

Hydrogen production via chemical looping steam methane reforming process: Effect of cerium and calcium promoters on the performance of Fe₂O₃/Al₂O₃ oxygen carrier



A. Hafizi^a, M.R. Rahimpour^{a,b,*}, Sh. Hassanajili^a

^a Chemical Engineering Department, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran

^b Department of Chemical Engineering and Materials Science, University of California, Davis, 1 Shields Avenue, Davis, CA 95616, United States

HIGHLIGHTS

- Effect of Ce/Ca promoters, its loading and temperature are studied in CL-SMR process.
- The OC with 5 wt.% promoter exhibited an excellent activity for CH₄ conversion.
- High activity is obtained during 15 oxidation–reduction cycles.
- The formation of carbon nanotube is observed in 15Fe–5Ce/Al₂O₃ oxygen carrier.

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ABSTRACT

High purity hydrogen can be produced through chemical looping with making use of the reaction between steam and lattice oxygen of an oxygen carrier. Since choosing a suitable oxygen carrier significantly affects the efficiency of this process, different oxygen carriers have been proposed. In this work, alumina supported Fe₂O₃ promoted with cerium or calcium oxides is assessed as an oxygen carrier. The effect of promoter type (M = Ca and Ce) and its loading weight percentage ($x = 0, 5, 10$) on the cyclic redox performance of 15Fe– x M/Al₂O₃ oxygen carrier is investigated. In addition, the reaction temperature (823–1023 K) and the oxygen carrier cyclic lifetime (up to 15 cycles) are studied at steam to methane ratio of 1.5. Surface and structural properties of some samples were characterized by various techniques such as X-ray diffraction, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, and Brunauer–Emmett–Teller. The results show that the activity, long-term stability and coke formation resistance of the oxygen carrier are significantly affected by the promoter type. The catalytic activity of oxygen carrier improves successfully in the presence of 5% cerium or calcium promoter. At 923 K, the methane conversion is about 100% for 15Fe–5Ca/Al₂O₃ and 15Fe–5Ce/Al₂O₃ oxygen carriers, which is the highest conversion among all the tested samples. However, 15Fe–5Ca/Al₂O₃ oxygen carrier is consistently stable in chemical looping reforming with high hydrogen producing capacity.

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1. Introduction

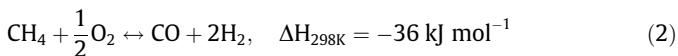
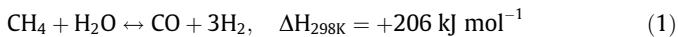
These days, one of the main concerns of the world is the global warming phenomenon that mainly results from fossil fuels burning. This issue along with the reduction of natural fossil fuels and the dependency of human life to energy explain the importance

of green energy sources development with the advantages of low emission of pollutants. Hydrogen, which is known as a green energy source, is a great candidate for this purpose [1–3]. From the time when Henry Cavendish discovered the hydrogen in 1766, many technical progresses have been made in its production and applications. In recent times, many scientific researchers are focused on the hydrogen production with lower costs by applying novel technologies [1–5]. The reforming of fossil fuels could usually produce this energy source. The non-reforming processes such as water gas shift reaction, water electrolysis and biomass gasification are also other hydrogen production approaches [1,2,6–8]. Due to the high availability of methane and its low cost, methane

* Corresponding author at: Chemical Engineering Department, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran.

E-mail addresses: rahimpour@shirazu.ac.ir, mrahimpour@ucdavis.edu (M.R. Rahimpour).

reforming is commonly applied in industries. In addition, hydrogen production from methane has received much consideration because it is a promising energy source that is also environmentally benign [9]. The most important methane feedstock reforming processes for hydrogen production are steam reforming (SMR), partial oxidation reforming (POR), CO₂ reforming and autothermal reforming (ATR) [10–14]. The main methane reforming reactions are:



Conventionally, in the partial oxidation of methane to hydrogen and carbon monoxide or in the oxidation of carbon monoxide to carbon dioxide, the oxygen source comes from both pure oxygen and air. The usage of pure oxygen needs a costly oxygen plant while the utilization of air results in the dilution of produced synthesis gas with N₂. In addition, it has been shown in the previous reports that nearly half of the capital investment in the gas-to-liquid (GTL) process is required for synthesis gas production which is due to the considerable capital cost of the oxygen plant or synthesis gas purification [15,16]. Thus, avoiding the use of pure oxygen or air and substituting them with lattice oxygen of solid oxygen carriers could significantly reduce the reforming and consequently hydrogen production or GTL costs. In chemical looping reforming (CLR), methane is partially oxidized to hydrogen and carbon monoxide without the consumption of elemental oxygen [17]. In this process, a suitable oxygen carrier (OC) is circulated between two interconnected reactors and methane is oxidized to synthesis gas by the lattice oxygen of the oxygen carrier in the “fuel reactor”. Then, the reduced oxygen

carrier is re-oxidized by air in the second reactor named “air reactor”. The CLR process concept is indicated in Fig. 1.

In the fuel reactor, the oxygen carrier (MeO) is reduced to its metallic form (Me) by methane while CH₄ is partially oxidized to H₂ and CO as mentioned in the following reaction.



In the air reactor, the oxygen carrier is oxidized to its initial state (MeO) with O₂ from the combustion air according to reaction 5, which is the partial oxidation of methane with an oxygen carrier:



Chemical looping steam reforming (CL-SR) in a fixed bed reactor is a process with two-step cyclically changing feeds to a reactor filled with oxygen transfer material (OTM) [18]. The feeds are fuel (hydrocarbon source mixed with steam) in reduction period and oxidant (air or oxygen) in oxidation step. Nevertheless, with chemical looping reforming, the H₂ and CO produced is not diluted with N₂, consequently the cost of a nitrogen and oxygen separation unit is avoided. It can significantly reduce capital costs of reforming units.

The chemical looping steam methane reforming (CL-SMR) process can be applied widely in large-scale industrial processes because of its lower cost, easier accessibility and environmental nature of this process [19,20]. Development of OC with high reactivity and adequate rates of oxidation and reduction is a vital issue in the CL-SMR process [21]. The oxygen carrier particles should be thermodynamically capable of converting a large amount of methane to synthesis gas, have adequate stability over cycles of oxidation/reaction at high temperature and have low tendency for fragmentation, agglomeration, attrition and other mechanical or thermal degeneration types. The OCs should also be capable of converting the fuel to synthesis gas in low oxygen to methane ratios [22–26].

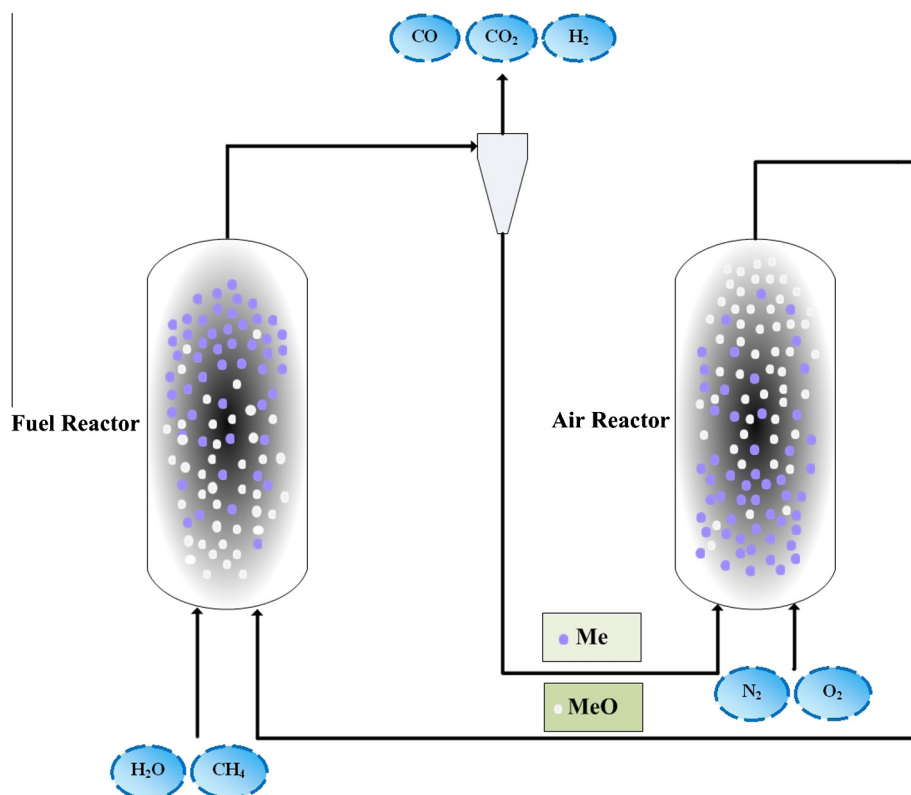


Fig. 1. Conceptual scheme of CL-SMR for hydrogen and carbon monoxide generation.

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