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Modeling of a metal monolith catalytic reactor for methane steam reforming–combustion coupling

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Abstract

A novel metal monolith reactor for coupling methane steam reforming with catalytic combustion is proposed in this work, the metal monolith is used as a co-current heat exchanger and the catalysts are deposited on channel walls of the monolith. The transport and reaction performances of the reactor are numerically studied utilizing heterogeneous model based on the whole reactor. The influence of the operating conditions like feed gas velocity, temperature and composition are predicted to be significant and they must be carefully adjusted in order to avoid hot spots or insufficient methane conversion. To improve reactor performance, several different channel arrangements and catalyst distribution modes in the monolith are designed and simulated. It is demonstrated that reasonable reactor configuration, structure parameters and catalyst distribution can considerably enhance heat transfer and increase the methane conversion, resulting in a compact and intensified unit.

Keywords: Catalytic reactors; Autothermal coupling; Monolith catalyst; Mathematical modeling; Parameter analysis; Performance simulation

1. Introduction

Owing to thermodynamic and kinetic limitations, endothermic reactions like hydrocarbon cracking, dehydrogenation, and reforming have to be carried out at high temperatures, which ask for a very efficiency heat supply and a heat recovery. Autothermal multifunctional reactors offer an attractive solution for implementing high-temperature reactions by coupling strong endothermic reaction with exothermic reaction, which has been a subject of vital research and development. Many methods are often found to combine the endothermic process and the exothermic one. A system in which oxidation and steam reforming reactions of hydrocarbons run in parallel by mixing two kinds of catalysts in one bed has been studied in experiment (Choudhary et al., 2000a,b; Ma and Trimm, 1996; Rane et al., 2004; Li et al., 2004) and simulation (Hoang and Chan, 2004; Avci and Trimm, 2001). The mixed catalysts that promote both endothermic and exothermic reactions at the same temperature range are required in this system, which is a design challenge. A bi-directional fixed-bed reactor concept was developed by means of heat storage in a fixed bed. During the exothermic semi-cycle the fixed bed is heated and the stored heat is consumed in the next semi-cycle when the endothermic process takes place. The experimental results showed that endothermic and exothermic reactions can be integrated inside the reactor and periodic steady state can be obtained under proper conditions (Sint Annaland and Nijssen, 2002). The effects on operability and energy efficiency of the reaction conditions, front velocities, switching during reaction phase were discussed in the modeling researches (Glockler et al., 2003; Kulkarni and Dudukovic, 1996, 1997). The dynamic nature of the fixed-bed reactor is complicated and inefficient heat integration can cause hot spots. Spatially segregated system was another novel design that allows indirect heat exchange using a thermally conductive substrate (Polman et al., 1999; Frauhammer et al., 1999). Several novel reactor configurations with co- and counter-current flow in the reaction zone were discussed (Kolios et al., 2002). How the maximum temperature can be reduced and the thermal efficiency of the integrated reactor can be improved were investigated using reactor model (Kolios et al., 2001). Besides the application of the catalytic heat-exchanging tubular reactor (Tonkovich et al., 2004; Ioannides and Verykios, 1998; Ismagilov et al., 2001) in this concept, a plate heat

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exchanger known as catalytic plate reactor (CPR) has attracted a lot of interest. Zanfir and Gavriilidis (2001, 2002a,b, 2003) carried out theoretical study in which the influence and sensitivity of parameters such as catalyst loading, wall thickness and thermal conductivity, flowrates, temperature, composition were analyzed in detail so that the design and operating parameters are kept within an acceptable range. A transient simulation exhibited the dynamic relationship between the catalytic combustion and catalytic steam reforming of CH_4 during transient start-up (Robbins et al., 2003). Also, a novel compact plate-fin reformer based on the CPR with crosscurrent flow was verified to integrate endothermic and exothermic reactions (Pan and Wang, 2005).

Recently, metal monolith catalyst with high thermal conductivity is considerably attractive (Groppi and Tronconi, 2005). Accordingly, a series of investigations for the metal monolith catalyst and reactor, such as the preparations, characterizations and reactive performance evaluation (Yin et al., 2005, 2006), simulations of heat transfer and reactive performance (Mei et al., 2005, 2006; Liu et al., 2005), are carried out in our research group. As a part of systematic studies, a novel jacket metal monolith reactor is proposed and used as autothermal reactor in this work to couple methane steam reforming with catalytic combustion. A model based on the whole reactor, in which the oxidation and reforming reactions take place at different parts, is developed to explore the influence of operating and structure parameters.

2. Studied system

A picture of the jacket metal monolith reactor shown in Fig. 1. Other than the extruded honeycomb monolith, it is made by wound waved metal sheet and the catalysts are deposited on the channel walls. For coupling the endothermic reaction with the exothermic one, the reactor contains two parts, one of which is inner pipe and the other is annular part between outer and inner pipes. The reactant mixtures of endothermic and exothermic reactions flow through the different parts, separately.

It is assumed that the steam reforming and the catalytic combustion of methane are carried out over a $Ni/MgAl_2O_3$ catalyst (Xu and Froment, 1989) and a Pd/Al_2O_3 catalyst (Hayes and Kolaczkowski, 1999), respectively. The main chemical reactions and the rate equations involved in the processes are shown in Table 1.

In Table 1, $Den = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O}/p_{H_2}$, and α is the multiple factor used to express the change of the catalyst loading.

3. Mathematical model

The simulated monolith reactor is designed similar to the picture of the above jacket metal monolith reactor. Owing to the axial symmetry of the reactor, the simulated region is chosen as one-sixth of the reactor as shown in Fig. 2. To reduce the heat loss, the reactant mixture of exothermic reaction is passed through the inner pipe and the reactant mixture of endothermic reaction is introduced to annular part. Taking account of considerable difference under real operation conditions for different channels of a monolith reactor as pointed out elsewhere (Mei et al., 2006), a three-dimensional stationary model based on the whole monolith reactor is derived for a co-current flow arrangement and given in Table 2. The model considers the flow, convective heat transfer, and mass transfer of the gas and the conduction of the solid. A set of governing equations can be obtained, including momentum, energy and mass balances for gas phase, energy balance for solid phase and state equation.

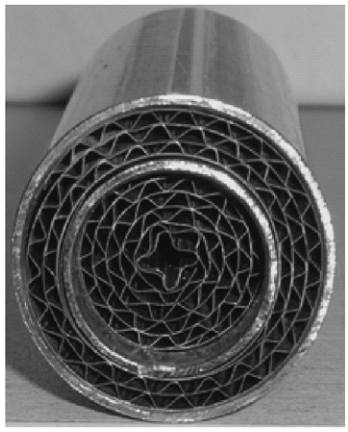

Fig. 1. Metal monolith catalyst and reactor for coupling.

The simplified assumptions are as follows: steady state is considered for reactor in a co-current flow arrangement; laminar flow is employed in both endothermic and exothermic sides; ideal gas is assumed; owing to the complicated structure of the reactor and minor thickness of the porous catalyst layer, the diffusion in the catalyst layer is not taken into account, the reaction appears as a source or a sink of material and energy in the boundary cell at the channel wall; homogeneous reactions, and heat radiation are neglected.

The following boundary conditions are adopted: uniform gas velocity, temperature and concentration at the entrance of the reactor; fully developed gas velocity, temperature and concentration profiles at the outlet of the reactor; axially adiabatic solid boundary at the entrance and the outlet; radially adiabatic at the external wall of the reactor; no slip condition and zero radial concentration gradient at the impermeable wall of the channel. The boundary conditions, as a necessary part of the model, are also listed in Table 2.

The physical properties of solid phase are assumed to be constant. The CH_4/air mixture acts as reactant of the exothermic reaction and the reactant mixture of endothermic reaction contain CH_4, H_2O, and small amounts of CO_2, H_2, and N_2. Since a large amount of the flowing gas is N_2 on the combustion side while water steam on the reforming side, the composition dependency of diffusion properties can be neglected and the values of the binary diffusion coefficients D_{i,N_2} and D_{i,H_2O} can be used for the two sides, respectively. The other properties are simply taken as the properties of N_2 and water steam