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ABSTRACT:

Biogas Dry Reforming in Pd/YSZ Membrane Reactors: A Process Intensification Strategy for Carbon-Negative Hydrogen Production

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The continuous rise in atmospheric concentrations of anthropogenic greenhouse gases, particularly carbon dioxide (CO_2) and methane (CH_4), is the primary driver of global temperature increase.
Biogas dry reforming (BDR) presents a viable approach for the simultaneous utilization of two greenhouse gases, CO_2 and CH_4 by converting them into synthesis gas, a mixture of H_2 and CO widely used in downstream chemical processes like methanol synthesis. The BDR reaction is highly endothermic (ΔH°298 = +247 kJ.mol-1) and typically operated at high temperatures (800–1000 °C) and pressures (15–30 bar) to overcome thermodynamic constraints [1,2].

The overall reaction is shown in Eq. 1:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H°298 = +247 \text{ kJ mol}^{-}. \qquad (1)$$

Despite its potential, BDR is challenged by several side reactions that lower CH_4 and CO_2 conversion, decrease H_2 yield, and alter the H_2/CO ratio. These include methanation, the reverse water-gas shift (RWGS), methane decomposition, and the Boudouard reaction [1,2].

Side Reactions:

$CO2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	ΔH°298 = −165 kJ.mol-1	(Methanation)	(2)
$CO_2 + H_2 \leftrightarrow CO + H_2O$	ΔH°298 = +41.4 kJ.mol-1	(RWGS)	(3)
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	ΔH°298 = +206 kJ.mol-1	(Steam Reforming)	(4)
$CH_4 \leftrightarrow 2H_2 + C(s)$	ΔH°298 = +75 kJ.mol-1	(Methane Decomposition)	(5)
$2CO \leftrightarrow CO_2 + C(s)$	ΔH°298 = −173 kJ.mol-1	(Boudouard Reaction)	(6)

To enhance BDR performance, membrane reactors (MRs) have been investigated due to their ability to integrate reaction and separation in a single unit. Hydrogen-permeable membranes, particularly Pd-based ones, are able to selectively remove H_2 from the reaction zone, thereby shifting reaction equilibrium toward further product formation, increasing CH_4 and CO_2 conversion, and suppressing side reactions. Pd-based membranes offer complete H_2 selectivity, high thermal stability, and chemical resistance under reforming reactions conditions [3,4].

Noble metals (Pt, Rh, Ru) and non-noble metals (Ni, Fe, Co) have been widely studied for catalyst development in BDR. Noble metals are particularly valued for their high catalytic activity, thermal stability, and resistance to carbon deposition, ensuring long-term performance under harsh conditions. Ceria (CeO_2) is an effective support material due to its ability to enhance metal dispersion, suppress sintering, and provide strong metal–support interactions. Its high oxygen storage capacity and Ce^{4+}/Ce^{3+} redox cycling help remove surface carbon via lattice oxygen, thereby improving coke resistance and maintaining catalyst activity [5–7]

In this study, a novel Ru/CeO_2 catalyst was employed in combination with a Pd/YSZ membrane to evaluate the performance of the BDR reaction for syngas (H_2 and CO) production under various temperature and pressure conditions. The membrane not only continuously removes hydrogen from the reaction zone but also helps suppress carbon deposition. This synergistic integration of a selective membrane with an advanced catalyst offers a promising strategy for scalable and stable BDR operation for hydrogen and syngas production.

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