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Coating of steam reforming catalysts in non-porous multi-channeled microreactors

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Abstract

Our previous work [T. Conant, et al., Wall coating behavior of catalyst slurries in non-porous ceramic microstructures. Chem. Eng. Sci. 61 (17) (2006) 5678] described how the inertial effects limit the catalyst wall-coating thickness in a single microchannel. In this work, we demonstrate the inherent benefit of multichanneled structures in avoiding inertial effects during the process of coating catalyst slurries. Our microreactor consists of 25 capillaries of 530 μm in diameter housed within a 1/4 in. o.d. stainless steel housing. The maximum fraction coated within the parallel-channel microstructure was found to be 40% which is a significant improvement over the 25% achieved with single 530 μm capillaries. Transmitted-light optical microscopy shows that the channels are plug-free. The thick coatings may lead to some loss of cohesion within the coating layer, resulting in non-uniform coating thicknesses. The catalyst layer within the reactors was tested for the steam reforming of methanol, confirming the viability of coating catalysts slurries in pre-fabricated microreactors.

Keywords: Methanol reforming; Microreactor; Catalyst wall coating; Capillary number; Reynolds number; Gas-assisted fluid displacement

1. Introduction

Due to its high energy density and low reforming temperature, methanol is often considered the best choice of a liquid fuel to generate hydrogen for fueling portable proton-exchange membrane (PEM) fuel cells [2]. It has been shown that $CuO/ZnO/Al_2O_3$ catalysts are able to produce hydrogen while maintaining a high selectivity to CO_2 at relatively low temperatures (230 °C), keeping CO from poisoning the PEM anode electrocatalyst. However, the steam reforming of methanol is a highly endothermic process, and recent research has shown that packed-bed reactors as small as 1 mm can have a ΔT as high as 20 K across the reactor leading to lowered overall catalyst performance [3]. For portable devices, using a micro-packed-bed reactor would drastically increase the pressure drop across the reactor and result in a larger balance of plant and lower the efficiency of the fuel cell stack. A wall-coated reformer system benefits from an inherently low ΔP, as well as isothermal operation, which maximizes the catalyst performance and minimizes the amount of catalyst required to produce a given amount of hydrogen.

Unlike the porous materials used in the catalytic converter industry, microreactors are typically fabricated with non-porous materials including silicon wafers [4–6], glasses [7], and tape-cast ceramics [8]. All of these fabrication methods involve harsh conditions which are harmful to commercially available steam-reforming catalysts. Therefore, the challenge becomes how to achieve adherent coatings within pre-fabricated non-porous microstructures. Taylor [9] explored the coating behavior of Newtonian fluids in tubes down to 1.5 mm using the gas-assisted fluid displacement technique. This technique is a two step process in which the tube is first filled with the coating material and then purged, leaving a fraction left coated on the wall of the tube. Taylor was able to correlate the fraction coated (m) as a function of the capillary number Ca. The capillary number is defined as the ratio of viscous effects and surface tension effects:

$$\mathrm{Ca} = \frac{U_\mathrm{b}\mu}{\sigma}$$

where μ is the fluid viscosity, U_b the velocity of the air/liquid interface (bubble) moving along the tube, and σ is the surface

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Table 1
Summary of coating behavior of fluids in various diameters and their correlating Reynolds numbers

Coating fluid	Channel diameter	m	Re
Newtonian	530 μm	0.57	<20
Slurry	1.75 mm	0.45	16
Slurry	530 μm	0.25	250
Slurry	250 μm	0.17	450

tension of the coating fluid in air. The fraction coated can be defined as the fraction of the open area remaining coated after the capillary is purged, and it was reported that the maximum fraction possible was 0.57. Polynkin et al. [10] then reported a model for predicting the maximum fraction coated for a shear-thinning fluid, absent of inertial effects, using the same gas-displacement method in tubes with millimeter diameters.

Our previous research addressed the issues associated with proper adhesion when coating glassy surfaces [11], and understanding the coating behavior of shear-thinning catalyst slurries in single cylindrical channels with dimensions well below 1.0 mm [1]. It was determined that the coating behavior was controlled by the coupled effects of the fluid rheology and the dramatic increase in inertial effects as the diameter was decreased. With a decrease in capillary diameter, the purging fluid Reynolds number (Re) would increase accordingly resulting in a lower fraction coated. These results are summarized in Table 1. The Reynolds number is defined as

$$Re = \frac{\rho U_b r}{\mu}$$

where ρ is the density of the coating fluid, U_b the bubble velocity, r the capillary radius, and μ is the coating fluid limiting viscosity.

Table 1 shows that the maximum fraction of cross-section area coated drops from 0.57 down to 0.45, primarily as a result of fluid rheology. Inertial effects were more dominant and caused a drop from 0.45 down to as low as 0.25 for a 530 μm single capillary and 0.17 for a 250 μm single capillary. We calculated the expected Re versus the number of channels for a channel diameter of 530 μm and a constant purge flow of 200 sccm. Fig. 1 shows that we would need at least 10 parallel channels to circumvent the effects of inertia by keeping $Re < 50$.

2. Multi-channel structure design and fabrication

The microreactor consists approximately 25 capillaries 530 μm in diameter or 60 capillaries 250 μm in diameter housed within a stainless steel housing, sealed with a high temperature epoxy (Cotronics General Purpose Room Temperature Cure Epoxy). We fabricated two different lengths of reactors: one for the coating behavior studies which was about 2.5 cm in total length, and one for the activity studies which was about 15 cm in length. The microreactor designed for the coating studies was so short in order to keep the ΔP required for purging below 60 psi.

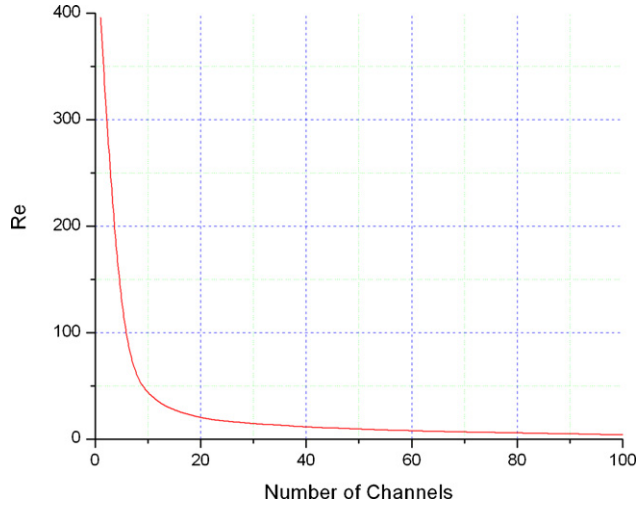

Fig. 1. Calculated Re vs. number of channels assuming a constant flow of 200 sccm and a channel diameter of 530 μm. In order to minimize inertial effects ($Re < 50$) 10 parallel channels are required.

For the 530 μm microreactor, a 1/4 in. o.d. stainless steel (s.s.) tube was cut to 2.5 cm in length, and approximately 25 fused-silica capillaries 530 μm in diameter were cut to a length of 8 cm (Fig. 2A). The ends of the capillaries were sealed by dipping them into the epoxy and allowing the epoxy to draw up approximately 1 cm from each end. The capillaries were then placed in an oven at 140 °C for 5 min to facilitate a full cure of the epoxy in a short time. After the capillaries are removed from the oven and allowed to cool, they were bundled together and coated with epoxy (Fig. 2B). The epoxy-coated bundle was then forced through the housing. The reactor was again heated to 140 °C in an oven to allow the epoxy to cure. In order to ensure that there was a leak-tight seal between the capillaries and the housing; epoxy was forced into the housing to fill in all voids using a syringe. A small amount of epoxy was also used along the interface between the capillaries and the housing to ensure that there were no voids on the outer edge, and the sealed

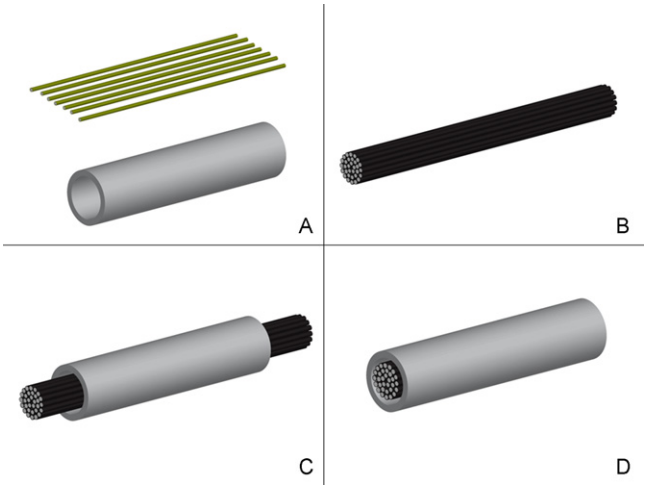

Fig. 2. (A) Fused-silica capillaries and 1/4 in. o.d. stainless steel tube (housing). (B) Fused-silica capillaries bundled with high temperature epoxy. (C) Capillary bundle placed within housing and voids are filled with high temperature epoxy. (D) Capillary ends cut to be nearly flush with the housing.

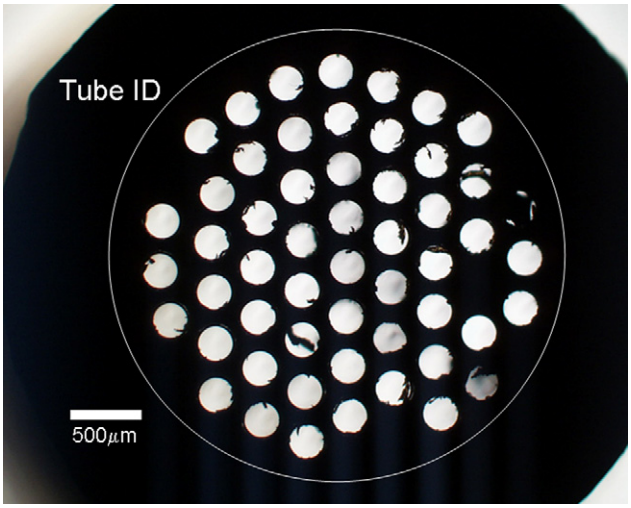

Fig. 3. Transmitted-light optical microscope image of an un-coated MR with about 60 250 μm capillaries. The white line shows the ID of the metal housing, and debris from the cutting process can be seen across the face of the reactor.

reactor was again heated to allow for curing. The sealed reactor is illustrated in Fig. 2C. The overhanging ends of the capillaries were then cut, with a glass-cutting saw, as close the housing as possible. Typically, the capillaries were cut to within 1 mm of the housing. The completed reactor is illustrated in Fig. 2D.

We were able to examine the assembled microreactor using a transmitted-light optical microscope in order to be sure that all of the voids between the open capillaries were filled. Fig. 3 shows an optical microscope image of an uncoated microreactor consisting of approximately 60 capillaries of 250 μm diameter. The image clearly shows that all of the voids between the capillaries are completely filled with the epoxy, yet debris from the cutting process can be seen across the face of the reactor. The white line drawn on the figure shows the ID of the housing to give an idea of how closely packed the capillaries are within the housing. We then tested the reactor at 60 psig for leaks and found that the reactor was leak-tight along the open face.

3. Experimental

3.1. Slurry preparation and characterization

The catalyst slurry was made by adding Boehmite (Catapal B from Sasol), deionized (DI) water, and nitric acid to a 300 ml ball mill jar containing 6 mm zirconia grinding media to prepare the sol-gel. Initially, 10–25 wt% Boehmite was deflocculated using 1 wt% nitric acid in a balance of DI water. This solution was milled for approximately 10 min to properly disperse the Boehmite. A commercially available BASF 13456 $CuO/ZnO/Al_2O_3$ catalyst was crushed and sieved to <25 μm in diameter, and then added to the dispersed boehmite solution. The slurry was then milled overnight. A 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 viscosity of the slurry was measured using a plate and cone viscometer (Brookfield DVII + pro), and was found to be shear-thinning with a limiting viscosity of 15 cP. The surface tension of 135 mN/m was measured using a Krüss tensiometer. The average particle size of the catalyst within the slurry was found to be about 4 μm using a Microtrac S3500 Particle Size Analyzer.

3.2. Coating procedure

The microchannels were first cleaned by flowing piranha etch through the uncoated microreactor. Piranha etch consists of a solid oxidizer (NOCHROMIX® from GODAX laboratories) and sulfuric acid. Water was flowed though next, followed by ethanol, and then the cleaned reactor was dried in an oven at 80 °C. This process served to remove any organic materials on the non-porous surface to ensure proper wetting of fluid on the inner-wall surface. As previously stated, the coatings were done using the two-step, gas-assisted fluid displacement method [1]. The microreactor is first completely filled with the shear-thinning catalyst slurry using a syringe, and then the majority of the fluid is forced out of the capillary using metered air at a flow rate of 200 sccm. The masses of the empty, full, and coated microreactor were measured throughout the coating procedure. The coatings were then dried in a programmable oven, under static conditions, at a maximum temperature of 230 °C.

3.3. Coating analysis

The fraction coated of the wet coating is then found using the following equation:

$$m = \frac{\text{coated mass} - \text{empty mass}}{\text{full mass} - \text{empty mass}}$$

After the drying process, the integrity of the coating was analyzed via optical microscope to determine if there were any plugged channels or if there were any adhesion or cohesion problems. Both optical microscopy (Olympus BX60) and scanning electron microscopy (JEOL JSM-5800LV) were used in the analysis of the dried coatings.

3.4. Activity studies

The in-house microreactors were also tested for their steam reforming of methanol performance. 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 reactor was placed in a convection oven which was heated to the reaction temperature, and a thermocouple was placed on the surface of the reactor to monitor the temperature. The inlet and outlet temperatures of the reactor were also monitored. The 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 from 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. Material balance was done as follows: using the methanol conversion and CO_2 selectivity and the reaction network stoichiometry, the total theoretical dry gas flow rate was calculated and compared to the reading of the mass flow meter [3].

4. Results

In this current study, we were interested in achieving the maximum fraction coated, therefore we chose a high enough flow rate to ensure that we were in the region where viscous effects were dominant (at a $Ca > 2.0$). We were also uninterested in the exact value of Ca since the fraction coated reaches its asymptotic maximum value after this point [9].

4.1. Coating behavior

Table 2 summarizes the results of the coating studies in a microreactor consisting of 25 parallel 530 μm capillaries. In a single 530 μm channel which is purged at 100 sccm the fraction coated was found to be 0.25, well below that of Polynkin et al.'s [10] ideal behavior of 0.44 for a highly shear-thinning fluid. This was attributed to the fact that in a single channel of small diameters, the flow was exceedingly high with a Reynolds number of approximately 250, resulting in less slurry being deposited due to its inertia [1,10]. In our in-house microreactor, we were able to achieve fractions coated around 0.40 at a flow of 200 sccm, which is much closer to the ideal behavior. With 25 parallel channels, and at a doubled total flow, we have cut the flow through the individual channels down ten-fold, resulting in the fluid having less inertia ($Re = 27$). We also found that the ΔP required for the purge step was raised from 40 psig for an individual channel to 60 psig for the 25 parallel channels due to the increase in slurry volume being purged.

4.2. Coating integrity and uniformity

Analysis of the coatings via SEM and optical microscopy show that the coatings within the microreactors are adherent and that the channels are free of plugs. Fig. 4 shows that the coatings are very thick (>75 μm) and adherent to the non-porous surface of the fused-silica capillaries, however there are issues with the cohesion of the layer. The coating shrinks substantially during the drying process, since the slurry is nearly 75 wt% water, and such a high loss in volume results in large stresses within the layer causing cracking in the layer.

Table 2
Summary of factors attributed to controlling coating behavior in single channels and multiple channels

Diameter (μm)	No. of channels	m	Purge flow (sccm)	Re	ΔP (psig)
530	1	0.25	100	250	40
530	25	0.40	200	27	60

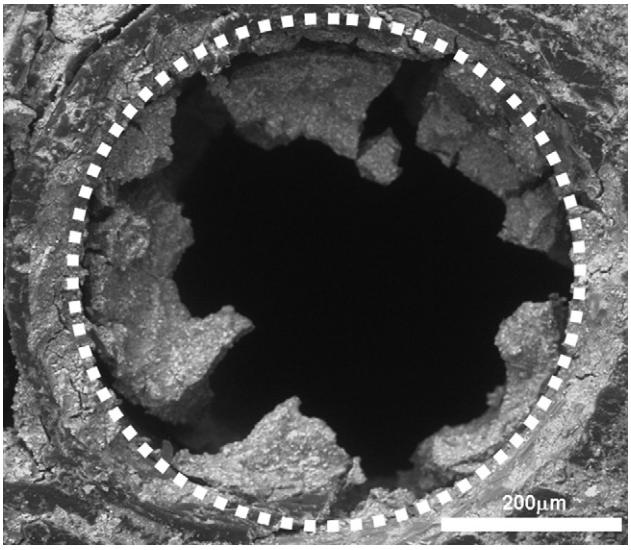

Fig. 4. SEM image showing that the coatings are adherent to the fused-silica surface, however there is a loss of cohesion in the layer resulting in non-uniform coating thicknesses. The fraction coated for this reactor was found to be 0.40 which is drastically improved from the 0.25 for the single 530 μm capillaries ($Re = 27$). The dotted white line shows where the inner diameter of the fused-silica capillary is located.

In order to be sure that the reactor has no plugged channels, the coated reactor was analyzed using a transmitted-light optical microscope. With a transmitted-light optical microscope we get a projection of the coating along the entire length of the channel, as opposed to just the surface with the SEM. Fig. 5 illustrates that all of the channels are plug-free leading to an even flow distribution throughout the reactor. Therefore, we can expect that all of the loaded catalyst is accessible for catalyzing the reforming reaction. However, this optical microscope image represents a superposition along the axial direction, exaggerating the extent of non-uniformity.

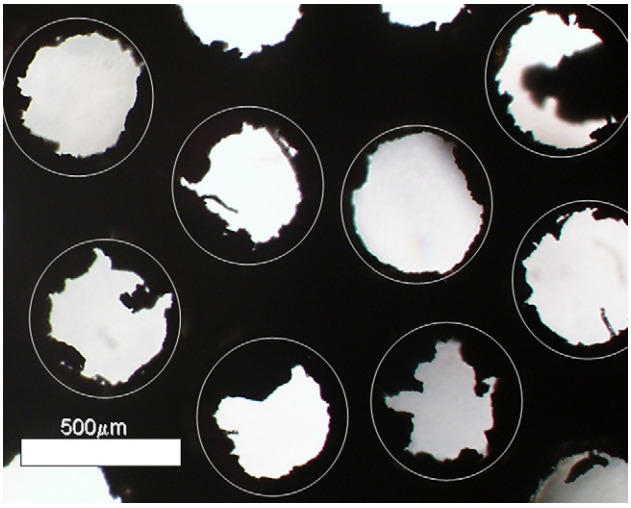

Fig. 5. Transmitted-light optical microscope image of a coated MR with about 25 530 μm capillaries. The white lines indicate the ID of the 530 μm capillaries. The benefit of the transmitted-light optical microscopy is that it definitively shows that no channels are plugged meaning that all of the loaded catalyst is accessible for reaction.

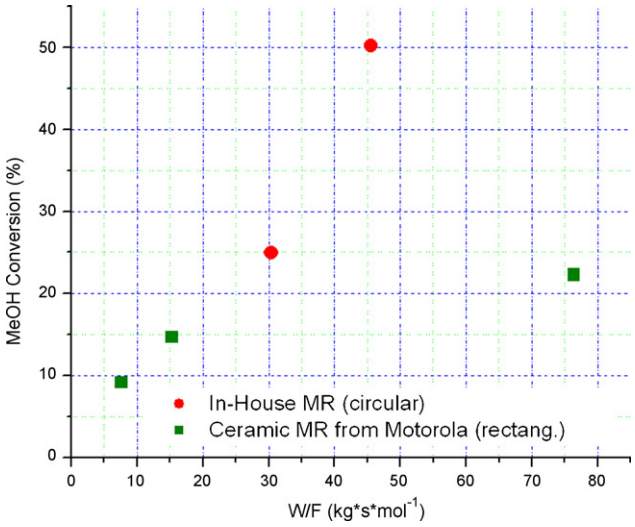

Fig. 6. Reactivity data for the in-house microreactor with circular channels vs. that of our previously reported data using a ceramic reactor with rectangular channels.

4.3. Microreactor reactivity data

Fig. 6 shows the methanol conversion of our in-house microreactor compared to our previously published data versus *W*/*F*, where *W* is the weight of the catalyst (kg) and *F* is the methanol flow rate (mol/s). The maximum methanol conversion obtained was 50% at a *W*/*F* of 46 kg s mol^{-1}, where our previously reported data only reached a maximum conversion of 23% at a much higher *W*/*F* of 77 kg s mol^{-1}. The dramatic increase in the catalyst activity is attributed to the accessibility of the catalyst. We confirmed through optical microscopy (see Fig. 5) that none of the channels are plugged, meaning that all of the catalyst weighed is accessible to the reactants. The non-uniformity of the coating thickness could lead to small variations in the flow rates through the individual channels slightly decreasing the overall performance of the reactor. Our previously published data showed that some of the square channels seem to be plugged or coated over resulting in a fraction of the catalyst being inaccessible. This, undoubtedly led to lower conversions for a given weight. The CO_2 selectivity, $P_{CO_2}/(P_{CO_2} + P_{CO})$, of both samples was higher than 97%.

5. Conclusions

We have used in-house microreactors made of a number of fused-silica capillaries housed in a 1/4 in. o.d. stainless steel tube in order to test the possibility of avoiding the adverse effects of inertia on achieving thick catalyst coatings. The results showed that the maximum fraction coated for the multi-channeled structure was approximately 0.40 up from the 0.25 for the single 530 μm channel. The resulting flow through the individual channels within the microreactor was decreased an order of magnitude resulting in a Reynolds number ten-fold lower than that of the single channels. The inherent compact design of multi-channeled microreactors leads to the possibility of loading more catalyst than a single channel of the same total reactor length. Microscopy showed that the coatings were adherent although drying stresses led to cracks and loss of cohesion within the relatively thick coatings. The catalyst-coated microreactor was found to be active towards the steam reforming of methanol reaching 50% methanol conversion while keeping a high selectivity towards CO_2.

Acknowledgments

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References

[1] T. Conant, et al., Wall coating behavior of catalyst slurries in non-porous ceramic microstructures, Chem. Eng. Sci. 61 (17) (2006) 5678.
[2] D. Browning, P. Jones, K. Packer, An investigation of hydrogen storage methods for fuel cell operation with man-portable equipment, J. Power Sources 65 (1/2) (1997) 187.
[3] A. Karim, et al., Comparison of wall-coated and packed-bed reactors for steam reforming of methanol, Catal. Today 110 (1/2) (2005) 86.
[4] S. Srinivas, et al., A scalable silicon microreactor for preferential CO oxidation: performance comparison with a tubular packed-bed microreactor, Appl. Catal. A: Gen. 274 (1–2) (2004) 285.
[5] A.V. Pattekar, M.V. Kothare, A microreactor for hydrogen production in micro fuel cell applications, J. Microelectromech. Syst. 13 (1) (2004) 7.
[6] S.K. Ajmera, et al., Microreactors for measuring catalyst activity and determining reaction kinetics, Sci. Technol. Catal. 145 (2003) 97.
[7] Y. Kikutani, et al., Pile-up glass microreactor, Lab. On A Chip 2 (4) (2002) 193.
[8] X. Wang, et al., Fabrication of micro-reactors using tape-casting methods, Catal. Lett. 77 (4) (2001) 173.
[9] G.I. Taylor, Deposition of a viscous fluid on the walls of a tube, Fluid Mech. 10 (161) (1961).
[10] A. Polynkin, J.F.T. Pittman, J. Sienz, Gas displacing liquids from tubes: high capillary number flow of a power law liquid including inertia effects, Chem. Eng. Sci. 59 (14) (2004) 2969.
[11] J. Bravo, et al., Wall coating of a CuO/ZnO/AI(2)O(3) methanol steam reforming catalyst for micro-channel reformers, Chem. Eng. J. 101 (1–3) (2004) 113.