SYNGAS PRODUCTION FROM STEAM AND DRY REFORMING OF METHANE OVER NI-BASED CATALYST IN MICROCHANNEL REACTOR: CFD MODELING WITH ELEMENTARY KINETICS

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Abstract

The major obstacles in syngas production from methane reforming are coking of catalyst and low process efficiency, which could be addressed by microchannel reactor technology with optimized process design. We built comprehensive CFD models coupled with microkinetics regarding steam and dry reforming of methane over Ni-based catalyst to guide the reactor design and process optimization. It was found that high space velocity and near-isothermal operation are crucial for reducing coking risk and increasing process efficiency. Design rules and operating strategies were proposed accordingly.

Keywords

Hydrogen and syngas production, Steam/dry reforming, Microchannel reactor, CFD, Elementary kinetics.

Introduction

In recent years, tremendous efforts have been paid to convert methane to syngas, which serves as a crucial intermediate in the chemical industry. Steam and dry reforming (SR and DR) of methane are among the most applicable technologies for the conversion. SR is the most preferable for producing hydrogen-rich syngas ($H_2/CO > 3$), while DR is preferred for other downstream processes such as methanol synthesis and Fischer-Tropsch synthesis with favorable $H_2/CO$ ratio below 2. The industrial fixed-bed based process, however, has low productivity due to severe heat transfer limitation. Also, coke formation over Ni-based catalyst leading to catalyst deactivation is inevitable except for using feedstock of rather high steam or carbon dioxide to methane ($S/C$ or $CO_2/CH_4$) ratios, which leads to considerable additional energy consumption. Moreover, the large footprint plant is unsuitable for the ever-growing potential distributed or portable applications.

The current obstacles have stimulated huge interests in process intensification with microchannel reactor, which features excellent heat and mass transfer, easy scalability and rapid startup (Tonkovich et al., 2004, Johnson et al., 2007). As a result, microchannel reactor can be operated at ultra-high space velocities together with better temperature control across the catalyst bed, which increases the process efficiency and could potentially decrease coking.

CFD simulation greatly improves the design and optimization of microchannel reactor. In our previous work (Zhai et al., 2011), a CFD model coupled with elementary kinetics has been proposed for SR over Rh in microchannel reactor. However, Ni is much more economically feasible than Rh in an industrial scale. In this work, we focused on syngas production from methane over Ni-based catalyst in microchannel reactor. We extended

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the model to SR, DR and their possible combinations. The overall target is a highly energy-efficient, compact and lightweight system that is capable of long-cycle stable operation, adaptable to various feedstock, and produces syngas with tunable composition.

Methods

Different CFD models were adopted in a hierarchical simulation scheme. In the first 2-D single-channel model, an isotropic porous media with finite thickness was imposed on the channel wall to describe momentum and heat transfer in catalytic washcoat, within which diffusion was described by means of effective diffusivity, which was composed of molecular and Knudsen diffusions. In the second 2-D multichannel model, heat coupling was incorporated in, while catalytic washcoat was simplified by an effectiveness factor approach. The full 3-D geometry model allowed the investigation of the overall efficiency of the integrated microchannel reactor system. The modeling and simulation were conducted in the commercial software FLUENT. The elementary reaction kinetics network was solved by an externally linked in-house stiff ODE integrator. All properties used in the simulation consider temperature-dependent real physics, and no lumped coefficient is used for modeling heat and mass transfer. Elementary reaction kinetics of Ni for \( \text{CH}_2\text{H}_2\text{O}_2 \) system was used in this work, which enables to incorporate a transient coking model, and extend model applications to cover SR and DR processes.

Results and discussion

We demonstrated the feasibility of high velocity operation based on Ni catalyst. SR over Ni in microchannel reactor is not external mass transfer limited with channel gap less than 1 mm at pressures from 1 - 2.5 atm. Over a practical range of pressure, temperature, and catalyst loading, the process is controlled by reaction and internal mass transfer. Based on detailed modeling of the catalytic washcoat, the upper limit of washcoat thickness was determined and preferable pore structure was proposed for increasing space velocity as much as possible.

Figure 1 shows the surface carbon concentrations on catalyst under various operating conditions for SR. Higher risk in coke formation was revealed at high pressure, low S/C, with CO\(_2\) addition, and with the existence of hotspots. A transient coking model accounting for catalyst properties such as crystal size was further developed. Aside from surface carbon formation, carbon deposition resulted from gas phase radicals was found noticeable at high pressure or with CO\(_2\) addition. High space velocity prevents coking from both gaseous and surface reactions. Also, the hotspot leads to high coking potential kinetically.

Heat management was thoroughly studied to eliminate the hotspot. Matching exothermic and endothermic heat was found more difficult using Ni than Rh, because the slower intrinsic reforming rate over Ni induced higher hotspot temperature. Different fuel composition and operating strategies were compared in terms of temperature profiles. In general, lower concentration and higher space velocity of fuel are beneficial for weakening hotspot temperature. Effective catalyst distribution in cross-current and co-current designs could be also be useful for minimizing hotspot temperature. Counter-current-like design was unsuitable because of the improper overlap of reaction zones leading to inevitable hotspot formation.

Conclusions

SR at low S/C or combined SR and DR over Ni with alleviated coke formation are feasible in microchannel reactor, allowing for high efficiency, low cost and flexible syngas production. Of primary importance, sufficiently high space velocity and near-isothermal condition should be guaranteed. SR and DR over Ni in microchannel reactors are free from transverse heat and mass transfer limitations, which ensures operation at ultra-high space velocity. On this basis, precisely matching heat in flow direction and optimizing the properties of catalytic washcoat help to achieve near-isothermal operation.

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References

