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Parametric study of methane steam reforming to syngas in a catalytic microchannel reactor

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ABSTRACT

The aim of this work is the parametric investigation of methane steam reforming (MSR) to synthesis gas (syngas, $CO + H_2$) in a wall-coated catalytic microchannel reactor. Methane conversion and CO selectivity on coated Rh, Ru, Pt and Ni catalysts, all supported on Al_2O_3, are compared in the parameter ranges of 12.86–77.14 ms residence time, 600–800 °C temperature and 0.5–3.0 M steam-to-carbon ratio at the reactor inlet. Among the active metals, Rh is the best one in terms of both methane conversion and productivity (rate of methane consumption per weight of catalyst). Productivity decreases in the order of Rh > Ru > Pt ≈ Ni. For all catalysts, conversion increases with residence time, temperature and steam-to-carbon ratio. CO selectivity is highest in all cases on Rh, and increases with increasing temperature and decreasing steam-to-carbon ratio. However, in the range of residence times considered, a maximum CO selectivity for each catalyst is encountered where the water–gas shift equilibrium becomes significant, and converts more of the CO produced by MSR to CO_2. Time-on-stream runs conducted on Rh and Ni show that the former has excellent chemical and mechanical stability for 72 h even at extreme conditions such as steam-to-carbon ratio of 0.5 and residence time of 12.86 ms. Activity of Ni starts to decrease after 20 h even though it is operated at a steam-to-carbon ratio of 3.0. Comparative tests conducted between microchannel and packed-bed reactors show that the former outperforms the packed bed in terms of productivity and CO selectivity.

1. Introduction

Methane steam reforming (MSR: $CH_4 + H_2O = CO + 3H_2$, $\Delta H^\circ = 206.2\ kJ\ mol^{-1}$) is one of the commercially established routes to produce syngas ($CO + H_2$), which is used as a feedstock for industrially important processes such as the Fischer–Tropsch or methanol syntheses and hydrogen production [1]. Tubular reactors packed with Ni-based catalysts are used for carrying out MSR, for which the endothermic heat is supplied either by a direct-firing furnace or by heat exchange with a hot stream [1]. Although MSR is well known and widely used, its efficiency is limited by heat and mass transfer resistances [2]. Distribution of external heat to the catalyst bed may not be uniform, and the resulting local fluctuations in temperature and reactant concentrations can affect the product distribution. With ever increasing know-how throughout the past decade [3,4], and emerging commercial applications at various scales [5], microchannel reaction technology has come out to offer potential solutions to problems that are challenging to resolve using conventional technology.

Microchannel reactors, consisting of parallel, identical channels with characteristic dimensions less than 1 mm, permit better control of the process under laminar flow conditions [6,7]. Since the transport distance is reduced, the reactants and heat can be delivered uniformly to the catalyst, which is mostly in the form of a thin, porous layer coated on the inner channel walls. Miniature dimensions also allow for high surface area-to-volume ratios and enhanced heat transfer coefficients that are 50–100 times higher than those in conventional reactors [8]. These factors lead to significant improvements in process efficiency and throughput, and ascertain a desired product range. Because catalyst utilization is improved, only a thin layer of catalyst is usually sufficient to drive the reactions to almost completion with negligible pressure drop [9].

MSR has been studied in catalytic microchannel reactors by several groups. Wang et al. [10] investigated methods of coating $Rh/MgO\text{-}Al_2O_3$ on Al-containing porous metal substrates that make up the engineered microchannel, and evaluated the performances of the resulting reactors using MSR at 850 °C as the model reaction. The catalyst was coated either on an interfacial oxide layer previously coated on the surface of the substrate or on the substrate itself with a native aluminum oxide layer. They concluded that engineered catalysts with an interfacial layer provided

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