Supporting Information

Toward high-effective and sustainable hydrogen production: bio-ethanol oxidative steam reforming coupled with water splitting in a thin tubular membrane reactor

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1. Experimental details

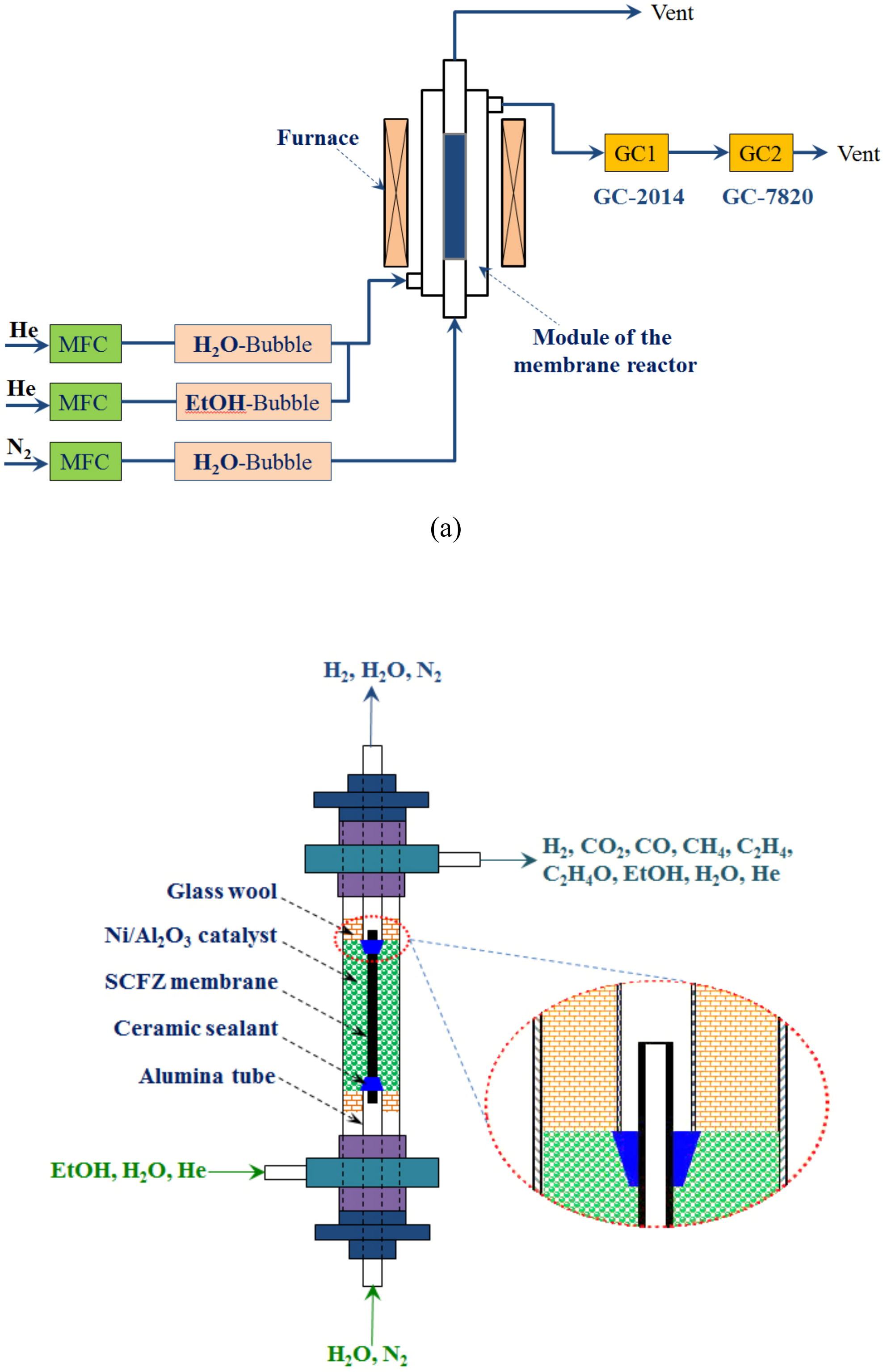
1.1 Sample preparation

$SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) was synthesized by the solid-state reaction method. First, stoichiometric amounts of $SrCO_3$, Co_2O_3, Fe_2O_3, and monoclinic ZrO_2 were mixed and ball-milled in ethanol for 24 h, followed by calcinations in air at 950 °C for 5 h. The starting extrusion mixture was composed of 76 wt% SCFZ powders, 10 wt% PVA solution, 10 wt% Dextrin and 4 wt% Tung oil. The green thin tubular membrane was prepared by the plastic extrusion and a die with an orifice diameter and inner diameter of 3.4 and 2.2 mm was used. The green thin tubular membranes were dried at room temperature for several days and sintered in air at 1250 °C for 2 h to form dense thin tubular membranes. The detailed procedure was described in our previous work.[1]

1.2 Membrane reactor set-up

The reaction of hydrogen production from oxidative steam reforming of ethanol (OSRE) and water splitting coupled with OSRE were performed on a high temperature apparatus. The reactor module and the experimental apparatus used in this study are shown in Fig. S1. A thin SCFZ tubular membrane with the ID/OD of 1.0/1.6 mm was sealed with two Alumina tubes (2 mm ID, 3 mm OD) at both ends of membrane. The effective length of the tubular membrane was 14 mm. A quartz tube (8 mm OD) surrounding the two quartz tubes formed the shell side of the membrane. 0.8 g Ni/Al_2O_3 catalyst was packed on the shell side of the tubular membrane. Nitrogen bubbled through a water bath at a fixed temperature or air was introduced to the tube side of the membrane. Helium was bubbled through a water bath and an ethanol bath at a fixed temperature, and then flowed over the shell side of the membrane. The flow rates of nitrogen and helium, and the temperatures of water and ethanol were adjusted to control the amounts of the feed water and ethanol, and their partial pressures. The gas flow rates were controlled by mass flow controller (Model AI-708PA, Xiamen Yudian automation technology Co.,Ltd.).

The effluent streams at the shell side of the membrane were analyzed by two on line gas chromatographs: Shimadzu, model GC-2014 equipped with a Porapak Q column (for the analysis of CO_2, C_2H_5OH, C_2H_4O) and Agilent, model GC-7820 equipped with a Haysep-DB column (for the analysis of H_2, N_2, CO, CH_4, CO_2, C_2H_4). CO_2 was used to relate the Porapak Q column and the Haysep-DB column to calculate the mass balances.



(a)

(b)

Fig. S1 Schematic diagrams of a membrane reactor for coupling OSRE with water splitting: a) schematic diagram of a complete reactor set-up; b) module of a thin tubular membrane reactor.

1.3 Definitions

The ethanol conversion and product selectivities were calculated by:

$$X_{Ethanol} = \frac{F_{Ethanol,in} - F_{Ethanol,out}}{F_{Ethanol,in}}$$

We define H_2 selectivity as the fraction of H atom in the ethanol molecule converted into H_2, so that 3 H_2 molecules from C_2H_5OH represent 100% H_2 selectivity. Because the H atoms from H_2O can also be converted into H_2, complete conversion of the ethanol and water could generate 5 H_2 per C_2H_5OH, which gives a maximum H_2 selectivity of 5/3 or 167%.[2]

$$S_{H_2} = \frac{F_{H_2}}{3 \times F_{Ethanol,in} \times X_{Ethanol}}$$

$$S_i = \frac{m \times F_i}{2 \times F_{Ethanol,in} \times X_{Ethanol}}$$

Where *F* is the flow rate of species *i*, in ml·min^{-1} and *m* is the number of carbon atoms in a product molecule.

The water of outstream, oxygen flux was calculated by the mass balance on the basis of the components of C_2H_5OH, C_2H_4O, C_2H_4, CO, H_2, CH_4, CO_2 and H_2O in exit stream:

$$F_{H_2O,out} = 3 \times F_{Ethanol,in} \times X_{Ethanol} + F_{H_2O,in} - 2 \times F_{CH_4} - 2 \times F_{C_2H_4O} - 2 \times F_{C_2H_4} - F_{H_2}$$

$$F_{O_2} = \frac{1}{2} F_{H_2O,out} + \frac{1}{2} F_{CO} + F_{CO_2} + \frac{1}{2} F_{C_2H_4O} - \frac{1}{2} F_{Ethanol,in} \times X_{Ethanol} - \frac{1}{2} F_{H_2O,in}$$

For water splitting coupled with OSRE, the hydrogen production rate at the tube side of the membrane was calculated through oxygen flux.

According to $H_2O \leftrightarrow H_2 + 1/2O_2$,

$$F_{H_{2,core}} = 2 \times F_{O_2}$$

Reference

[1] C. Zhang, Z. Xu, X. F. Chang, Z. C. Zhang, W. Q. Jin, *J. Membr. Sci.*, 2007, **299**, 261.

[2] G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios, *Science*, 2004, **303**, 993.

2. The performance of OSRE with air as oxygen source

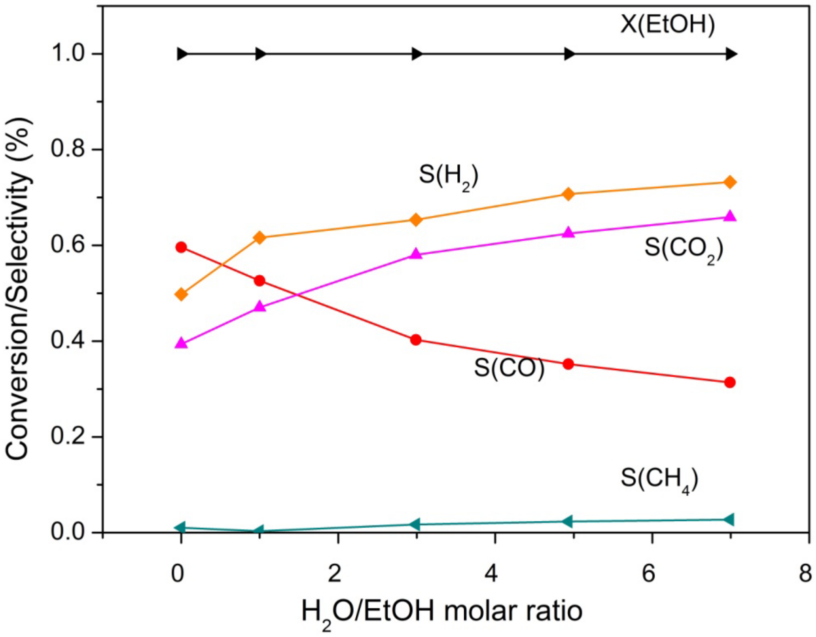


Fig. S2 Effect of H_2O/EtOH molar ratio on the performance of OSRE at 900 °C. **X**: ethanol conversion, **S**: selectivities to the reaction products. Shell side: $F_{EtOH} = 7$ ml·min^{-1}, $F_{He} = 120$ ml·min^{-1}; Tube side: $F_{air} = 200$ ml·min^{-1}.

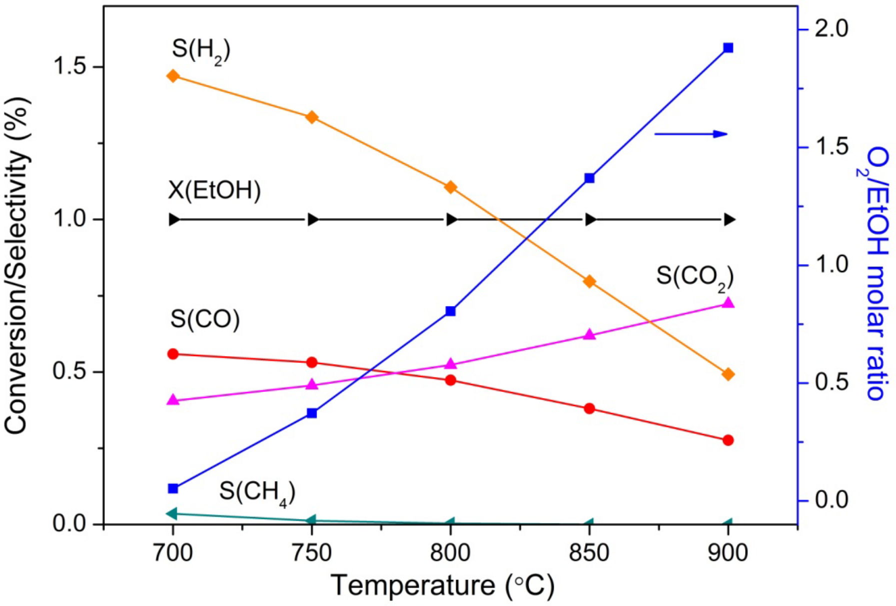


Fig. S3 Temperature dependence of oxygen permeation, ethanol conversion (**X**) and selectivities (**S**) to the reaction products for OSRE. Shell side: p_{EtOH} = 0.06 atm, F_{EtOH} = 7 ml·min^{-1}, n(H_2O)/n(EtOH) = 4.8; Tube side: $F_{air} = 200$ ml·min^{-1}.

Table S1. Temperature dependence of hydrogen production rate and oxygen flux for OSRE. Shell side: p_{EtOH} = 0.06 atm, F_{EtOH} = 7 ml·min^{-1}, n(H_2O)/n(EtOH) = 4.8; Tube side: F_{air} = 200 ml·min^{-1}.

Temperature (°C)	Oxygen permeation flux (ml·cm^{-2}·min^{-1})	H_2 production rate (ml·cm^{-2}·min^{-1})
700	0.6	54.2
750	4.6	49.2
800	9.9	40.8
850	16.8	29.4
900	23.6	18.2

3. Blank experiments

In order to demonstrate the simultaneous participation of water splitting and steam reforming of ethanol in the coupling reaction process, following two blank experiments have been conducted. Experiment 1: feeding water at the tube side and ethanol (with no water) at the shell side. Experiment 2: feeding ethanol and water at the shell side and no water (only inert) at the tube side.

For experiment 1: The performance of the reactor was tested at 750 °C, 800 °C and 850 °C. The relative contents of CO, CO_2, CH_4, H_2 and H_2O in the shell side were listed in Table S2. The selectivities of CO, CO_2, CH_4 and H_2 in the shell side and the production rate of H_2 in the tube side were listed in Table S3. From table S2 and S3, an obvious oxidation reforming of ethanol (ORE) was observed in the shell side. Moreover, the oxygen provided by the membrane was excess, thus part of the produced H_2 reacted with O_2 to H_2O (see table S2). In other words, the water splitting (WS) reaction really occurred in the tube side. This result was further confirmed by the high H_2 production rate in the tube side (see table S3).

Table S2 The relative contents (%) of CO, CO_2, CH_4, H_2 and H_2O in the shell side. Tube side: $p_{H2O} = 0.69$ atm, $F_{N2} = 100$ ml·min^{-1}; Shell side: $F_{EtOH} = 0.9$ ml·min^{-1}, $p_{EtOH} = 0.06$ atm.

Temperature (°C)	CO	CO_2	CH_4	H_2	H_2O
750	35.67	3.67	3.32	48.06	9.28
800	34.80	5.09	0.53	47.81	11.77
850	33.21	6.77	0.08	44.85	15.09

Table S3 The performance of the reactor. Tube side: $p_{H2O} = 0.69$ atm, $F_{N2} = 100$ ml·min^{-1}; Shell side: $F_{EtOH} = 0.9$ ml·min^{-1}, $p_{EtOH} = 0.06$ atm.

Temperature (°C)	Shell side Selectivities (%)				Tube side
	CO	CO_2	CH_4	H_2	H_2 Production rate (ml·cm^{-2}·min^{-1})
750	83.60	8.60	7.80	75.10	2.33
800	86.10	12.60	1.30	78.86	4.51
850	82.90	16.90	0.20	74.62	4.96

For experiment 2: The performance of the reactor was also tested at 750 °C, 800 °C and 850 °C. The selectivities of CO, CO_2, CH_4 and H_2 in the shell side were listed in Table S4. A steam reforming of ethanol (SRE) indeed occurred in the shell side to produce H_2, CO, CO_2 and minor CH_4. Relatively high hydrogen selectivity was obtained.

Table S4 The selectivities (%) of CO, CO_2, CH_4 and H_2 in the shell side. Shell side: $F_{EtOH} = 0.9$ ml·min^{-1}, $p_{EtOH} = 0.06$ atm, $n(H_2O)/n(EtOH) = 4.8$

Temperature (°C)	CO	CO_2	CH_4	H_2
750	70.10	29.60	0.30	155.90
800	77.80	22.20	0	151.70
850	80.10	19.90	0	148.80

4. The simulation of OSRE in the Gibbs reactor model

ASPEN PLUS 11.1 (Aspen Technology, Inc., MA, USA) was uesd to simulate the OSRE in the Gibbs reactor model for comparison with the experimental results. Gibbs reactor model calculates the product composition by minimizing Gibbs free energy. In the simulation, the reaction products of H_2, CO_2, CO, C_2H_5OH, O_2, H_2O, CH_4, C_2H_4O and C_2H_4 are considered in the equilibrium system.

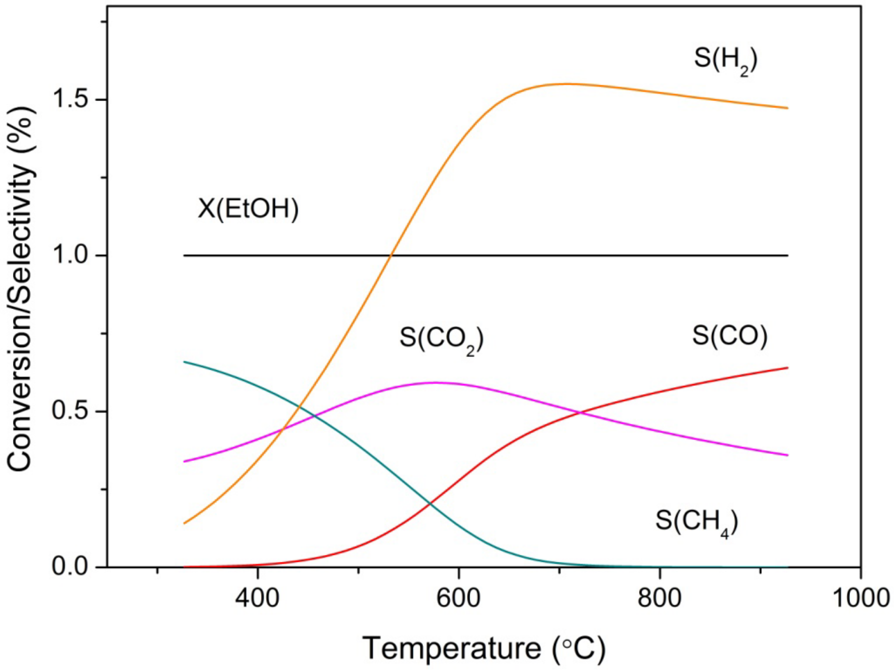


Fig. S4 Temperature dependence of equalibrium ethanol conversion and selectivities to the reaction products for OSRE. $n(H_2O)/n(EtOH) = 4.8$; $n(O_2)/n(EtOH) = 0.1$; Pressure=1 atm.

Fig. S4 shows the performance of the OSRE from 330 ^{o}C to 930 ^{o}C calculated at thermodynamic equilibrium in Gibbs reactor. Ethanol was converted completely over the whole temperature range. As the temperature increases, the selectivity to H_2 dramatically increases until reaches a maximum at around 710 ^{o}C then steadily decreases. The CO_2 selectivity increases first and has a maximum at around 580 ^{o}C then decreases. The CO selectivity increases with increasing the temperature.