Supplementary information for

# Enhanced Decomposition of Sulfur Trioxide in the Water-Splitting Iodine-Sulfur Process via a Catalytic Membrane Reactor

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# Experimental

### *Fabrication of microporous silica membranes*

Porous $SiO_2$ glass tubular substrates with a pore diameter of 500 nm, an outside diameter of 8.5 mm and a length of 100 mm were employed as supports. Tetraethoxysilane (TEOS) was used as a silica precursor and was mixed with ethanol, followed by the addition of water and HCl to obtain a silica sol. The molar ratio of the above reagents (TEOS/$H_2$O/HCl) was controlled at 1/200/0.1, and the concentration of TEOS was kept at 0.05-1.0 wt%. The silica sol was deposited onto the porous substrates which were then calcined at 600 °C to form a thermally stable intermediate layer. For the separation top layer, the silica sol was coated onto the intermediate layer, followed by a calcination at 350 °C in air.

### *Gas permeation measurement*

Single gas (He, $H_2$, $N_2$, $CF_4$ and $SF_6$) permeation testing was conducted using a setup schematically shown in Figure S1. The feed gas was introduced to the upstream of the membrane under a temperature that varied between 300 and 600 °C. The pressure at the retentate side was controlled with a pressure regulator while the permeate side was maintained at atmospheric pressure. The gas flow rates were obtained by film flow meters (SF-2U, Horiba, Japan).
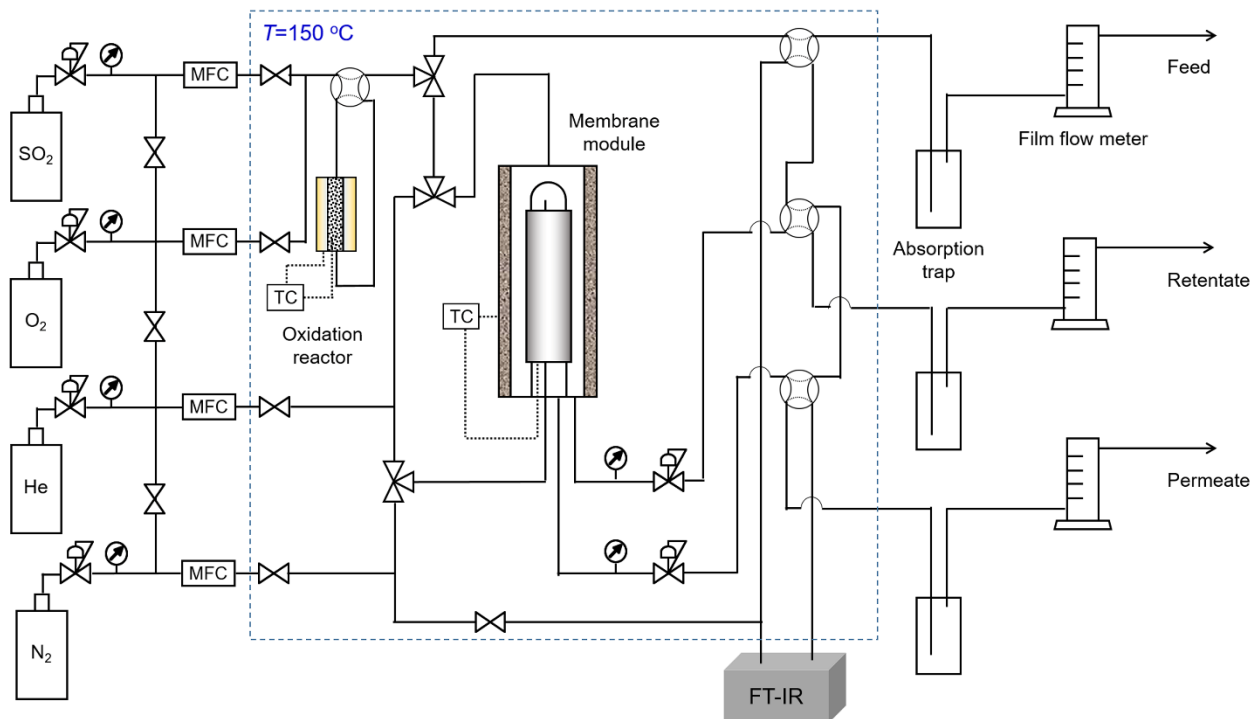


Figure S1. Schematic diagram of the experimental setup for gas permeation and catalytic membrane reactor.

In the present study, $SO_3$ was generated from the oxidation of $SO_2$ at 400 °C with $Pt/Al_2O_3$ catalysts. The concentrations of $SO_3$ and $SO_2$ in mixed gas were determined using a Fourier transform infrared (FT-IR) analyzer (IRTracer-100, Shimadzu, Japan). Figure S2 shows the time-course of FT-IR analysis for $O_2/SO_3$ separation with a microporous silica membrane at 600 °C. First, $SO_2$ was detected when $SO_2$ and $O_2$ were mixed and introduced into the FT-IR analyzer. After feeding $SO_2$ and $O_2$ into the oxidation reactor, the peak height for $SO_3$ increased while that for $SO_2$ decreased to zero indicating that the $SO_2$ conversion reached 100%. The stable $SO_3$ flow was then introduced into the shell side of the membrane. By switching the 4-way valves, the FT-IR analyzer could be connected to either the retentate or the permeate side which offered a quick-response and stable measurement of $SO_3$ concentration in $O_2/SO_3$ mixed gas. The absorption trap filled with hydrogen peroxide (0.1 mol/L) was employed for trapping $SO_3$ and $SO_2$, while $O_2$ passed through the traps and was measured by a film flow meter.
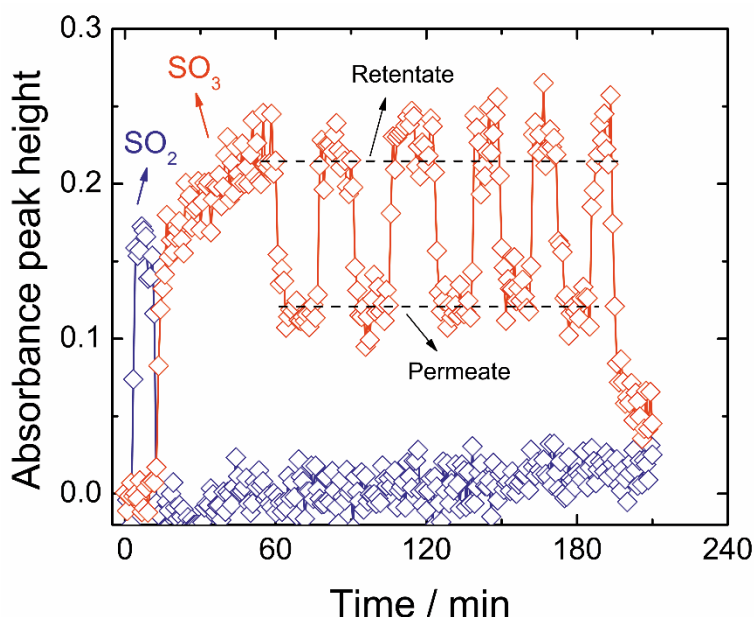


Figure S2. Time-course of FT-IR analysis for $O_2/SO_3$ separation with a microporous silica membrane at 600 °C.

In binary-component gas permeation, the selective permeation causes a partial pressure distribution of the component along the membrane surface. Here, the logarithmic mean pressure difference for the component, $i$ ($\Delta p_{i,lm}$) was employed to calculate the driving force for gas permeation:

$$\Delta p_{i,lm} = \frac{\Delta p_{i,in} - \Delta p_{i,out}}{\ln(\frac{\Delta p_{i,in}}{\Delta p_{i,out}})} \tag{1}$$

where $\Delta p_{i,in}$ and $\Delta p_{i,out}$ refer to the difference in the partial pressure of component $i$ between the retentate and the permeate side at the inlet and at the outlet, respectively.

### *Estimation of the effective molecular size of SO₃ via NKP*

The normalized Knudsen-based permeance (NKP) method has been a useful tool for the determination of the average pore size of a microporous membrane, $d_p$ [1-5]. NKP is the ratio of the permeance of component $i$ to the permeance predicted using He, which is the smallest molecule, under the Knudsen diffusion mechanism, as expressed in Eq. (2).

$$NKP = \frac{P_i}{P_{He}} \frac{\sqrt{M_i}}{\sqrt{M_{He}}} = \frac{(d_p - d_{k,i})^3}{(d_p - d_{k,He})^3} \exp(-\frac{E_{P,i} - E_{P,He}}{RT}) \qquad (2)$$

where $P_i$, $M_i$, $E_{P,i}$, $d_{k,i}$ represent the gas permeance, molecular weight, activation energy and molecular size for the permeating components, respectively. Herein, the $E_{P,i}$ for different gases is assumed to be similar to $E_{P,He}$ due to the large pore size of the microporous silica membrane [3]. Thus, the membrane pore size, $d_p$, can be calculated by the following equation (Eq. (3)).

$$NKP = \frac{(d_p - d_{k,i})^3}{(d_p - d_{k,He})^3} \qquad (3)$$

Table S1 summarizes the gas physical and permeation properties used for NKP calculation. These gas permeation data for the microporous silica membrane were measured at 600 °C. Based on Eq. (3), the NKP fitting curve that is based on the experimentally obtained NKP with a best fitted pore size ($d_p$) of 0.505 nm was plotted as a function of the molecular size of gas molecules. Then the effective molecular size of SO₃ permeates through the microporous membrane could be obtained by simply fitting the value of SO₃ permeance to the curve.

Table S1 Gas properties and NKP at 600 °C for the microporous silica membrane

| Gas | Molecular size [nm] | Molecular weight [g mol$^{-1}$] | Permeance [$10^{-8}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$] | NKP |
|---|---|---|---|---|
| He | 0.260 | 4.00 | 247.34 | 1.0000 |
| O₂ | 0.346 | 32.00 | 23.24 | 0.2657 |
| N₂ | 0.364 | 28.02 | 13.15 | 0.1407 |
| SO₂ | 0.429 | 64.07 | 3.15 | 0.5098 |
| CF₄ | 0.480 | 88.00 | 0.81 | 0.1540 |
| SO₃ | | 80.07 | 0.94 | |

### *SO₃ decomposition in the catalytic membrane reactor*

0.7 g Pt/Al₂O₃ catalysts were packed into the core side of the membrane. The temperature inside the membrane was maintained at 600 °C, and the membrane module was placed in an oven controlled at 150 °C to avoid any possible condensation. The flow rate of SO₃, O₂ in feed and O₂ as sweep gas in the permeate stream were 2.5, 43.6 and 8.8 ml/min, respectively. The pressure at the retentate side was controlled with a back-pressure regulator and pressurized from 130 to 140 kPa, while the permeate stream was kept at a

pressure of 108 kPa. $SO_3$ conversion ($X$) in the catalytic membrane reactor is defined as the percentage of reacted $SO_3$, and is expressed in the following equation:

$$X = \frac{F_{SO_3,0} - F_{SO_3,r} - F_{SO_3,p}}{F_{SO_3,0}} \tag{4}$$

where $F_{SO_3,0}$, $F_{SO_3,r}$, and $F_{SO_3,p}$ refer to the flow rates of $SO_3$ in the feed stream, at the outlet of retentate side and at the outlet of permeate side, respectively.

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