Compact, Efficient Microreactors for Steam Reforming of Methanol

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Introduction

Compact fuel cell systems operating with hydrocarbon fuels possess high volumetric and gravimetric energy density and could outperform batteries in low-power, portable electronics [1]. The challenge is to develop efficient micro reformers for converting the chemical fuel into H_2 which can be fed to a proton exchange membrane fuel cell to produce electricity. Among the fuels considered, methanol is an attractive candidate since it is sulfur free, and most importantly, can be reformed at low temperatures (200-250°C). For methanol steam reforming (MSR), in order to achieve high conversions, the reformer has to operate with low gas velocity. The vast majority of studies on MSR have been done using packed-bed reactors of inner diameters ≥ 4mm and reactor to particle diameter ratio of less than 25. The low gas velocity dramatically lowers the effective thermal conductivity of the catalyst bed [2]. Furthermore, the low ratio of reactor to catalyst particle diameter, and the low gas velocity tends to introduce a large heat transfer resistance between the wall and the catalyst particles where the void fraction is largest [3] and in turn lead to temperature gradients in the bed. For an endothermic reaction such as MSR, temperature gradients in the packed-bed lead to lowered catalyst activity and could also lead to falsified kinetics.

The importance of heat transfer from the wall, particularly at low gas velocities is not well appreciated and is often neglected. There are no reported experimental measurements of the impact of heat transfer on the MSR reaction, or recommendations for reactor dimensions that would overcome transport limitations. In this work, we have performed an experimental study of the rate of MSR under conditions where we attempt to minimize the effect of transport limitations. The work was complemented by reactor modeling using a 2-D pseudo homogeneous model that allows us to calculate temperature profiles and to assess their impact on catalyst reactivity. The agreement between the experimental data and the reactor model confirms our initial hypothesis that MSR can be subject to severe heat transfer limitations in packed-bed reactors.

Materials and Methods

Measurements of the steam reforming of methanol were performed in tubular packed-bed and wall-coated reactors. For the wall-coated reactors, the catalyst was coated on the walls of quartz capillary tubes [4]. The reactor tube was positioned in an aluminum block heated by two cartridge-heaters. The inner diameters of the quartz tubes used in the experiments were 4.1mm down to 230µm. The effluent of the reactor was analyzed using gas chromatography. A commercial $Cu/ZnO/Al_2O_3$ catalyst from BASF (F13456) was used in all the experiments. The catalyst was used in its as-received, calcined state.

Results and Discussion

The apparent catalyst activity increased significantly with smaller reactor diameter as shown in Figure 1 (a). This suggests that the reactors suffer from large temperature gradients which lower the measured catalyst activity. A 2-D pseudo-homogeneous reactor model was fit to the experimental data assuming a first order reaction and adjusting the pre-exponential factor to fit the observed data for the packed-bed. Using these kinetics, we calculated the performance of the 1.75 and 1mm diameter reactors. Figure 1 (a) shows that excellent agreement was obtained between the 2-D model predictions and experimental data. Figure 1 (b) shows the temperature profile for the 1mm reactor. The temperature difference between the reactor wall and the cold spot was 19°C, indicating the severity of heat transfer limitation. These results suggest that future experiments be directed at wall coated reactors that may help overcome these heat transfer limitations. We have therefore wall-coated the MSR catalyst into quartz capillary tubes ranging from 1mm diameter down to 230µm. The presentation will compare the performance of wall-coated and packed-bed microreactors.

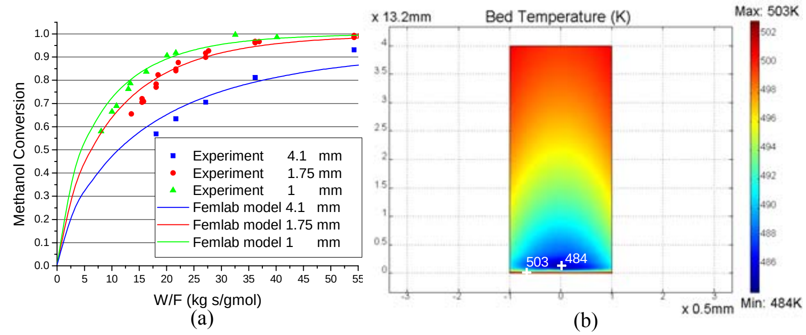

Figure 1 (a) Effect of reactor diameter on measured catalyst activity, W/F = weight of catalyst/methanol molar flowrate, P = 640 Torr, T = 230°C, H_2O/CH_3OH molar ratio = 1.1 **(b)** Temperature profile in the 1mm ID reactor, U_0 = 0.26 m/s, W/F = 16 kg s/gmol

Significance

This study clearly shows that the majority of activity measurements for the steam reforming of methanol reaction reported in the literature could be influenced by temperature gradients within the reactor. The analysis presented here can be easily extended to other endothermic or exothermic reactions to check for heat transfer limitations. This study will also present a method to determine the reactor size needed for elimination of temperature gradients and their adverse effects on measured kinetics for endothermic or exothermic reactions.

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