiO₂ (A1), α -Al₂O₃ (B1), ZrO₂ (C1) powders. (A2), (B2) and (C2) were those powders after H₂SO₄ (100 kPa) exposure at 600 °C, respectively.

Fig. 5 Time course of N₂ permeance for α -Al₂O₃ membrane support (M1) and membrane prepared by Al₂O₃ particle layer (M2, M3), and SiC particle (M4, M5) after the treatment under H₂SO₄ vapor at 600 °C.

shows the time course of the N_2 permeance with increases in the treatment time under H_2SO_4 vapor. The N_2 permeance of the $\alpha-Al_2O_3$ membrane support (M1) was decreased only slightly even after 22 h of exposure to H_2SO_4 vapor at 600 °C, since the membrane support provided only moderate chemical stability, as shown in Fig. 3F (XRD) and Table 2, and the large pores changed very little even after sulfate formation. M2, M3, and M4 prepared with different particles (SiC, $\alpha-Al_2O_3$) and binders (SiO_2-ZrO_2 , SiO_2) showed N_2 permeance at the same level ($10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) as before the stability test, which provided a fair comparison and verified good reproducibility of the membrane fabrication. Values were drastically decreased for the permeance of both M2 and M3 Al_2O_3 particle layers following H_2SO_4 exposure for 4 h. The permeance of M2 was further decreased, however, confirming that the high Zr content in the binder (Si/Zr = 5/5) was more unstable due to the formation of $Zr(SO_4)_2$ with H_2SO_4 , similar to high Zr content SiO_2-ZrO_2 (Si/Zr = 5/5) in SO_3 .⁵ These results were reasonable, and strongly suggested that the membranes should be prepared using Si-rich SiO_2-ZrO_2 (Si/Zr = 7/3) as a binder. M4 and M5 SiC particle layers showed a very small decrease and high relative permeance over all the particle membranes, M2–M5. That indicated that the membrane prepared by SiC with Si-rich SiO_2-ZrO_2 (Si/Zr = 7/3) increased both the chemical and hydrothermal stability compared with that of the Al_2O_3 particle layers with Zr-rich SiO_2-ZrO_2 used to fabricate M2 and M3. The morphology changed less for membranes fabricated with SiC layers following exposure to H_2SO_4 (ESI-3†), which corresponds to the stability confirmed by XRD and BET results. These results suggested that the SiC was stable for fabricating a particle layer for membrane preparation in the IS process.

Catalytic membrane reactor for H_2SO_4 decomposition, liquid H_2SO_4 (98%) was fed at a flow rate of 1.0 ml h^{-1} and He was used as the carrier gas with a flow rate of 24.5 ml min^{-1} controlled by a mass flow controller. Fig. 6 shows the time course for the total flow rate of the outlet gas in both the retentate and permeate, and the conversion of H_2SO_4 decomposition at 600 °C in a SiC particle-derived membrane reactor. A brief flow sheet with or without extraction is shown in ESI-4.† The membrane reactor with extraction, O_2 with low molecular weight was transferred faster than SO_2 and SO_3 , and SO_3 , and the largest molecular weight, permeated at the slowest speed by Knudsen diffusion through the

mesoporous SiC membrane.⁴⁶ Therefore, the equilibrium of the reaction (R4) ($SO_3 \leftrightarrow SO_2 + 0.5O_2$) was forwarded to the product side by removing O_2 . In a comparison with a membrane without extraction, the membrane reactor with extraction achieved higher conversion at the same temperature of 600 °C. The catalytic membrane reactor obtained conversion of 25% without extraction, which approximated the equilibrium (theoretical) conversion of SO_3 decomposition (eqn (4)) of 28% at 900 K.³ Comparison with membrane without extraction, the conversion of H_2SO_4 decomposition was increased to 45%, which was much higher at the same temperature of 600 °C. Additionally, the H_2SO_4 decomposition conversion remained constant at around 41% after membrane exposure to H_2SO_4 vapor for 10 h. Moreover, after decomposition for 10 h, He permeance was approximately the same as that before the decomposition reaction, which indicated that the SiC particle layer (with SiO_2-ZrO_2) had high hydrothermal and chemical stability under H_2O and SO_3 . However, the separation properties of M4 membranes was still poor; the He/ N_2 permeance ratio was 2.3 with N_2 permeance of $4.5 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, since the SiC membrane was fabricated using SiC particles, and the gaps between particles were large enough to allow gas to pass through.

4. Conclusions

SiC mesoporous membranes were successfully prepared using an $\alpha-Al_2O_3$ support and a SiC particle layer. The gas permeance of the SiC membrane was stable for 20 h under H_2SO_4 vapor at 600 °C, which indicated its high chemical stability. Regarding the H_2SO_4 decomposition reaction, the SiC membrane achieved a conversion of 41% at 600 °C, which was much higher than that of the membrane without extraction (25%). Our previous work involved the preliminary use of SiC membranes in a catalytic membrane reactor for hydrogen production in the iodine-sulfur process, and a desirable design for a SiC subnanoporous membrane with a combination of high O_2 permeance and O_2/SO_2 selectivity will be a major objective in the future.

Conflicts of interest

There are no conflicts to declare.

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