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Oxidative steam reforming of methane to synthesis gas in microchannel reactors

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ABSTRACT

Oxidative steam reforming of methane to synthesis gas (syngas) over an alumina supported bimetallic Pt–Rh catalyst was comparatively investigated in coated and packed microchannel reactors. In the first configuration, thin layers of catalysts are coated on opposite walls of a single microchannel, while the second one is described by particulate catalysts packed into an empty microchannel of dimensions identical with the first one. Both geometries are compared on the basis of methane conversion and CO selectivity measured at different values of parameters, namely reaction temperature (773–923 K), molar steam-to-carbon (S/C = 0–3.0) and oxygen-to-carbon (O_2/C = 0.47–0.63) ratios in the feed, and contact time (0.36–0.71 mg min cm^{-3}). Although methane conversions are found to be comparable, the coated catalyst gave significantly higher CO selectivities than the packed counterpart in the whole parameter range. Increase in all of the parameter values led to improvement in methane conversion, while CO selectivity increased only with temperature and contact time. Molar H_2/CO ratios obtained in the coated microchannel reactor are found to vary between 1.0 and 3.0 which are at least three times smaller than those produced in the packed microchannel reactor. Catalyst deactivation is not detected in both configurations. Stable operation up to 72 h over coated microchannel verified mechanical and chemical stability of the Pt–Rh coating that produced syngas with H_2/CO ratio of 2.12 at temperatures lower than employed in industrial reformers. Different flow distribution properties of coated and packed microchannels seem to play roles in affecting the product distribution.

1. Introduction

Syngas, a mixture of hydrogen and carbon monoxide, is an important feedstock in industrial chemicals production processes such as Fischer–Tropsch (FT) and methanol syntheses. It is mainly produced by steam reforming (SR) of natural gas, composed mostly of methane, in tubular reactors packed with Ni-based catalysts:

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H^\circ = 206.2\ \text{kJ/mol} \tag{1}$$

SR is a strongly endothermic reaction requiring the external heating of the reactor tubes which is carried out either by direct firing (as in radiant reformers) or by heat exchange with a hot stream (as in convective reformers) [1]. The process is limited by the inherently weak heat transport capabilities of a packed-bed reactor that hinders the distribution of external

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heat to the catalyst bed. The end result is lower average bed temperatures that lead to H_2-rich syngas production by the suppressed CO formation via the exothermic water–gas shift (WGS), an important side reaction affecting the SR product distribution:

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^\circ = -41.2\ \text{kJ/mol} \tag{2}$$

Syngas composition is critical as it significantly affects the product distribution in operations such as FT synthesis that requires molar H_2/CO equal to ca. 2 [1,2]. In order to reduce the syngas ratio, part of the fuel (e.g. methane) is combusted to supply heat to SR (Reaction 1) in the same reactor volume. In this process, which is known as autothermal or oxidative steam reforming (OSR), fuel combustion can supply heat sufficient to raise the Ni-based catalyst bed temperature well above ca. 1273 K to produce syngas by reforming the remaining fuel with steam that is co-fed with oxygen to produce H_2/CO ratio lower than those obtained from SR alone [1,3]. Despite its capability in delivering desirable feedstock quality to FT synthesis, high temperatures (up to ca. 2500 K) caused by combustion may lead to hot-spot formation in industrial autothermal reformers, which, in turn, causes deactivation of the Ni-based catalyst present in particulate form [4].

Emerging microchannel reactor technology can be a promising option for the solution of the heat transfer related problems in SR and OSR. Microchannel reactors are defined by parallel, identical channels with typical dimensions in the 1×10^{-6}–1×10^{-3} m range, and are made of metallic substrates to give ca. 50–100 times increased compaction versus the conventional counterparts with surface areas varying between $\sim 1 \times 10^2$–1×10^3 $m^2\ m^{-3}$. Increased surface areas ($\sim 1 \times 10^4$–5×10^4 $m^2\ m^{-3}$), sub-millimeter dimensions and use of thermally conductive materials of construction provide enhanced heat transfer rates that are a few orders of magnitude greater than those possible with conventional reactors [4–6]. Therefore, heat generated locally or supplied externally can rapidly be spread over the entire catalyst volume, which can exist either as a layer coated on the interior channel walls or as particles packed into the channels, and nearly isothermal operating conditions without the risk of hot-spot formation can be guaranteed [4–6]. Due to the negligible pressure drop benefit of the microchannel flow, operation at the microscale also offers the possibility to reduce residence times down to millisecond levels at which undesired and slow side reactions such as carbon formation cannot take place.

Syngas production from methane in microchannel or structured reactor geometries was investigated by several research groups. Fichtner et al. [7] studied partial oxidation of methane over Rh foils with honeycomb geometry which gave high methane conversions and CO selectivities. The results were linked with the improved heat dissipation along the flow direction provided by the high thermal conductivity of the metal foils. Use of Rh as catalyst in methane partial oxidation was also tested over microchannels made of FeCr alloy and Nicrofer materials in terms of catalytic activity and stability [8]. The former material was found to end up with a thin but stable layer of alumina that provided increased number of sites for the Rh particles. Methane partial oxidation was also demonstrated over a Pd-based catalyst with good reaction control that allowed operation without safety issues [9]. Makarshin et al. [10] tested the impact of flow strategy, counter-current and co-current flows, in a microchannel reactor, and reported that the former configuration delivered higher methane conversion and CO selectivity, especially at high heat loads, due to better heat dissipation over the catalytically active zone. Carbon deposition during methane-to-syngas conversion in catalytic microchannels has also been investigated in several studies which reported stable, coke-free operation even at feed conditions involving very low S/C ratios [11–13]. Apart from methane, microchannel OSR conversions of ethanol over Rh [14], of methanol over Pd–Zn [15] and Cu/ZnO [16], of propane over Rh [17] and of iso-octane over Pt [18] were reported.

Several studies that aim to understand the operational differences of microchannel/structured reactors with their conventional packed counterparts report that the former configuration delivers better catalytic performance. Wang et al. [19] comparatively tested methane steam reforming in a packed bed reactor and in an engineered, FeCrAlY made microchannel reactor involving the same catalyst, and showed that the latter delivered higher methane conversions and CO selectivities. Ryu et al. [20] compared Ni-catalyzed methane steam reforming over wash-coated monolith and coarsely powdered reactor geometries that involved equal volumes of catalyst. They reported higher methane conversions in the monolith reactor and observed that the difference between both configurations became more notable at GHSV values above 28,000 h^{-1} where no pressure drop was seen in the monolith [20]. Karakaya and Avci [11] compared wall-coated microchannel and conventional packed bed reactors in the context of methane steam reforming run over alumina supported Rh, Ru, Pt and Ni based catalysts at equal weight hourly space velocities. They reported that methane conversions and CO selectivities obtained over the microchannel reactor outperformed the packed bed performance. Apart from methane, steam reforming of methanol [21] and autothermal reforming of iso-octane [22] were comparably tested in wall-coated microchannel and packed bed reactor configurations. Both studies reported that the microchannel reactor operated without any transport limitations, whereas packed bed operation was hindered mainly by heat transfer. Propane OSR over Pt/CeO_2 catalyst conducted in monolithic, packed-bed and jellyroll reactors showed that the circular concentric design of the jellyroll configuration, which, compared with the monolith, involved higher channel density, smaller channel diameter and thinner walls between the channels, exhibited better performance in terms of fuel conversion, hydrogen production and low by-products formation [23].

The studies summarized above take the conventional packed bed reactor as the basis of comparison. However, microchannel reactors can also be designed by packing the particulate catalyst with appropriate size range into empty microchannels. Studies addressing the comparison of two microchannel reactor configurations, wall coated and packed microchannels, are scarce. Simsek et al. [24] reported a comparative investigation of two catalytic microchannel configurations for syngas production by methane steam