Supplementary Information (SI) for Reaction Chemistry & Engineering.

A highly stable asymmetric hollow fiber catalytic membrane reactor for selective oxidation of ethane to ethylene

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1. Performance the catalytic membrane reactor for ODHE

To assess the performance of oxidative dehydrogenation of ethane (ODHE), the CGO/CSO-SSAF catalytic membrane was installed in a homemade setup with a vertical high-temperature furnace, as described in our previous work. As illustrated in Fig. S1, the CGO/CSO-SSAF catalytic membrane was positioned within an alumina tube, with approximately 3 cm of the membrane extending outside on one side, which was subsequently sealed using glass adhesive. The glass adhesive is cheaper than sliver slurry, which exhibits a good application prospect. The effective membrane area was determined by manual measurement and calculation, given that the hollow fiber membrane has a diameter of approximately 0.3 cm and an effective length of 3 cm, the area was calculated as $A = \pi dl = 3.14\times0.3\ cm\times3\ cm \approx 2.8\ cm^2$. The ethane mixture (32 mL min^{-1} ,10% C_2H_6-5% N_2-85% Ar) was supplied to the shell side. The Air (15 mL min^{-1}) was supplied to the inside of the hollow fiber membrane. The gas flow rates were adjusted by gas mass flow meters. Regular calibration of the flow rates was measured by a bubble flow meter. The gas composition at the reactor outlet was analyzed by an A91 on-line gas chromatography. After examining the effects of various operating conditions, a long-term stability test was conducted on the CGO/CSO-SSAF catalytic membrane reactor under ethane mixture at 625 °C for a duration of 500 h.

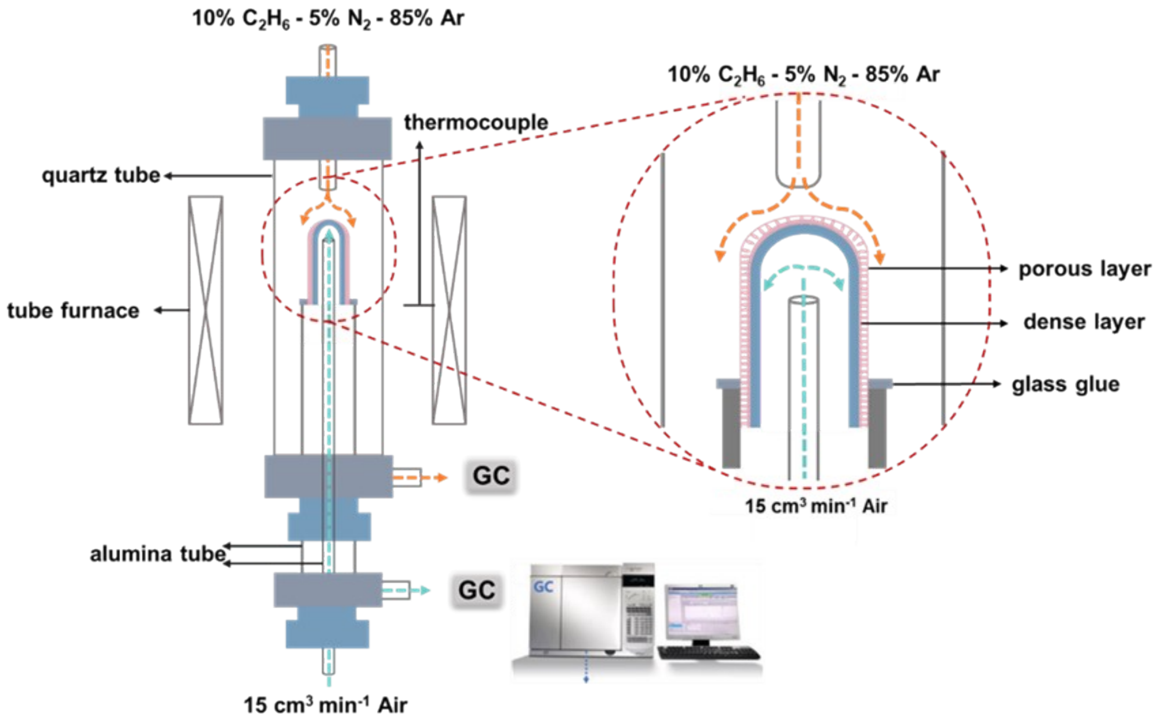

Fig. S1 Diagram of catalytic membrane reactor for ethane dehydrogenation to ethylene.

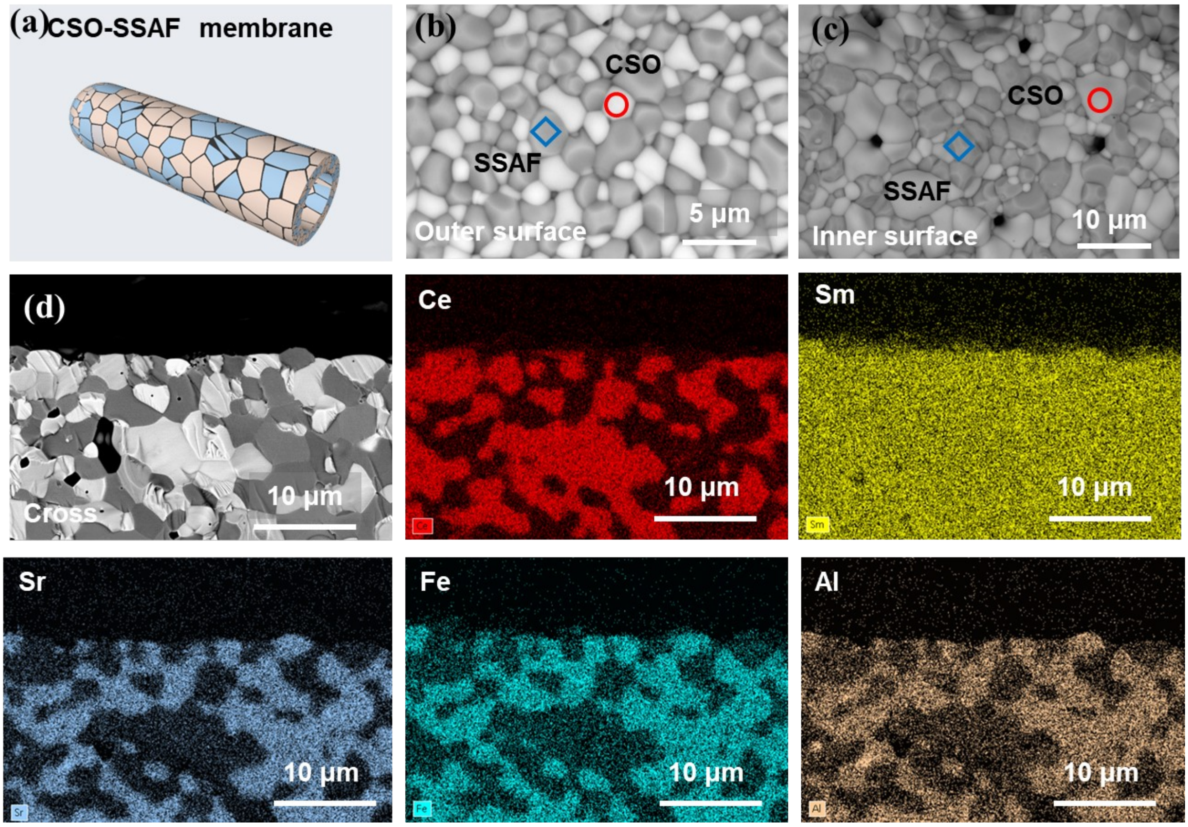

Fig. S2 The structure and morphology of CSO-SSAF hollow fiber membranes. (a) The schematic illustration of CSO-SSAF membrane; (b) BSE images of the outer surface (c) and the inter surface about the CSO-SSAF membrane; (d) the BSEM images and EDX-mapping of cross section about the CSO-SSAF membrane.

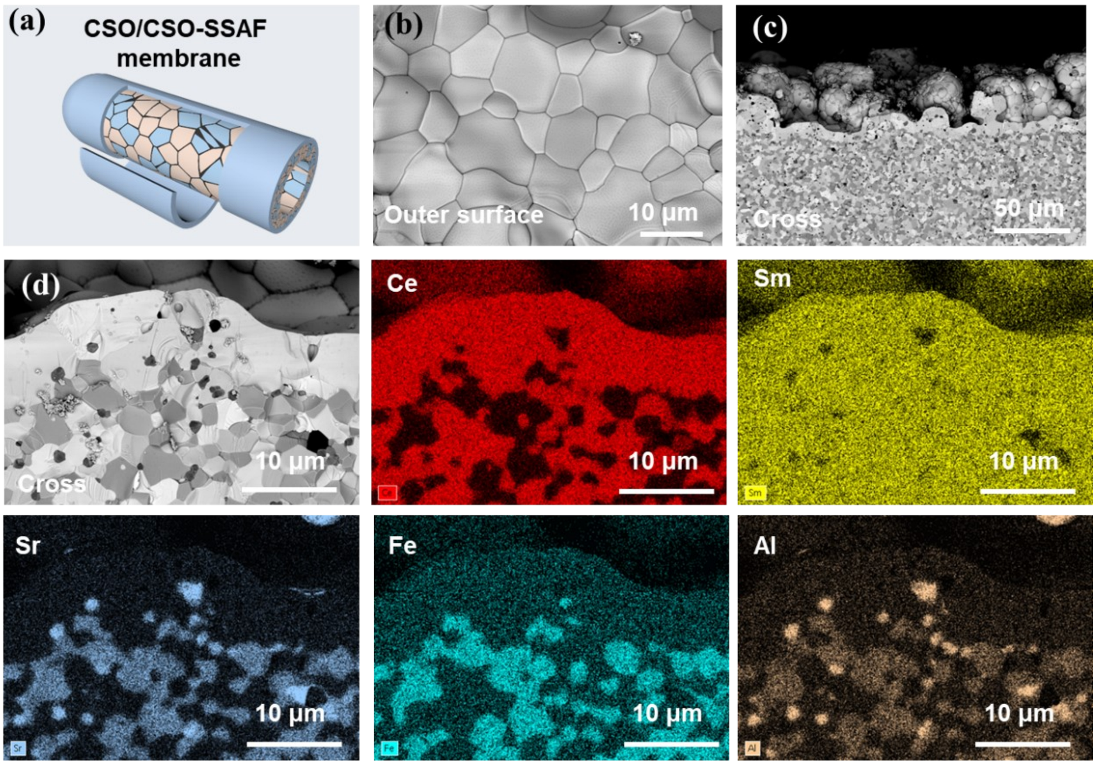

Fig. S3 The structure and morphology of CSO/CSO-SSAF hollow fiber membranes. (a) The schematic illustration of CSO/ CSO-SSAF membrane; (b) BSE images of the outer surface (c) and the inter surface about the CSO/ CSO-SSAF membrane; (d) the BSEM images and EDX-mapping of cross section about the CSO/CSO-SSAF membrane.

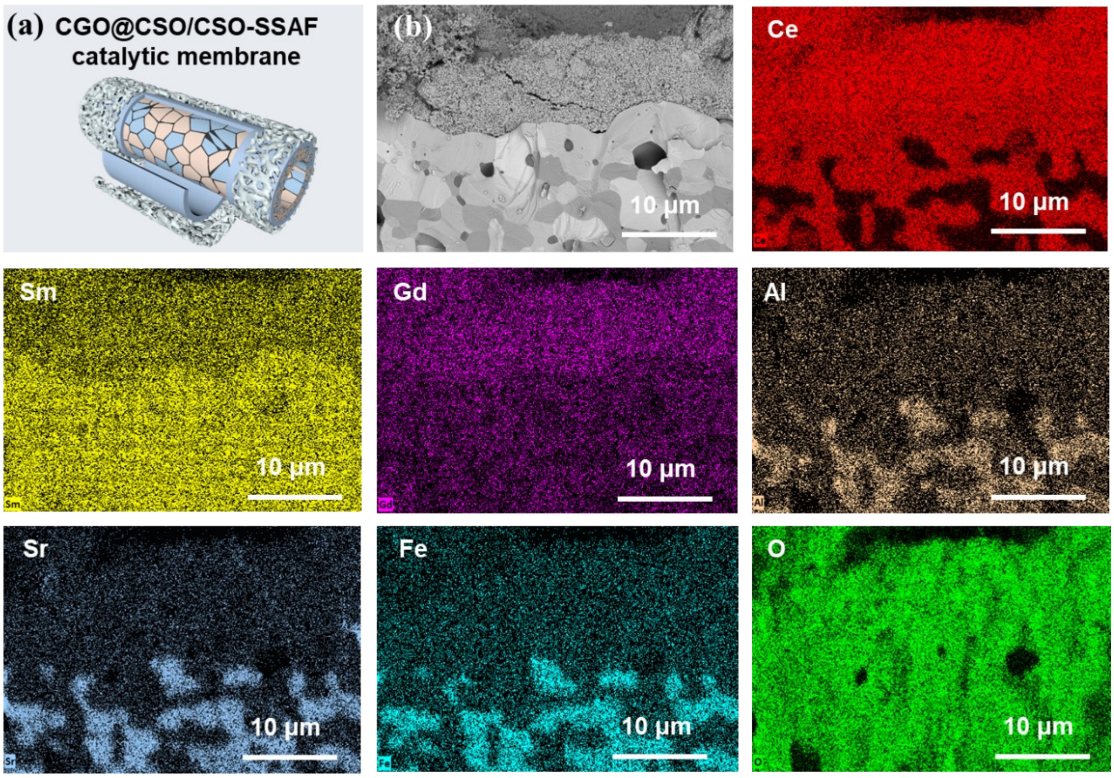

Fig. S4 The structure and morphology of CGO@CSO/CSO-SSAF hollow fiber membranes. (a) The schematic illustration of CGO@CSO/CSO-SSAF membrane; (b) BSE images of the outer surface (c) and the inter surface about the CGO@CSO/ CSO-SSAF membrane; (d) the BSEM images and EDX-mapping of cross section about the CGO@CSO/CSO-SSAF membrane.

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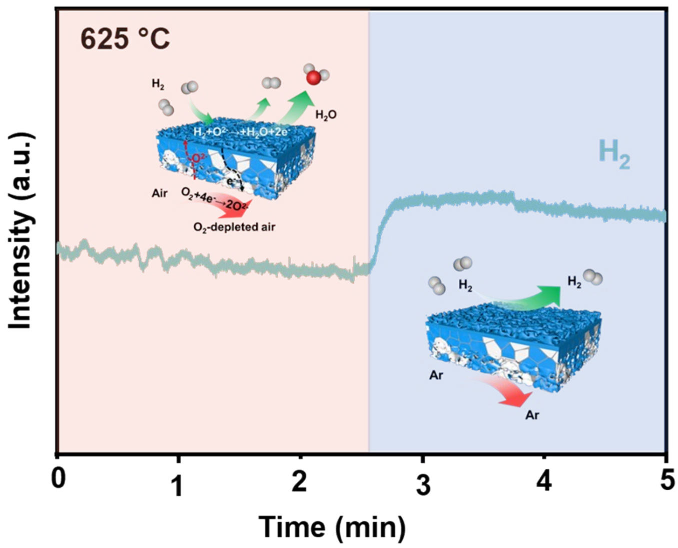

Fig. S5 In-situ mass spectrometry of H_2 consumption under different operating conditions in the CGO@CSO/CSO-SSAF catalytic membrane reactor.

The experiment was performed at 625 °C. The feed side was first supplied with air at 15 mL min^{-1}; after the signal stabilized, the feed gas was switched to Ar at 15 mL min^{-1}. The sweep gas was 5% H_2/Ar at 32 mL min^{-1}, which carried the permeated oxygen to the detector. The experimental setup and catalytic membrane reactor were the same as those used under other test conditions in this study.

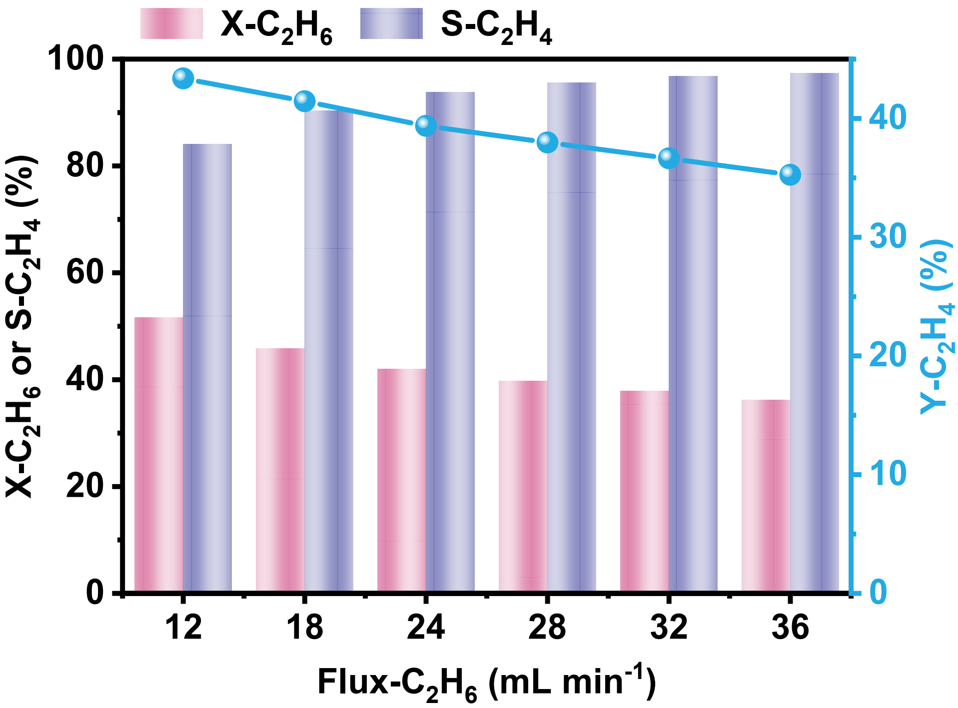

Fig. S6 The performance of ODHE reaction in the CGO@CSO/CSO-SSAF catalytic membrane reactor with different ethane flux at 675 °C.

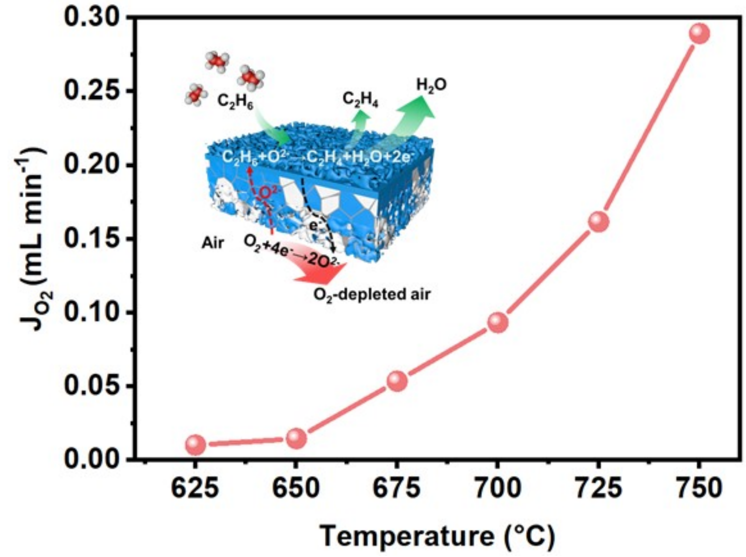

Fig. S7 Oxygen permeation flux of CGO@CSO/CSO-SSAF membranes at different temperatures.

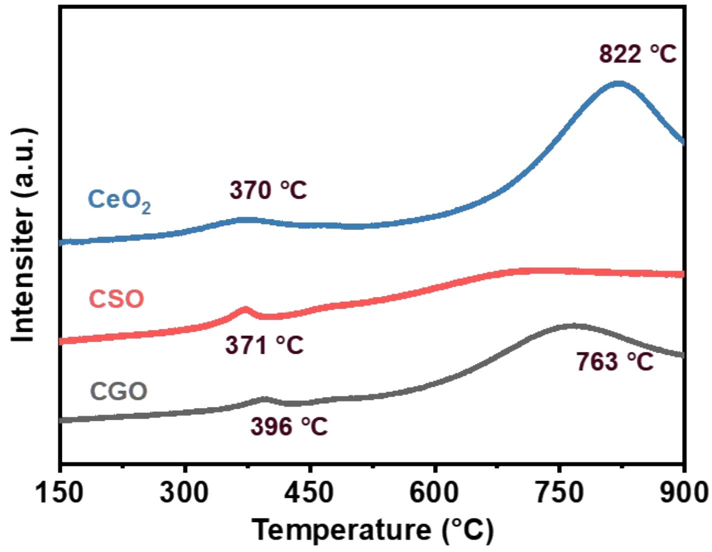

Figure S8. Temperature-programed reduction profiles of CGO, CSO and CeO_2 under 10%H_2/Ar.

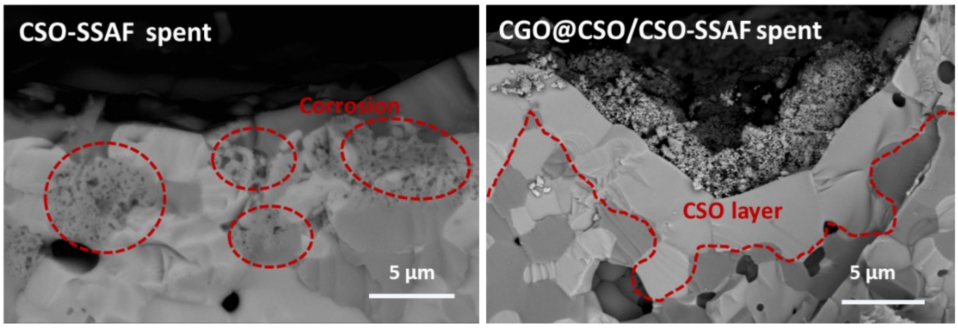

Figure S9. SEM images of the spent membranes with and without CSO protection layer

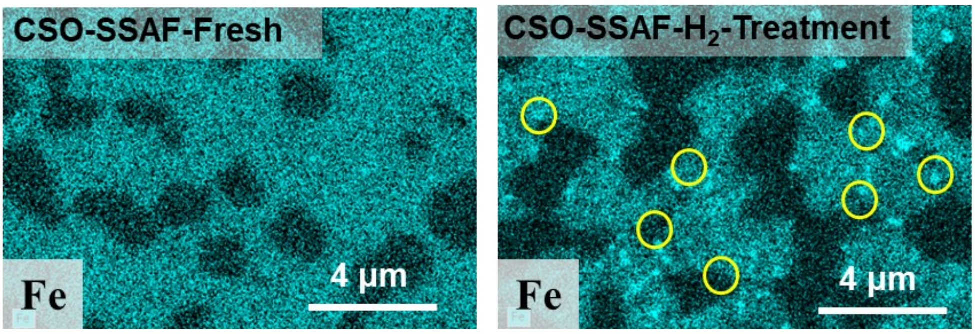

Figure S10. EDX images of the CSO-SSAF membrane before and after a 30 h treatment at 950 °C under a 10 vol% H_2/Ar atmosphere.

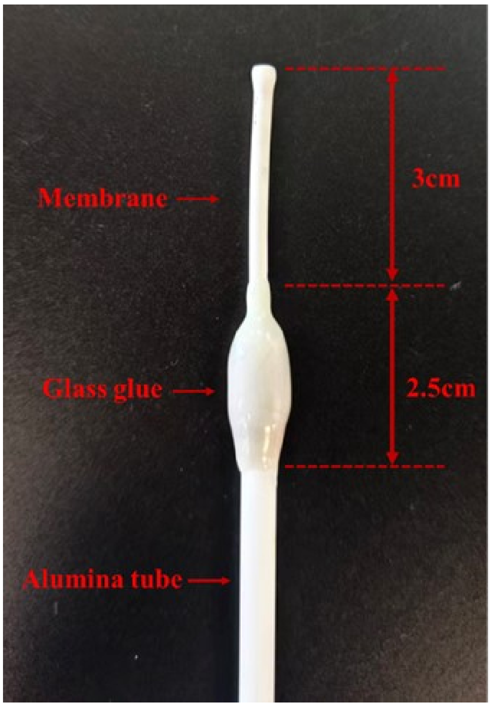

Figure S11. Macroscopic diagram of catalytic membrane and component sealing

Table S1 A review of different membrane systems for ODHE synthesis utilizing oxygen permeable membranes

Membrane material	Catalyst	Temperature [°C]	Conversion/selectivity	Stability	Reference
CSO/CSO-SSAF	CGO	625	0.19/0.99	500 h	
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	V/MgO Pd	775 775	0.9/0.83 0.88/0.85	--	1
$BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ)	No catalyst	800	0.62/0.63	--	2
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}$ $O_{3-\delta}$(BSCF)	V/MgO Pd	775 775	0.91/0.8 0.87/0.86	--	3
$BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ)	Cr_2O_3	725	0.89/0.58	60 min	4
$BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ)	No catalyst	800	0.63/0.64	--	5
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	No catalyst	850	0.9/0.85	--	6
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	$Ce_{0.8}Tb_{0.2}O_{2-\delta}$	850	0.89/0.93	--	7
$SrFe_{0.85}W_{0.15}O_{3-\delta}$	No catalyst	860	0.9/0.43	115 h	8

[1] Rebeilleau-Dassonneville, M.; Rosini, S.; Veen, A. C. v.; Farrusseng, D.; Mirodatos, C. Oxidative activation of ethane on catalytic modified dense ionic oxygen conducting membranes. *Catalysis Today* **2005**, *104* (2), 131-137. DOI: https://doi.org/10.1016/j.cattod.2005.03.071.

[2] Wang, H.; Tablet, C.; Schiestel, T.; Caro, J. Hollow fiber membrane reactors for the oxidative activation of ethane. *Catalysis Today* **2006**, *118* (1), 98-103. DOI: https://doi.org/10.1016/j.cattod.2005.11.093.

[3] Dalmon, J.-A.; Cruz-López, A.; Farrusseng, D.; Guilhaume, N.; Iojoiu, E.; Jalibert, J.-C.; Miachon, S.; Mirodatos, C.; Pantazidis, A.; Rebeilleau-Dassonneville, M.; et al. Oxidation in catalytic membrane reactors. *Applied Catalysis A: General* **2007**, *325* (2), 198-204. DOI: https://doi.org/10.1016/j.apcata.2007.03.024.

[4] Czuprat, O.; Werth, S.; Schirrmeister, S.; Schiestel, T.; Caro, J. Olefin Production by a Multistep Oxidative Dehydrogenation in a Perovskite Hollow-Fiber Membrane Reactor. *ChemCatChem* **2009**, *1* (3), 401-405. DOI: https://doi.org/10.1002/cctc.200900176 (acccessed 2026/02/05).

[5] Kondratenko, E. V.; Wang, H.; Kondratenko, V. A.; Caro, J. Selective oxidation of CH4 and C2H6 over a mixed oxygen ion and electron conducting perovskite—A TAP and membrane reactors study. *Journal of Molecular Catalysis A: Chemical* **2009**, *297* (2), 142-149. DOI: https://doi.org/10.1016/j.molcata.2008.09.015.

[6] Lobera, M. P.; Escolástico, S.; Serra, J. M. High Ethylene Production through Oxidative Dehydrogenation of Ethane Membrane Reactors Based on Fast Oxygen-Ion Conductors. *ChemCatChem* **2011**, *3* (9), 1503-1508. DOI: https://doi.org/10.1002/cctc.201100055.

[7] Lobera, M. P.; Balaguer, M.; Garcia-Fayos, J.; Serra, J. M. Rare Earth-doped Ceria Catalysts for ODHE Reaction in a Catalytic Modified MIEC Membrane Reactor. *ChemCatChem* **2012**, *4* (12), 2102-2111. DOI: https://doi.org/10.1002/cctc.201200212.

[8] Bragina, O. A.; Shubnikova, E. V.; Arapova, M. V.; Novikov, A. D.; Cherendina, O. V.; Khokhlova, M. O.; Kovalskii, V. Y.; Zilberberg, I. L.; Jiang, H.; He, G.; et al. Oxygen transport SrFe0.85M0.15O3-δ (M=Mo, W) hollow fiber membranes for ethylene production by ODHE. *Surfaces and Interfaces* **2025**, *76*, 107833. DOI: https://doi.org/10.1016/j.surfin.2025.107833.