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Comparison of wall-coated and packed-bed reactors for steam reforming of methanol

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Abstract

The kinetics of methanol steam reforming on a commercial $CuO/ZnO/Al_2O_3$ catalyst in packed-bed and wall-coated microreactors were compared experimentally. Different dimensions of both reactor configurations were tested and the transport limitations were analyzed using 2D reactor models. Packed-bed reactors of dimensions from 4.1 down to 1 mm i.d. were found to be heat transfer limited and temperature gradients of up to 40 K could exist in the bed. The reactor diameter required to eliminate temperature gradients was estimated to be 300 μm, which clearly is not practical. On the other hand, the wall-coated reactor was found to be free from any mass or heat transfer limitations in dimensions from 4.1 mm down to 200 μm i.d. Our modeling results showed that the reactor volumetric productivity increases with thicker catalyst wall-coatings for the same reactor diameter. We also show that the wall-coated reactor offers a better solution to achieve low pressure drop and high catalyst activity compared to a packed-bed microreactor.

Keywords: Methanol steam reforming; Heat transfer limitations; Packed bed microreactor; $CuO/ZnO/Al_2O_3$ catalyst; Reactor modeling; Wall coated microreactor

1. 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 microreformers 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) [2]. The low reforming temperature results in low CO concentration (1.5%) in the product gases. This makes it possible, with elevated-temperature (180 °C) PEM fuel cells, to feed the reformate directly to the fuel cell without subsequent CO clean up. Fuel cell membranes made of polybenzimidazole (PBI) polymer allow high temperature operation of up to 200 °C and performance is not affected by CO concentrations up to 3% [3].

Although methanol steam reforming (MSR) is less endothermic than steam reforming of other fuels, it is heat transfer limited in a packed bed reactor and significant axial and radial temperature gradients can exist in the bed [4–6]. This, in part, is due to the low gas velocities used to achieve high conversions. For a packed bed, the low gas velocity dramatically lowers the bed effective thermal conductivity [7], which will cause cold spots in the bed, in turn leading to low volumetric efficiency. By eliminating temperature gradients, we make full use of the intrinsic activity of the catalyst.

Microreaction technology makes it possible to achieve near isothermal operation [8]. Karim et al. showed that a reactor of 300 μm diameter would be needed to achieve isothermal operation in a packed-bed reactor for MSR [6]. However, pressure drop would limit the use of such small dimensions to testing small amounts of catalyst. For a commercial reformer, a packed-bed reactor would not be favored due to practical issues like bed redistribution leading to gas channeling and the availability of a micro-pump capable of overcoming a high pressure drop. Alternatively, isothermal operation could be achieved using wall-coated reactors, since the heat has to be

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Nomenclature

a_c	external catalyst surface area $= \frac{\pi(d_t-2\delta_c)L}{\pi[d_t^2-(d_t-2\delta_c)^2]L}$ (m^2/m^3)
C_A	concentration of species A ($gmol/m^3$)
C_p	heat capacity (J/kg K)
d_p	catalyst particle diameter (m)
D_{Am}	binary diffusion coefficient (m^2/s)
E_a	reaction activation energy (J/gmol)
F	methanol molar flowrate (gmol/s)
h_w	heat transfer coefficient at the wall (W/m^2 K)
k_1	reaction rate constant (s^{-1})
k_1'	reaction rate constant (m^3/kg s)
P	pressure (N/m^2)
$-r_A$	rate of disappearance of species A per unit volume ($gmol/m^3$ s)
R	ideal gas constant (8.314 J/gmol K)
T	temperature (K)
U	superficial gas velocity based on the tube cross-sectional area (m/s)
W	catalyst weight (kg)
X	conversion $= \frac{\text{Moles reacted}}{\text{Moles fed}}$
y_A	mole fraction of species A

Greek letters

δ	the increase in the total number of moles per mole of CH_3OH reacted
ρ	density (kg/m^3)
ϕ	void fraction
ε	change in number of moles for complete conversion/total number of moles fed to the reactor
λ	thermal conductivity (W/m K)

Subscripts

0	inlet
A	methanol
eff	effective
g	gas
s	solid
w	wall

transferred through the walls rather than to the catalyst bed [9]. In addition to their isothermal operation, wall-coated reactors offer a much lower pressure drop than packed-bed microreactors.

The objective of this study is to compare the performance of a packed-bed to a wall-coated reformer. We performed experimental measurements of the reactivity of packed-bed and wall-coated reactors of different sizes. We developed a 2D pseudo-homogeneous model to calculate temperature profiles in the packed-bed reactors. The model allowed us to study the impact of reactor size on the apparent catalyst activity. We also used a 2D model for the wall-coated reactor to study the effect of catalyst wall-coating thickness and that of reactor diameter on the apparent catalyst activity.

2. Experimental

Measurements of the steam-reforming of methanol were performed in tubular reactors. The reactor consisted of a quartz tube positioned in an aluminum block heated by two cartridge-heaters. The space between the quartz tube and the aluminum block was filled with sand for better heat transfer. The temperature of the aluminum block was controlled by a temperature controller. The temperature of the reactor outer surface was measured and was equal to that of the aluminum block. The inlet and outlet temperatures of the reactor were also monitored. The reactor effluent stream passed through a gas-sampling valve, then through a condenser to trap unreacted water and methanol before reaching a digital mass flow meter which allowed for total product dry gas flow to be monitored. The effluent of the reactor was analyzed using a Varian CP-3800 gas chromatograph (GC) equipped with a Porapak Q column and a TCD detector, using helium as the carrier gas. The analysis of the gas phase species CO_2, CO and CH_3OH along with a carbon balance allowed the methanol conversion and CO_2 selectivity to be calculated. The GC was programmed to sample reactor product gases at 20 min intervals around the clock. The entire system was automated by Labview software and appropriate data acquisition hardware. Material balance was done as follows: Using the methanol conversion and CO_2 selectivity and the reaction network stoichiometry, the total theoretical dry gas flowrate was calculated and compared to the reading of the mass flow meter. The error was less than 10% in all experiments. A commercial $CuO/ZnO/Al_2O_3$ catalyst from BASF (F13456) was used in all the experiments. For the packed-bed reactors, the catalyst was crushed and sieved to 100–250 μm particle size. The same particle size was used for the different reactor sizes. A different aliquot from the crushed catalyst was used for each experiment. For the wall coated reactors, the commercial catalyst was crushed and sieved to less than 25 μm in diameter. The catalyst particles were then added to boehmite, deionized (DI) water, and small amounts of nitric acid in a 300 ml ball mill jar containing 6 mm zirconia grinding beads to prepare a sol–gel slurry. The typical slurry formulation consisted of 100 ml of DI water, 25 mg of catalyst, 10 mg of boehmite, and 0.5 ml of nitric acid. The water and boehmite were initially combined, and the nitric acid was added to disperse the flocculated boehmite powder creating a colloidal suspension. The pH was measured at this point and the solution was found to be fairly acidic (pH = 3). The catalyst powder was then added to the dispersed solution and then rotated overnight, during which time gelation of the sol occurs. The sol–gel slurry was coated onto the walls of the capillaries using the gas displacement method [10]. The $CuO/ZnO/Al_2O_3$ was used in its as-received, calcined state. The reactor was heated to the reaction temperature of 200 °C under helium flow of 4 sccm at 15 °C/min. The helium was left to flow for an hour after the temperature reached 200 °C before the water methanol mixture was introduced to the reactor. A mixture of 1.1:1 molar water/methanol was pumped using an injection pump (Cole Parmer 74900) at 0.2 ml/h to an in-house built vaporizer operating at 130 °C. The vaporizer was optimized to get a stable flow rate and minimize fluctuations in the water-methanol molar ratio [11]. After starting the methanol/water flow, 30 min were allowed for catalyst reduction. Kinetic data point collection was done by changing the flowrate of the liquid water/methanol mixture from low to high flowrate (high to low W/F). Since catalyst activity decayed with time on stream, all data points reported here were collected during the first 3 h period after starting the methanol/water flow. Tests showed that the extent of deactivation during this initial period was 5–10% and will not affect the conclusions of this paper.

3. Results

3.1. Effect of packed-bed reactor diameter on apparent catalyst activity

In a previous study, we measured the catalyst activity in three reactors having an i.d. of 4.1, 1.75 and 1 mm to assess the effect of reactor diameter on catalyst apparent activity [6]. The reactors were loaded with 100, 50 and 30 mg catalyst. The same range of catalyst particle sizes (100–250 μm) was used in the different size reactors. The measured catalyst activity increased significantly with decreasing reactor diameter as shown in Fig. 1. The disadvantage of using smaller diameter reactors is the higher pressure drop across the catalyst bed. The high pressure drop and the difficulties of catalyst packing prevented us from using reactors with diameter less than 1 mm.

3.2. 2D packed-bed reactor modeling

The software program Femlab 2.3a (Comsol Inc.) was used to develop a 2D pseudo-homogeneous model for the packed-bed reactors used in this study.

3.2.1. Model description

A comprehensive reaction network model that accounts for the all the reactants and products would significantly increase the computational requirements. Also, since we are mainly focusing on the impact of heat transfer effects on the measured methanol conversion, the type of the reaction rate law used will not change the conclusions of this work. Therefore, the MSR reaction rate law will be taken to be first order in methanol and zero order in water. Preserving the change in number of moles with reaction, the methanol steam reforming reaction can be simplified to the following [6]

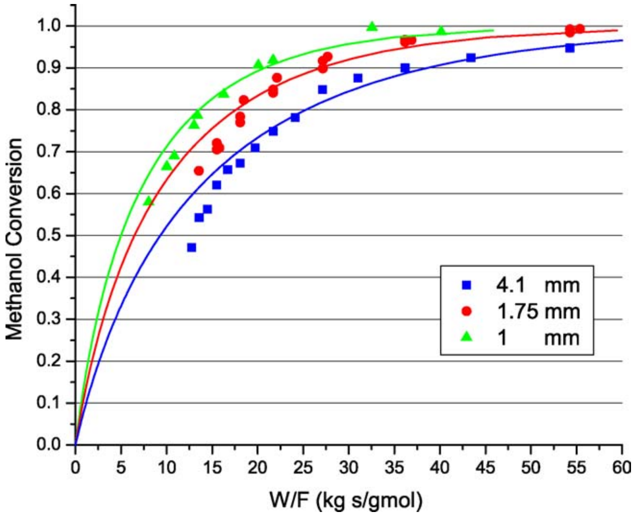

Fig. 1. Effect of decreasing reactor i.d., W/F = weight of catalyst/methanol molar flow rate, $P = 640$ Torr, $T = 230\ ^{\circ}\mathrm{C}$, H_2O/CH_3OH molar ratio = 1.1, Solid lines correspond to a first order kinetic model with respect to methanol. Reprinted with permission from Ref. [6]. Copyright 2005 Elsevier.

$$A \rightarrow 3D \qquad (1)$$

The reaction rate is taken to be first order in methanol and zero order in water and neglecting the pressure drop in the reactor [6]

$$-r_A = k_1 \frac{C_{A_0}(1-X_A)}{(1+\varepsilon X_A)} \frac{T_0}{T}(1-\phi) \qquad (2)$$

where $\varepsilon = \delta y_{A_0} = 2 \times \frac{1}{2.1} = 0.9524$ (H_2O/CH_3OH molar ratio = 1.1). The first order reaction rate constant k_1 is evaluated using the Arrhenius equation.

$$k_1 = A \exp \frac{-E_a}{RT} \qquad (3)$$

where $E_a = 82$ kJ/gmol. The volumetric flowrate change with conversion and temperature is accounted for in the gas velocity expression as follows

$$U = U_0(1+\varepsilon X_A)\frac{T}{T_0} \qquad (4)$$

Properties of the gas and catalyst bed are given below, the gas physical properties are taken as an average of the mixture over several methanol conversions between 0 and 1. Further details on calculating these properties is given elsewhere [6]

$$\rho_g = 0.5\,\mathrm{kg/m^3}; \qquad C_p = 2000\,\mathrm{J/kg\ K};$$

$$\lambda_g = 0.04\,\mathrm{W/m\ K}; \qquad \lambda_{\mathrm{eff}} = 0.17\,\mathrm{W/m\ K};$$

$$d_p = 150\,\mu\mathrm{m}; \qquad h_w = 320\,\mathrm{W/m^2\ K};$$

$$\rho_{\mathrm{bulk}} = 890\,\mathrm{kg/m^3}$$

The boundary conditions for the energy and mass balance equations are as follows

- At the reactor inlet

  $$T = T_0 = 503\,K; \qquad C_A = C_{A_0} = 11.6\,\mathrm{gmol/m^3}$$

- At the reactor walls

  $$\vec{q}\cdot\vec{n} = h_w(T - T_w), \quad T_w = 503\,\mathrm{K}; \qquad \vec{N}_i\cdot\vec{n} = 0$$

- At the reactor outlet

  $$\vec{q}\cdot\vec{n} = \text{convective flux}; \qquad \vec{N}_i\cdot\vec{n} = \text{convective flux}$$

3.2.2. Isothermal packed-bed performance

The model described above has only one adjustable parameter, the pre-exponential factor A in the Arrhenius equation. A was fit to the experimental data obtained in the 4.1 mm i.d. packed-bed reactor to get $A = 22 \times 10^9\ \mathrm{s^{-1}}$. This value was fixed and the dimensions of the reactor were adjusted to model the 1.75 and 1 mm i.d. reactors. Fig. 2 shows the agreement between the model results and the experimental data. The figure also shows the performance of an isothermal packed-bed reactor with $A = 22 \times 10^9\,\mathrm{s}^{-1}$. The diameter needed for the reactor to be isothermal is 300 μm [6]. It is clear that the reactors used in our experiments suffer from large temperature gradients. We calculated the temperature drop in the reactors to be 40 K in the 4.1 mm reactor, 27 K in the 1.75 mm reactor and 22 K in the 1 mm reactor.

3.3. 2D wall-coated reactor modeling

The software program Femlab 2.3a (Comsol Inc.) was used to develop a 2D axisymmetric model for the wall-coated reactors used in this study.

3.3.1. Model description

The wall-coated reactor consists of two domains, the empty space and the catalyst coat. For the empty space the gas velocity is given by

$$U = U_0(1 + \varepsilon X_A)\frac{T}{T_0} \tag{5}$$

The Stefan–Maxwell equations were used to calculate the mean effective binary diffusivity [12].

$$D_{\mathrm{Am}} = 6.8 \times 10^{-5}\,\mathrm{m^2/s} \tag{6}$$

this value for the mean effective binary diffusivity (D_{Am}) is weakly dependent on the methanol conversion and is taken to be constant in the model. Properties of the gas are given below, the gas physical properties are taken as an average of the mixture over several methanol conversions between 0 and 1.

$$\rho = \rho_g = 0.5\,\mathrm{kg/m^3}; \qquad C_p = 2000\,\mathrm{J/kg\ K};$$

$$\lambda = \lambda_g = 0.04\,\mathrm{W/m\ K}$$

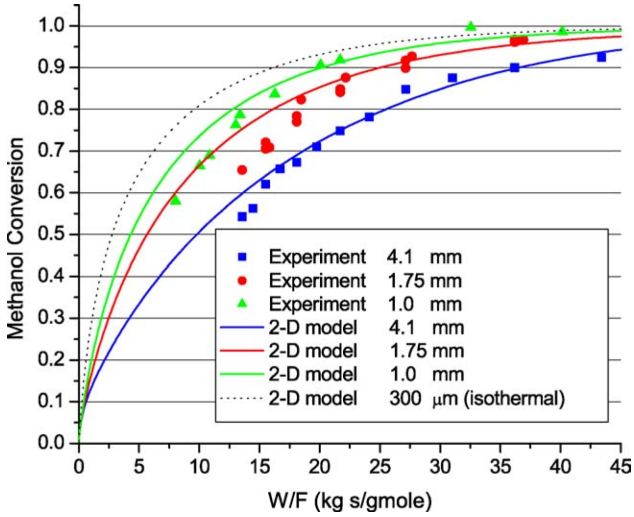

Fig. 2. Isothermal packed-bed performance compared to experimental data.

For the catalyst coat

$$-r_A = k_1 \frac{C_{A_0}(1 - X_A)}{(1 + \varepsilon X_A)}\frac{T_0}{T} \tag{7}$$

The first order reaction rate constant k_1 is evaluated using the Arrhenius equation.

$$k_1 = A \exp\frac{-E_a}{RT} \tag{8}$$

where $E_a = 82$ kJ/gmol

$$\rho = \rho_s = 1480\,\mathrm{kg/m^3}; \qquad C_p = 1000\,\mathrm{J/kg\ K};$$

$$\lambda = \lambda_s = 0.3\,\mathrm{W/m\ K}$$

The diffusion coefficient in the catalyst is taken to be isotropic (same value in r and z directions)

$$D_{\mathrm{Am}} = 6.8 \times 10^{-6}\,\mathrm{m^2/s} \tag{9}$$

The boundary conditions for the energy and mass balance equations are as follows

- At the reactor inlet

  $$T = T_0 = 503\,K; \qquad C_A = C_{A_0} = 11.6\,\mathrm{gmol/m^3}$$

- At the interface between the catalyst coat and the empty space

  $$\vec{q}\cdot\vec{n} = \frac{-r_A}{a_c}; \qquad \vec{N}_i\cdot\vec{n} = \frac{-r_A|\Delta H_R|}{a_c}$$

- At the interface between the catalyst coat and the reactor walls

  $$T = T_w = 503\,\mathrm{K}; \qquad \vec{N}_i\cdot\vec{n} = 0$$

- At the reactor outlet

  $$\vec{q}\cdot\vec{n} = \text{convective flux}; \qquad \vec{N}_i\cdot\vec{n} = \text{convective flux}$$

The 4.1 and 1.75 mm diameter reactors were 16 cm long. All smaller diameter reactors were 4 cm long. The catalyst

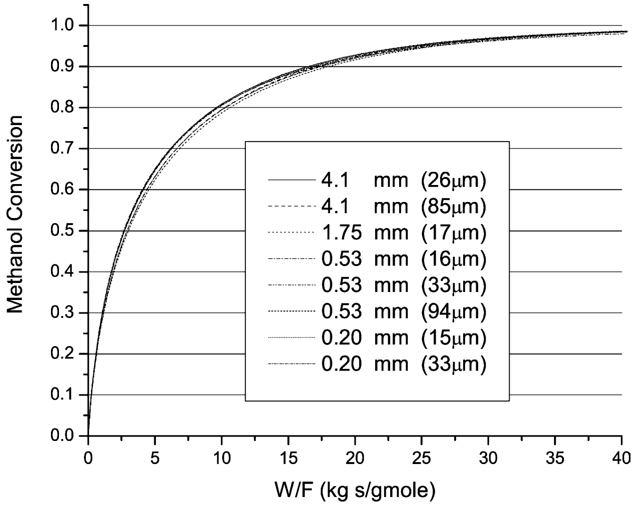

Fig. 3. Modeling results for wall-coated reactors of diameters from 4.1 mm down to 200 μm, values in parentheses represent the catalyst coating thickness, $A = 22 \times 10^9\,\mathrm{s}^{-1}$.

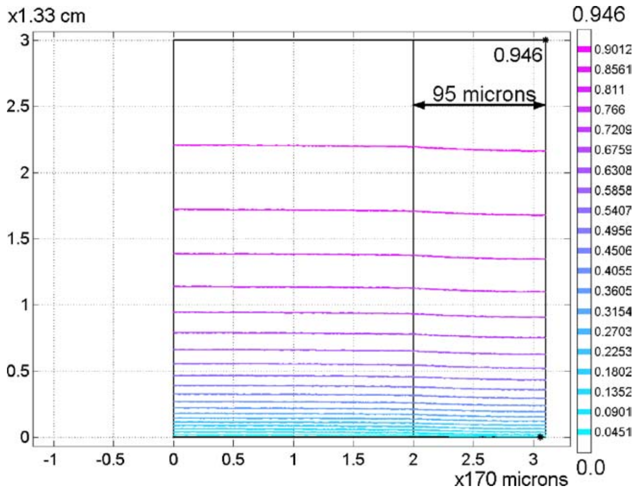

Fig. 4. Conversion profile for the 530 µm reactor with a coating thickness of 95 µm at a methanol conversion of 95%, $A = 22 \times 10^9\ s^{-1}$, the center of the reactor is at $x = 0$.

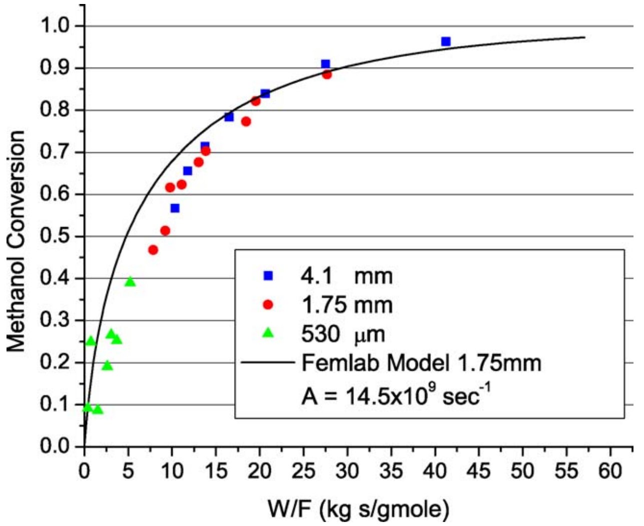

Fig. 6. 2D model ($A = 14.5 \times 10^9\ s^{-1}$) compared to the experimental data for the wall-coated reactor.

weight is calculated using the catalyst density ($\rho_s = 1480$ kg/m^3) and the volume of the catalyst (using the catalyst coating thickness (δ_c) reported in the figures).

3.3.2. Modeling results

In the absence of any heat or mass transport limitations, the wall-coated reactor should perform the same as an isothermal packed-bed reactor (see Fig. 2). In order to confirm that the wall-coated reactor is free from any transport limitations, we studied the effect of different reactor diameters and catalyst coating thicknesses. Fig. 3 shows that the reactor diameter and coating thickness do not affect reactor productivity per unit catalyst weight. Figs. 4 and 5 show the concentration and temperature profiles in the 530 µm reactor with a coating thickness of 95 µm, the methanol conversion was 95%. The profiles are shown for half the reactor diameter since the other half is symmetric. The profiles confirm that the 530 µm reactor is free from transport limitations. This is also true for the different reactor diameters from 4.1 mm down to 200 µm.

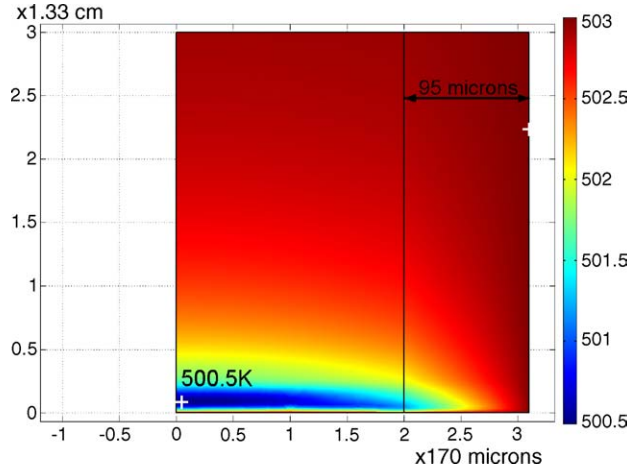

Fig. 5. Temperature profile for the 530 µm reactor with a coating thickness of 95 µm at a methanol conversion of 95%, $A = 22 \times 10^9\ s^{-1}$, temperature scale in Kelvin, the center of the reactor is at $x = 0$.

3.4. Wall-coated reactor experimental results

The heat transfer limitation for packed-bed reactors could alternatively be solved by coating a thin layer of the catalyst on the inner walls of the reactor, thus avoiding the pressure drop associated with packed bed reactors. The temperature could be easily controlled and the reactor will operate near isothermally. In order to test the catalyst activity in a wall-coated reactor, the inside walls of quartz tubes of inner diameters 4.1, 1.75 and 0.53 mm were coated with a 5–25 µm catalyst coat using the method described previously [10]. The length of the coated tube was 16 cm in all reactors. Fig. 6 shows the measured catalyst activity in the different diameter reactors. Using the 2D model described above we fitted the data to get $A = 14.5 \times 10^9\ s^{-1}$, the 2D model results are also shown in Fig. 6. The overlap of experimental data for the 4.1 and 1.75 mm reactors confirms the absence of any diffusion limitation.

4. Discussion

The modeling results show that the reactor productivity per weight of catalyst is independent of reactor diameter and catalyst coating thickness. However, the reactor productivity normalized to the reactor volume is of great importance for the use in compact fuel cell systems. Therefore, if we normalize the previous results with respect to the total reactor volume instead of the catalyst weight we can conclude that for the same reactor diameter, the thicker the catalyst coat the higher the reactor volumetric productivity. However, we could achieve the same volumetric productivity using a smaller diameter reactor and a thinner catalyst coat. For example, a 530 µm reactor with a 95 µm catalyst coat has the same volumetric productivity as a 200 µm reactor with a 33 µm catalyst coat. In other words, reactors with the same percentage area coated (area coated/total cross-sectional area) have the same volumetric productivity. Studies are currently under way to determine the maximum percentage area that could be coated and the effect of reactor diameter on the ease of coating. This is particularly important to determine the optimum channel size for the reformer to achieve the highest volumetric productivity.

The apparent catalyst activity measured in the wall-coated reactor was 34% less than that for an isothermal packed-bed reactor. Since we have proved that the wall-coated reactor is free from any transport limitations, we expected to measure the same activity as in an isothermal packed-bed. We attribute the decrease in catalyst activity to the formation of a slurry from a preformed catalyst and the subsequent coating process. The low pH of the catalyst slurry caused the catalyst to dissolve and then reprecipitate during the drying step. The reprecipitation could have changed the original structure of the catalyst thus leading to a lower activity. We are currently working on modifying the coating procedure and on developing catalysts that may be less sensitive to the coating process than $CuO/ZnO/Al_2O_3$.

5. Conclusions

The activity of $CuO/ZnO/Al_2O_3$ for the steam reforming of methanol was measured in packed-bed and wall-coated reactors of different sizes. The reactivity results showed that the packed-bed reactor suffered from significant temperature gradients, and this was confirmed by the analysis of heat transfer limitation using a 2D pseudo-homogeneous model. The wall-coated reactor was shown to be free from any transport limitations. Our modeling results showed that a 530 μm reactor with 95 μm coating thickness is isothermal and free from diffusion limitation. We also found that our coating process does slightly lower the catalyst activity, however, we believe the wall-coated reactor still offers a better solution to achieve high catalyst activity without the penalty of pressure drop.

Acknowledgements

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References

[1] Jianli. Hu, Yong. Wang, Dave. VanderWiel, Cathy. Chin, Daniel. Palo, Robert. Rozmiarek, Robert. Dagle, James. Cao, Jamie. Holladay, Ed. Baker, Fuel processing for portable power applications, Chem. Eng. J. 93 (2003) 55–60.

[2] L.F. Brown, A comparative study of fuels for on-board hydrogen production for fuel-cell powered automobiles, Int. J. Hydrogen Energy 26 (2001) 381–397.

[3] O. Savadogo, B. Xing, Hydrogen/oxygen polymer electrolyte membrane fuel cell (PEMFC) based on acid-doped polybenzimidazole (PBI), J. New Mater. Electrochem. Syst. 3 (2000) 345–349.

[4] W. Lee Perry, Abhaya K. Datye, Anil K. Prinja, Lee F. Brown, Joel D. Katz, Microwave heating of endothermic catalytic reactions: reforming of methanol, AIChE J. 48 (4) (2002) 820–831.

[5] P.J. de Wild, M.J.F.M. Verhaak, Catalytic production of hydrogen from methanol, Catal. Today 60 (2000) 3–10.

[6] Ayman. Karim, Jaime. Bravo, Abhaya. Datye, Nonisothermality in packed bed reactors for steam reforming of methanol, Appl. Catal. A: General 282 (1–2) (2005) 101–109.

[7] Sakae. Yagi, Daizo. Kuni, Studies on effective thermal conductivities in packed beds, AIChE J. 3 (3) (1957) 373–381.

[8] Matthew W. Losey, Martin A. Shmidt, Klavs F. Jensen, Microfabricated multiphase packed-bed reactors: Characterization of mass transfer and reactions, Ind. Eng. Chem. Res. 40 (2001) 2555–2562.

[9] Hubert. Redlingshofer, Oliver. Krocher, Wolfgang. Bock, Klaus. Huthmacher, Gerhard. Emig, Catalytic wall reactor as a tool for isothermal investigations in the heterogeneously catalysed oxidation of propene to acrolein, Ind. Eng. Chem. Res. 41 (2002) 1445–1453.

[10] Jaime. Bravo, Ayman. Karim, Travis. Conant, Gabriel P. Lopez, Abhaya. Datye, Wall coating of a $CuO/ZnO/Al_2O_3$ methanol steam reforming catalyst for micro-channel reformers, Chem. Eng. J. 101 (2004) 113–121.

[11] A. Karim, A Comparison Between Packed Bed and Wall Coated Reactors for the Steam Reforming of Methanol, Master's Thesis, University of New Mexico, December, 2003.

[12] Gilbert F. Froment, Kenneth B. Bischoff, Chemical Reactor Analysis and Design, Second ed., John Wiley & Sons, Inc., 1990.