

Catalytic valorization of industrial residues for sustainable high-purity hydrogen production

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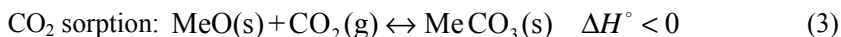
Highlights

- Promoted CaO sorbents show high performance over consecutive SESRG/regeneration cycles.
- Addition of metal stabilizers improved the hybrid materials stability over cyclic operation.
- The integrated process is a promising alternative for single-stage production of high purity hydrogen.

1. Introduction

Conversion of biomass (abundant, clean, and renewable) is one of the promising hydrogen production approaches. However, renewable vegetable oils&animal fats conversion into biofuels through catalytic transesterification (process that is undergoing a boom through new biorefineries worldwide as part of global efforts to combat climate change and reduce dependency on fossil fuels) produces glycerol, a significant by-product. The high surplus of glycerol on the market made it become a waste problem and opened significant areas of research for the development of technologies for its valorization into value-added compounds. Using glycerol as a feedstock for hydrogen production has two main advantages: valorizing a large amount of redundant glycerol produced as an inevitable by-product of biodiesel production and achieving the full environmental benefit of using hydrogen as an energy carrier by using a carbon-neutral source for its generation. In the context of a sustainable development, the sorption enhanced steam reforming of glycerol (SEGSR) integrating the reforming reaction with CO₂ chemisorption on high-temperature sorbents, is a promising technology and an opportunity to improve the economics of green H₂ production (the exothermic CO₂ adsorption provides the heat to the endothermic steam glycerol reforming) [1,2]. In-situ CO₂ removal allows high-purity H₂ production in a single step and decreases the risk of coke formation. Moreover, the pure stream of CO₂ produced during the sorbent regeneration is ready for further use or storage.

The overall SEGSR reaction (4) is a combination of the endothermic glycerol pyrolysis, the exothermic WGS and the CO₂ reaction with a metal oxide (MeO):



The mixing pattern of catalyst and sorbent is an important issue, particularly in large-scale hydrogen production units. In addition to physical mixing of catalyst and sorbent, hybrid catalyst-sorbent materials to integrate the catalytic reaction and CO₂ capture in a single pellet can eliminate the mass diffusional limitations and decrease the reactor volume [1]. This work aims to investigate the application of new Ni-CaO hybrid materials stabilized with different Metal-based industrial solid residues, for highly pure H₂ production by SEGSR.

2. Methods

The hybrid materials were synthesized by wet mixing and characterized by XRD, TEM and SEM. The materials were evaluated in CO₂ sorption/desorption (carbonation/calcination) cycles using the Intelligent Gravimetric Analyzer, IGA-003 (Hiden Isochema) and throughout cyclic sorption-enhanced steam reforming/regeneration using a fixed-bed reactor [3]. The exit flow of reactor was first passed through an ice bath to separate the condensable compounds and subsequently analyzed by an on-line Agilent 3000A Micro GC. The kinetics of CO₂ capture was investigated experimentally and described by a mathematical reaction-rate model. The performance of SEGSR process was investigated experimentally and using a two-scale, non-isothermal, unsteady-state model taking into account the gas dynamics which tied steam glycerol reforming/CO₂ capture kinetics, thermodynamics, thermal effects and variable gas flow rate due to chemical and physical contractions. Both hybrid sorbent-catalyst materials and homogeneous mixture of monodisperse particles of catalyst and sorbent were considered for comparison. The contribution of the reaction and CO₂ sorption was weighted according to the fraction of the corresponding functionalities.

3. Results and discussion

The CO₂ capture performance of the synthesized hybrid materials was first evaluated in a cyclic carbonation/calcination process. The carbonation process comprises a fast step, controlled by the chemisorption process and a slow step, controlled by CO₂ diffusion. The conversion was found almost independent on CO₂ partial pressure, but strongly affected by the carbonation temperature. Also, the increase in carbonation temperature improved the kinetics by the extension of the fast reaction step controlled by chemisorption, thus increasing the material sorption capacity due to the increase of chemisorption kinetics at elevated temperatures. The SEGSR is an integrated process involving the reforming reaction and in-situ CO₂ sorption; the CO₂ formation rate is therefore strongly related to the CO₂ sorption rate. The relationship between the two processes strongly depends on the sorbent/catalyst ratio: the prebreakthrough period (where the high purity hydrogen period is characterized by a match between CO₂ formation and CO₂ sorption rates) was found to decline with the decrease of the sorbent fraction due to the decrease of CO₂ removal efficiency. Lower inlet superficial gas velocity also led to longer prebreakthrough periods. At higher gas velocity CO₂ production rate in the glycerol reforming process is higher than CO₂ sorption rate of the adsorbent, thus decreasing the CO₂ removal efficiency (the integrated system is limited by the sorption capacity of the material). A similar behavior was observed in the case of the increase in glycerol partial pressure. Higher partial pressures (lower steam-to-glycerol ratio) led to shorter prebreakthrough periods. With the increase of glycerol partial pressure the integrated system is limited by the material sorption capacity. The length of the H₂ high purity time period also increases with the increase of inlet reactor temperature due to the improvement of the thermal behavior of SEGSR. Finally, the use of hybrid materials was found to offer a better performance. The presence of promoters and metal-stabilizers controlled the distribution of Ni active sites, the amount of coke deposition, and the degree of CaO sintering.

4. Conclusions

Coupling the reaction system with in-situ CO₂ separation substantially improved the reactant conversion and product selectivity, and enhanced the thermal efficiency of the reforming process. The process minimizes the amount of glycerol (waste by-products) and represents an energy efficient alternative for producing green hydrogen as the exothermic CO₂ adsorption provides the heat to endothermic steam glycerol reforming.

References

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Keywords

Hydrogen production; Sorption-enhanced steam reforming; Glycerol valorization; Hybrid sorbent-catalyst.