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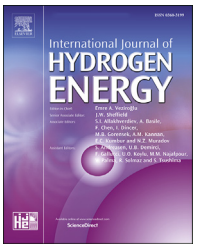

Effectiveness factor correlations from simulations of washcoat nickel catalyst layers for small-scale steam methane reforming applications

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ABSTRACT

In this paper, the effectiveness factors of $Ni/MgAl_2O_4$ washcoat catalyst layers under steam methane reforming (SMR) conditions relevant to small-scale hydrogen production systems (1–3 bar pressure, 600–800 °C temperature, and 2–4 steam-to-carbon ratio) are numerically investigated. The effects of the washcoat properties, including the layer thickness (20–80 μm), the mean pore diameter (10–40 nm), and the volume-specific catalyst surface area ($1.1–3.3 \times 10^7$ m^2/m^3), are also considered. The simulation is conducted by fully considering the intrinsic reaction kinetics (Xu and Froment model) and multicomponent mass diffusion (Maxwell-Stefan equation). The numerically obtained effectiveness factors are presented as a function of the methane conversion ratio and effective Thiele moduli, and simple correlation equations are proposed for easy evaluation of the effectiveness factors.

Introduction

Steam reforming is the primary process in the industrial (large-scale) production of hydrogen by the catalytic reaction of light hydrocarbons (mainly methane) obtained from natural gas [1]. A mixture of hydrocarbons and steam is passed through pipes containing nickel catalyst at high temperatures, where the gas mixture is converted to carbon monoxide and hydrogen. Then, the carbon monoxide is further converted to carbon dioxide, producing additional hydrogen. Hydrogen has been mainly used in the industrial synthesis of ammonia and the refining of petroleum oil. Recently, the fuel cell technology operated with hydrogen fuel has drawn considerable research attention as an alternative power source that is clean and renewable [2,3] Accordingly, the demand for small-scale (on-site) production of hydrogen by reforming for fuel cell applications is increasing [4–8].

Nickel (Ni) is the most commonly used catalyst material for the steam methane reforming (SMR) process because it is cost-effective and efficient [9,10]. In Ni-based catalysts, nanosized Ni particles are uniformly dispersed on porous support structures made of alumina (Al_2O_3) or spinel

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Nomenclature

A_{cat}	Volume-specific catalyst surface area ($m^2\ m^{-3}$)
A_k	Face area at grid point k (m^2)
D_{CH_4}	Average methane diffusivity in the washcoat layer ($m^2\ s^{-1}$)
D_{ij}	Binary diffusivity of species pair $i-j$ ($m^2\ s^{-1}$)
D_{iK}	Knudsen diffusivity of species i ($m^2\ s^{-1}$)
d_{pore}	Mean pore diameter (m)
$K_{eq,m}$	Equilibrium constant for reaction m (see Appendix A for units)
K_i	Adsorption coefficient of species i (see Appendix A for units)
K_v	Viscous flow permeability (m^2)
k_m	Reaction rate constant for reaction m (see Appendix A for units)
L_{cat}	Thickness of washcoat catalyst layer (m)
M_i	Molecular mass of species i ($kg\ kmol^{-1}$)
M_{wc,CH_4}	Nominal methane diffusion rate ($mol\ m^2\ s^{-1}$)
N	Number of volume cells
N_i	Molar flow rate of species i ($mol\ s^{-1}$)
n_i	Molar flux of species i ($mol\ m^{-2}\ s^{-1}$)
p_i	Partial pressure of species i (Pa)
p_t	Total pressure of species i (Pa)
R_g	Universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$)
$R_{wc,m}$	Nominal reaction rate of reaction m ($mol\ m^2\ s^{-1}$)
r_m	Reaction rate for reaction m ($kmol\ kg_{cat}^{-1}\ h^{-1}$)
SC	Steam-to-carbon ratio
s_i	Volumetric source for species ($mol\ m^{-3}\ s^{-1}$)
T	Temperature (K)
V_k	Cell k, or its cell volume (m^3)
v_i	Diffusion volumes of species i
x_i	Mole fraction of species i
z	Coordinate (m)
z_k	Grid point k, or its coordinate location (m)
Δz_k	Distance between two adjacent cell centers at grid point k (m)

Greek symbols

β_{CH_4}	Methane conversion ratio
$\beta_{CH_4}^{eq}$	Equilibrium methane conversion ratio
ε	Porosity
ϕ_m	Effective Thiele modulus for reaction m
ϕ_m^*	Modified Thiele modulus for reaction m
η_m	Effectiveness factor for reaction m
μ_{mx}	Viscosity of gas mixture ($kg\ m^{-1}\ s^{-1}$)
ρ_{cat}	Apparent catalyst density ($kg\ m^{-3}$)
τ	Tortuosity

Superscript/Subscripts

∞	Flow stream condition
eff	Effective value
I, II, III	Reaction index
i, j	Species index
k	Grid or cell index
o	Inlet or initial value

($MgAl_2O_4$), in which the Ni content generally ranges from 7 to 15 wt%. The SMR process with Ni catalysts is generally described by global three-step reaction [11,12]; (1) steam reforming, (2) water-gas shift, and (3) reverse methanation. The overall process is strongly endothermic, and thus, sufficient heat should be provided, such as through the use of multifunctional reactors [13] (composed of a reforming reactor, an exothermic reactor, and a heat exchanger).

Two broad types of reformer designs are used for small-scale hydrogen production systems for fuel cell applications [14,15]. The first is packed-bed reformers [16–18], where porous Ni catalyst pellets are packed in a container and the steam/methane gas mixture flows through it. In these reformers, relatively large size of pellets results in low catalyst utilization. In addition, heat transfer is often limited by the low thermal conductivity of the catalyst pellets. The second type of the reformer design is coated-wall reformers [19–25], where a thin catalyst layer (called the washcoat) is formed directly on the reactor walls. Typical coated-wall reformers include catalytic plate reformers (also called microchannel reformers) [19–21] and monolithic reformers [22–25]. In catalytic plate or microchannel reformers, the channels for gas combustion are placed next to the channels for the SMR process, which provides an efficient heat supply for reforming. In general, coated-wall reformers exhibit lower flow resistance and higher catalyst utilization than packed-bed reformers.

The effectiveness factor is a quantitative measure of the utilization of catalyst materials and is defined as the ratio of actual overall rate of reaction to the rate of reaction that would result if entire interior surface were exposed to the external washcoat surface conditions [26,27]. The active surfaces of porous catalyst pellets and washcoat layers cannot be fully utilized due to the relatively slow mass transport through the pores. The effectiveness factors of Ni catalyst pellets under industrial (large-scale) SMR conditions have long been studied by many researchers [12,28–30] because these factors are essential information for the proper design of SMR reactors. The authors have recently studied the effectiveness factors of Ni catalyst pellets under small-scale SMR conditions near atmospheric pressure and then proposed simple correlation equations [31,32]. However, few references that can be used for estimating the effectiveness factors of Ni washcoat catalyst layers under small-scale SMR conditions are currently available [19,33].

Thus, this study numerically investigated the effectiveness factors of thin washcoat catalyst layers made of $Ni/MgAl_2O_4$ in the SMR process. The reforming conditions for small-scale hydrogen production systems, such as a pressure range of 1–3 bar, a temperature range of 600–800 °C, and a steam-to-carbon ratio (S/C) range of 2–4, were considered. In addition, the effects of the washcoat properties, including the layer thickness (20–80 μm), the mean pore diameter (10–40 nm), and the volume-specific catalyst surface area ($1.1–3.3 \times 10^7\ m^2/m^3$), were also considered. For this purpose, a one-dimensional, isothermal reaction/diffusion process was simulated inside the washcoat layer by considering the intrinsic reaction kinetics for the steam reforming, water-gas shift, and reverse methanation reactions (Xu and Froment model [11,12]) and multicomponent mass diffusion (Maxwell-Stefan equation [34,35]). The standard composition of

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