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A theoretical comparison of multifunctional catalyst for sorption-enhanced reforming process

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HIGHLIGHTS

- Comparison of two one-pellet catalyst designs for sorption-enhanced processes.
- Both one-pellet designs had greater adsorbent utilization than a two-pellet design.
- Uniform-distributed design is recommended over core-shell due to better utilization.
- Core-shell design approaches uniform-distributed results at low catalyst thicknesses.
- Core-shell design mitigates hot-spot for an adiabatic sorption-enhanced WGS process.

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ABSTRACT

This work presents the first side-by-side comparison of the two leading multifunctional catalyst designs reported in the literature today for sorption-enhance reforming processes. Two-dimensional unsteady-state models were developed to compare the performance of a core–shell multifunctional catalyst, consisting of a calcium-based sorbent core enclosed in a porous shell of methane steam reforming or water-gas shift catalyst, against an equivalent case of a uniform-distributed multifunctional design in which catalyst and sorbent materials are uniformly distributed within the particle. Additionally, these two multifunctional catalyst designs were compared against the conventional two-pellet approach, where the capture and catalytic properties are distinguished into separate pellets. Both multifunctional catalyst designs (i.e. core-shell and uniform-distributed) had greater adsorbent utilization and higher H_2 outlet concentration up to breakthrough time than the conventional two pellet design. The uniform-distributed multifunctional catalyst design had greater adsorbent utilization up to breakthrough conditions as compared to the core-shell design. This behavior may be attributed to the fact that for the uniform-distributed multifunctional, the active catalyst is constantly producing CO_2 next to an adsorbent active site. For the core-shell multifunctional catalyst design, decreasing catalyst-shell thickness resulted in performance approaching the uniform-distributed case. For the case of exothermic water-gas shift reaction coupled with CO_2 chemisorption, the core-shell design mitigated local bed hot-spot magnitudes by $\sim$40 K.

1. Introduction

Sorption-enhanced reforming processes (SERPs), in which catalytic reaction is directly coupled with CO_2 adsorption, have received significant attention over the past two decades owing to a growing demand for high-purity H_2 and rising costs associated with CO_2 by-product emissions (Barelli et al., 2008; Ochoa-Fernández et al., 2007). Methane steam reforming (MSR) and water-gas shift (WGS) (Eqs. (1) and (2), respectively) are two key reactions in hydrogen production today (Holladay et al., 2009; Leiby, 1994). Both MSR and WGS are equilibrium-limited reactions and, therefore, require additional capital cost associated with multi-staged beds to maximize H_2 yield (Satterfield, 1991). The product reformate stream needs further purification to achieve H_2 purities $>95\%$ as required by many of refinery operations (Alves and Towler, 2002; Harrison, 2008; Zagoria and Huycke, 2003). Purification processes based upon the selective removal of H_2 from the reformate stream result in rejection losses which translate to H_2 waste, and do not offer a direct means to capture CO_2 for appropriate utilization or disposal. Process intensification via SERP addresses these challenges by isolating CO_2 from the reacting fluid, thereby removing equilibrium limitation on hydrogen yield while

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Nomenclature

B_0	permeability coefficient, m^2
c_i	concentration of component *i*, mol m^{-3}
C_p	specific heat capacity, J mol^{-1} K^{-1}
d	particle diameter, m
D_{ij}	binary diffusion coefficient of a mixture *i* and *j*, m^2 s^{-1}
$D_{i,k}$	Knudsen diffusion coefficient of component *i*, m^2 s^{-1}
$D_{z,i}$	axial dispersion coefficient of component *i*, m^2 s^{-1}
Da	Damköhler number, dimensionless
E_a	activation energy, J mol^{-1}
F_{press}	pressure scale-up factor, dimensionless
k	thermal conductivity, J m^{-1} s^{-1} K^{-1}
k_f	rate constant, mol m^3 s^{-1}
k_{gs}	mass transfer coefficient at gas-solid interface, mol m^{-2} s^{-1}
k_s	kinetic constant for surface reaction, m^4 $kmol^{-1}$ h^{-1}
K_{eq}	reaction equilibrium constant, dimensionless for WGS and (Pa) for MSR
M_i	molecular weight of species *i*, kg mol^{-1}
N_{Ca}	moles per unit volume of sorbent particle, kmol m^{-3}
N_i	flux of component *i*, mol m^{-2} s^{-1}
Nu	Nusselt number, dimensionless
p_i	partial pressure of component *i*, Pa
P	pressure, Pa
Q_r	rate of heat generation, J mol^{-1} s^{-1}
r_i	rate of appearance of component *i* via WGS/MSR reaction, mol m^{-3} s
r_p	pore radius, m
R_1	sorbent radius of core-shell design, m
R_2	sorbent plus catalyst radius of core-shell design, m
Re	Reynolds number, dimensionless
R_g	universal gas constant, J mol^{-1} K^{-1}
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
T	temperature, K
t	time, s
t_c	catalyst-shell thickness, m
u	velocity, m s^{-1}
V	molar volume, m^3 mol^{-1}
X	local extent of solid sorbent conversion, dimensionless
x_i	mole fraction of component *i*, dimensionless
z	axial coordinate, dimensionless
Z	molar volume ratio, V_{CaCO3}/V_{CaO}, dimensionless

Greek symbols

α	adsorbent-to-catalyst volume ratio, dimensionless
δ	average grain diameter, m
ΔH^0_{rxn}	heat of reaction, J mol^{-1}
ϵ	porosity, dimensionless
ε/κ	Lennard-Jones parameter, K
ζ	defined in Eq. (45), dimensionless
η	effectiveness factor, dimensionless
Θ	defined in Eq. (29), dimensionless
λ_T	axial bed conductivity, J m^{-1} s^{-1} K^{-1}
μ_i	viscosity of component *i*, Pa s
υ_i	diffusion volume of component *i*, dimensionless
Φ	modified Thiele Modulus, dimensionless
ρ	density, m^3 kg^{-1}
σ	Lennard-Jones parameter, Å
σ_{CaO}	grain surface area per unit particle volume, m^{-1}
τ	tortuosity factor, dimensionless
Ω	Lennard-Jones parameter, dimensionless

Subscripts

0	initial/inlet condition
b	bulk
CaO	calcium oxide
Cat	catalyst
CO	carbon monoxide
CO_2	carbon dioxide
MET	methanation
H_2	hydrogen
H_2O	steam
mix	mixture
MSR	methane steam reforming
p	pellet
sor	sorbent
WGS	water gas shift

Superscript

eff	effective

simultaneously purifying the product stream. Although SERPs eliminate the need for a separate purification stage, these processes generate an additional cost due to the need for adsorbent regeneration. The advantages of lower capital cost and reduced footprint resulting from the selection of the SERP technology must be weighed against the additional cost arising from the regeneration process in order to select the best approach.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \ \Delta H^0_{rxn} = 206 \text{ kJ/mol} \quad (1)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \ \Delta H^0_{rxn} = -41.1 \text{ kJ/mol} \quad (2)$$

The selected adsorbent must be capable of CO_2 adsorption at the conditions of the reactions (473–1023 K). CaO-based adsorbents are ideal candidates for SERP processes because they are inexpensive and abundant. However, the main disadvantage of adsorbents derived from natural sources is the decay of their capacity to capture CO_2 with each passing cycle as well as their poor mechanical stability (Anthony, 2008; Blamey et al., 2010; Grasa and Abanades, 2006). These disadvantages can be mitigated by blending CaO with refractory materials (e.g., MgO, ZrO, $CaTiO_3$) to prevent pore closure during the regeneration process and improve material's mechanical properties (Harrison, 2008).

Sorption of CO_2 occurs via the reversible exothermic reaction of CO_2 and CaO (Eq. 3) that yields to $CaCO_3$ in the solid phase (Abanades and Alvarez, 2003; Huijgen and Comans, 2003; Stendardo and Foscolo, 2009). Inspection of the equilibrium CO_2 pressure over CaO indicates that H_2 purification via CO_2 sorption using CaO-based adsorbents is compatible with MSR and WGS operating conditions (Harrison, 2008).

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \ \Delta H^0_{rxn} = -178 \text{ kJ/mol} \quad (3)$$

The majority of reports on sorption-enhanced methane steam reforming (SEMSR) and sorption-enhanced water-gas shift (SEWGS) have focused upon a two-pellet design, where the adsorptive and catalytic properties are distinguished into separate pellets (Jang et al., 2013; Jang et al., 2012; Stevens et al., 2010; Van