

A Novel Catalyst – Sorbent System for an Efficient H₂ Production with in Situ CO₂ Capture

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Introduction

Hydrogen is well perceived as a pollution-free primary energy carrier for future transportation as well as electricity generation. The sorption enhanced catalytic reforming of natural gas is an innovative concept of high purity hydrogen production and in-situ CO₂ capturing. In this contribution, the performance of a sorption enhanced catalytic reforming process is experimentally and mathematically investigated over a newly developed catalyst/sorbent system in a fixed bed reactor. Rh/Ce_{0.4}Zr_{1.6}O₂ is employed as an efficient low temperature catalyst for steam reforming (SR) and autothermal reforming of methane (ATR). K-promoted hydrotalcite (HTC), Zr-doped K-promoted hydrotalcite, and lithium zirconate (LZC) are employed as newly developed candidate carbon dioxide sorbents for high purity hydrogen production at temperatures lower than 550°C. Experimental and modeled results are compared to the results in conventional Ni – based catalytic reforming process. The study demonstrates a profit of the newly developed materials in improving the performance of catalytic methane reforming concerning mainly conversion enhancement, H₂ output purity, and productivity. The influence of major process parameters such as steam/carbon ratio, catalyst/sorbent ratio, feed and catalyst temperatures, gas space velocity (GHSV), feed contamination with CO, CO₂, and H₂ is examined.

Experimental

The sorption enhanced reforming experiments are performed in a 1.0 m in length and 4.0 mm internal diameter fixed bed tubular reactor setup. The reactor is quartz made and composed of three zones; two upper – part heating sections and one reaction/adsorption zone. The temperature is measured along the reactor and controlled at a temperature range of 100–750 °C. Gas flow rates of CH₄, CO, CO₂, and H₂ in a range of 0 – 50 nml/min can be applied. N₂ is used as an inert and a carrier gas in the flow range of 0 – 500 nml/min. Steam is applied to the system by evaporating distilled water in a static evaporator mixer at 80 °C up to a flow rate capacity of 1500 mg/hr. The gas composition is measured at the feed and product gas sections by online analysis using mass spectrometry (ESS II system) for dynamic experiments and gas chromatography (GC Varian CP-3800) for steady state experiments. Rh/Ce_{0.4}Zr_{1.6}O₂ catalyst used in sorption enhanced steam reforming experiments is prepared by dry impregnation of 1 wt% Rh loaded on a commercially available mixture of ceria – zirconia supports with a weight ratio of 60:40. Three sorbents are tested in the experiments; zirconium doped hydrotalcite, hydrotalcite promoted by potassium and doped by zirconium, and lithium zirconate. An average size of 300-µm catalyst and sorbent pellets is used throughout the experiments. The reactor is always fed by a mixture gas of steam, hydrogen, and nitrogen with a molar composition of 20 %, 20 %, and 60 %, respectively as initial reaction conditions. Base operational conditions used are as follows: temperature of 500°C, pressure of 4.47 bar,

steam/carbon ratio of 6, oxygen/carbon ratio of 0.45, gas feed mass velocity of 0.05 kg/m²s, and space velocity of 3071 hr⁻¹.

Mathematical Modeling

A 1-D heterogeneous dynamic model is constructed to simulate the process, accounting for mass and thermal dispersion in the axial direction, pressure drop, and intraparticle and interfacial transport resistances.

Results and Discussion

The simulation results revealed that a hydrotalcite-based sorption enhanced ATR system can achieve a conversion level of 84% with a 43% enhancement over the conventional ATR process, a H₂ purity of 95%, CO and CO₂ concentrations lower than 0.03%, a H₂ yield of 3.6, and a thermal reforming efficiency of 1.08 at the experimented base conditions. The lithium zirconate-based process enhances conversion and H₂ purity up to 99.5% and 99%, respectively at identical conditions. However, 2.5 times higher adsorption rates in the HTC-based process in comparison to the LZC-based process are obtained. The high CO₂ capacity of LZC over HTC can give a privilege in terms of adsorption cycle time in industrial operation. It was also found that the conversion and H₂ purity achieved do not benefit from the total effect of high pressure operation. Short residence time operation can result in lower conversion enhancement and lower purity hydrogen. More work, therefore, should be conducted on the particle design for high porosity and surface area to provide a higher capacity sorbent with faster adsorption kinetics.

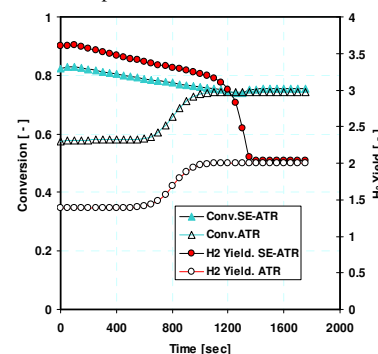


Figure 1. Dynamic profiles of effluent CH₄ conversion and H₂ yield obtained in ATR with and without HTC sorbent.

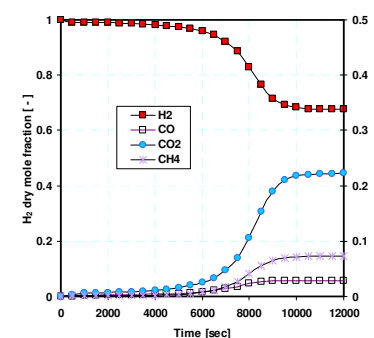


Figure 2. Dry basis effluent concentration profiles of LZC – based sorption enhanced ATR process.

Significance

This study presents a beneficial catalyst/sorbent system for pure H₂ production as green energy source with in situ CO₂ capture at low temperatures (<550°C). It is an efficient technique in terms of energy saving, production rates, and capital investment of the integrated reactor/adsorber.