A Comparison Between Ceramic Foam Catalyst and Packed-Beds for Methanol-Steam Reforming

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Abstract

Ceramic foams are sponge-like materials with open cells that are connected to each other through openings or windows that are formed from ceramic struts. The open cells collectively form tortuous continuous passages that are interrupted by the web of struts. The foam can accept a washcoat and thus becomes an attractive catalytic support. The foam has high porosity and offers little resistance to flow (low pressure drop). The tortuous flow path generates disturbances in the flow that enhances the heat and mass transfer between the pores in the washcoat and the flow. Recent work by Richardson and co-workers note the attractions of ceramic foam catalysts and their advantages over conventional porous pellets. In addition, they have measured rates of heat & mass transfer in ceramic foams and presented them as correlations suitable for reactor design & simulation.

The objective of this work is to examine the advantages of ceramic foams versus packed beds for steam reforming of methanol. Two reactors are simulated: one that is filled with either a 'cartridge' of catalytic foam or a bed of commercial pellets. The reactor geometry is designed to mimic a semi-commercial methanol reformer of about 1L volume, which has been studied in other publications from our labs. The pseudo-homogenous methodology, with appropriate modification, is used to simulate the two reactors.

A key assumption of the comparison is that the commercial catalyst can be deposited onto the ceramic foam support as a washcoat without altering the nature of the active sites and the associated pore structure. This implies that the reaction mechanism and kinetic expressions remains the same for the foam and porous pellet and that the ratio of active sites per unit surface area (BET) is constant. Since the BET surface area of the washcoat and porous pellet are different, the total number of active sites per unit volume of reactor will be different between the two reactors.

1   Introduction

The widespread adoption of fuel cells will require an economic technology for producing a hydrogen rich feed. The reforming of liquid fuels, especially conventional hydrocarbons, is one attractive means of generating a feed of the correct quality and quantity for a given fuel cell type and application. The reforming of hydrocarbons, conducted in conventional packed-bed reactors, is an established technology and there is a global infrastructure for the distribution of a many different types of liquid hydrocarbons such as methanol, ethanol, gasoline, diesel and other heavy oils.

Reforming technology tends to fall into three categories depending on the co-reactants that are feed with the hydrocarbon: steam reforming, catalytic partial oxidation and a combination of the two, auto thermal reforming (or oxidative steam reforming). Steam reforming can generate a feed with the greatest hydrogen concentration but requires external heating to drive the endothermic reactions. Steam reformers are recognized as having a slow thermal response especially during startup where the catalyst bed must be heated to some elevated temperature. Partial oxidation and autothermal reforming have more attractive thermal response than steam reforming since a portion of the feed is oxidized in the reactor. However the disadvantage is that the hydrogen concentration is usually significantly less than with steam reforming.

Many new reactors are being developed in order to improve rates of heat transfer during reforming compared to traditional packed-beds [1, 2, 3]. One of these new technologies [4 – 7] is based on catalytic ceramic foams. Ceramic foams have an open cell geometry similar to sponges yet are ceramics such as ZrO_2 or α-Al_2O_3, traditional catalyst supports. The foam can accept a washcoat forming a thin catalytic surface (i.e. catalytic ceramic foam). The open cells collectively form tortuous continuous passages that are linked by a web of struts. The combination of tortuous flow path and struts generates disturbances in the flow that enhances heat and mass transfer between fluid in the pores of the washcoat and the bulk flow.

The enhanced heat and mass transfer is a key advantage of foams versus packed beds. However, this is offset by two other factors. First, there is much smaller mass of active catalyst per reactor volume for a ceramic foam compared to packed bed. Second, the internal (BET) surface area of the washcoat foam is much smaller then that in a traditional porous pellet (20 – 40 m^2/g versus > 100 m^2/g for a pellet).

A direct calculation of the advantage (or disadvantage) of foams versus packed-beds is difficult due to the presence of mass transfer. For the packed-bed, diffusion of species within the pellet usually hinders the reaction and is accounted for by an effectiveness factor that is generally much less than one. In the case of foam, the effectiveness factor is usually assumed to be unity since the washcoat is quite thin (~50 μm). However, there is the possibility of the reaction being limited due to slow mass transfer from the bulk fluid to the surface of the washcoat.

The objective of this work is to determine, through simulation, the potential advantages of catalytic ceramic foams versus packed beds for the steam reforming of methanol. The basis for comparison is a constant wall temperature reformer that contains either a conventional packed-bed or a cartridge of catalytic ceramic foam. The reformer in both cases is simulated using a two dimensional model based upon the pseudo-homogenous methodology. Steam reforming of methanol is used as a model reaction since there is, firstly, a validated kinetic scheme [8, 9] and, secondly, changes in internal (BET) surface area can be considered in a logical manner.

The model for the packed-bed has been reported in an earlier publication [10]. It accounts for the radial porosity profile in the packed-bed so that the effective thermal conductivity is computed up to the reactor wall. A wall heat transfer coefficient is not required.

The model for the catalytic ceramic foam is founded upon recent work by Richardson and co-workers [11, 12]. They have measured heat and mass transfer in a number of catalytic and non-catalytic ceramic foams and presented them as correlations suitable for reactor design and simulation. In their modeling, they fitted a wall heat transfer coefficient to their data and this approach is used in this work.

2   Basis for Reactor Simulation & Kinetics

In previous work [10], we have reported experimental data gathered from a semi-commercial methanol reformer that had a maximum capacity of 4.4 kWe (1kWe = 10 SLPM of hydrogen) at a liquid feed rate of 70 cm^3/min of a 54% by weight methanol-water feed. The reactor was constructed from standard 2" diameter Schedule 5 stainless steel pipe and the catalyst bed occupies the central portion of the pipe. The bed was about 1.2L in volume (5.715 cm ID by about 47 cm long) and held about 1.5 kg of a commercial Cu/ZnO/Al_2O_3 catalyst. The reactor was electrically (tape) heated. Further details are available in [10].

We propose to use this experimental reformer as a guide for the geometry of and flows to the simulated reformer. An important reason for this decision is that packed-bed model mentioned above, adequately modeled the experimental reformer. Thus the predictions of the packed-bed model are founded upon experiment and provide a realistic benchmark.

We further propose to replace the pellets of the packed-bed with a catalytic ceramic foam with the same intrinsic activity (defined below) as that of the pellet. The question is then, if the reformer geometry diameter is kept constant, how does the quantity (and quality) of reformate change? By quality, we are principally referring to the concentration of CO in the reformate. Further questions naturally arise such as how sensitive is the reformate flow (and CO concentration) to changes in the various parameters of the catalytic ceramic foam? Or, better still, what changes in reformer operation and geometry would enhance the performance of a catalytic ceramic foam based reformer?

We now address the basis for equal intrinsic activity of foam and pellet. By intrinsic activity, we are referring to the number of active sites per unit of internal (BET) surface area. The assumption of equal intrinsic activity implies that the washcoat has the same number of active sites per unit of internal (BET) surface area as a pellet.

At first, this may seem to be an inappropriate or even speculative assumption. It is well known that the washcoat and pellet have different internal surface areas and indeed probably different pore size distributions - the washcoat is not simply a thin layer of the pellet draped over the surface of the foam.

We note that Bravo et al [3] have successfully applied a washcoat to glass where the washcoat contained coarse particles of a commercial $CuO/ZnO/Al_2O_3$ catalyst. The small particles were obtained by grinding 3 mm granules in a mortar and pestle. In this manner, the pore structure and active sites present in the pellet can be incorporated into a washcoat. Since the structure of the pellet is intact, it is reasonable that the kinetics developed for a pellet can now be used for the washcoat with some overall correction for the reduced surface area.

The kinetic scheme developed in our laboratory [8, 9] allows for the correction in surface area (see Section 4) as the rate expressions explicitly have a surface area (S_A) that multiplies the site concentrations ($C_{S_1}^T$, $C_{S_{1a}}^T$, $C_{S_2}^T$ & $C_{S_{2a}}^T$) (units are mols of active sites per m^2 of surface area).

The estimates for the site concentration were obtained in conjunction with the development of the packed-bed model. As explained more fully in [10], the packed-model was fit to experimental data (June 17th 'A' run) corresponding to the reactor operating at about 60% full capacity (feed flowrate is 35 cm^3/min; reformate flow of 34.9 SLPM). The fit described in [10] was done by 'hand' but for the present work superceded by a fit based on minimizing a sum of the squares of the temperature differences between the model and data. {Note to CPT: big/little change in site concentrations?}

3 Model Assumptions

3.1 Packed-Bed

Details of the packed-bed model are included in Section 5 in order to contrast with the model for the foam reactor. Additional information is provided in [10] regarding the development of the model and simulation of the experimental data.

3.2 Foam

Richardson and co-workers [11, 12] studied heat and mass transfer in a number of different foams but concentrated on 30 PPI foam of α-Al_2O_3 with and without washcoat. In particular, Richardson developed correlations [12, equations (25) & (26)] for a standard, two parameter (k_{eff}, h_{wall}) or (λ_e, α_w) model (two dimensional) pseudo-homogenous model for the 30PPI foam but without washcoat. In this work we will assume that these correlations are applicable for the 30 PPI foam with washcoat. Inspection of the one-dimensional models [12] shows that the washcoat increases the overall heat transfer coefficient (h_e) and it is reasonable to conclude these correlations are conservative.

We will assume, due to the thinness of the washcoat, that the effectiveness factor is unity [7].

It is possible for the foam to be mass transfer limited. Richardson et al [11] studied the oxidation of carbon monoxide over a 30 PPI foam impregnated with Pt. Temperatures ranged from 352°C to 580°C while the superficial velocity varied from 1 m/sec to 8 m/sec. Richardson et al was able to correlate the mass transfer coefficient with the classical j_D-factor with a simple power dependence on a Reynolds number (Re_s).

The procedure outlined by Froment & Bischoff [13] was used to correct the mass transfer coefficients to the reaction stoichiometry and operating conditions specific to methanol steam reforming. A one-dimensional simulation of methanol steam reforming was used to generate a number of combinations of temperature and bulk species concentrations that occur in

a packed-bed. It was assumed that these combinations would also approximate conditions in a catalytic ceramic foam. Detailed calculations, following Froment & Bischoff, were carried out to determine the rates of mass transfer and thus the difference in bulk and surface concentrations. Under most combinations, the difference between the bulk and surface concentrations of all species is small (< 1% in mole fraction) and it is concluded that steam reforming is kinetically controlled. Only near the front of the bed where the concentration of products is low, do the surface and bulk concentration of products differ. At the same location, the reactant concentrations at the surface and the bulk were effectively equal.

For the operating conditions in the present work, it is concluded that methanol steam reforming is not mass transfer limited for the catalytic ceramic foam and the bulk and surface concentrations of species can be assumed to be the same. Since the foam model neglects mass transfer, it can be considered a non-conservative model as it predicts the best performance of a catalytic ceramic foam.

4   Reactions & Rate Expressions of Methanol-Steam Reforming

There are three overall reactions and five species involved in the steam reforming of methanol [8]

$$CH_3OH + H_2O \underset{\leftarrow}{\overset{\rightarrow}{}} 3H_2 + CO_2 \qquad\qquad \text{Reforming} \qquad \text{(R)}$$

$$CO \;+\; H_2O \underset{\leftarrow}{\overset{\rightarrow}{}} H_2 + CO_2 \qquad\qquad \text{Water-gas shift} \quad \text{(W)}$$

$$CH_3OH \qquad \underset{\leftarrow}{\overset{\rightarrow}{}} 2H_2 + CO \qquad\qquad \text{Decomposition} \quad \text{(D)}$$

We have proposed a mechanistically based reaction scheme for methanol steam reforming based upon the Langmuir-Hinshelwood approach and developed corresponding (complex) rate expressions [9]. There are three rates, one for each reaction, denoted by r_i (moles-sec^{-1}-kg of catalyst^{-1}),

$$r_R = \frac{k_R K^*_{CH_3O'} \dfrac{p_{CH_3OH}}{p_{H_2}^{1/2}} \left(1 - \dfrac{p_{H_2}^3 p_{CO_2}}{K_R p_{CH_3OH} p_{H_2O}}\right) C^T_{S_1} C^T_{S_{1a}} S_A}{\left(1 + K^*_{CH_3O'} \dfrac{p_{CH_3OH}}{p_{H_2}^{1/2}} + K^*_{HCOO'} p_{CO_2} p_{H_2}^{1/2} + K^*_{OH'} \dfrac{p_{H_2O}}{p_{H_2}^{1/2}}\right) \left(1 + K_{H^{1a}}^{1/2} p_{H_2}^{1/2}\right)} \qquad \text{Eq. 1}$$

$$r_W = \frac{k^*_W K^*_{OH'} \dfrac{p_{CO} p_{H_2O}}{p_{H_2}^{1/2}} \left(1 - \dfrac{p_{H_2} p_{CO_2}}{K_W p_{CO} p_{H_2O}}\right) C^{T\,2}_{S_1} S_A}{\left(1 + K^*_{CH_3O'} \dfrac{p_{CH_3OH}}{p_{H_2}^{1/2}} + K^*_{HCOO'} p_{CO_2} p_{H_2}^{1/2} + K^*_{OH'} \dfrac{p_{H_2O}}{p_{H_2}^{1/2}}\right)^2} \qquad \text{Eq. 2}$$

$$r_D = \frac{k_D K^*_{CH_3O^{(2)}} \dfrac{p_{CH_3OH}}{p_{H_2}^{1/2}} \left(1 - \dfrac{p_{H_2}^2 p_{CO}}{K_D p_{CH_3OH}}\right) C^T_{S_2} C^T_{S_{2a}} S_A}{\left(1 + K^*_{CH_3O^{(2)}} \dfrac{p_{CH_3OH}}{p_{H_2}^{1/2}} + K^*_{OH^{(2)}} \dfrac{p_{H_2O}}{p_{H_2}^{1/2}}\right) \left(1 + K_{H^{(2a)}}^{1/2} p_{H_2}^{1/2}\right)} \qquad \text{Eq. 3}$$

In equations 1-3, S_A is the BET surface area of the catalyst, and $C^T_{S_1}$, $C^T_{S_{1a}}$, $C^T_{S_2}$ & $C^T_{S_{2a}}$ are total site concentrations (mole-m^{-2}). As discussed above, the site concentrations are determined by fitting the packed-model to experimental data as

described in [10]. Once determined, they are fixed and the same for both the packed-bed and foam reactor (equal intrinsic activity)

The rates of reactions are combined to give the rate of the species formation R_i (moles-sec^{-1}-kg of catalyst^{-1}):

$$-R_{CH_3OH} = r_R + r_D$$

$$-R_{H_2O} = r_R + r_W$$

$$R_{H_2} = 3r_R + 2r_D + r_W$$

$$R_{CO_2} = r_R + r_W$$

$$R_{CO} = r_D - r_W$$

5   Packed-Bed Reformer Model

5.1   Description of Model

The pseudo-homogenous approach yields the following equation for temperature (T) in the presence of reaction:

$$\rho u_s C_{p,gas} \frac{\partial T}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(rk_{eff}\frac{\partial T}{\partial r}\right) - \frac{1-\varepsilon}{1-\bar{\varepsilon}}\eta\rho_{cat}\sum_{rxn}\left(\Delta H_{rxn}\right)_i r_i \qquad \text{Eq. 4}$$

where ρ_{cat} is the bulk density of the catalyst, (kg m^{-3}), $C_{p,cat}$ is the heat capacity of the catalyst pellets (J-K^{-1}-kg^{-1} of catalyst), u_s the superficial velocity (m-sec^{-1}), ρ the total density of the reaction mix (kg m^{-3}), $C_{p,gas}$ the heat capacity of the reaction mix (J-K^{-1}-kg^{-1}), k_{eff} the effective thermal conductivity of the catalyst bed (J-K^{-1}-m^{-1}), ε the fraction of the reactor volume occupied by gas (void fraction) at a radial location, $\bar{\varepsilon}$ the average void fraction for the bed, η the effectiveness factor, r_i is the rate of ith reaction (moles-sec^{-1}-kg of catalyst^{-1}, see below) and $\left(\Delta H_{rxn}\right)_i$ is the heat of the reaction for the ith reaction (W-kg of catalyst^{-1}) at the given reaction conditions (temperature, pressure and composition).

The equation for species mass fraction (ω_i), again in the presence of reaction, is:

$$\rho u_s \frac{\partial \omega_i}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\rho D_{eff}\frac{\partial \omega_i}{\partial r}\right) + \frac{1-\varepsilon}{1-\bar{\varepsilon}}\eta\rho_{cat}M_i R_i \qquad \text{Eq. 5}$$

where R_i is the rate of production of the ith species (moles-sec^{-1}-kg of catalyst^{-1}, see below), M_i is the molar mass of the ith species, D_{eff} the effective mass diffusivity (m^2-sec^{-1}),

The axial superficial velocity is calculated from:

$$-\frac{dP}{dz} = 150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu}{d_p^2}u_s + 1.75\frac{(1-\varepsilon)}{\varepsilon^3}\frac{\rho}{d_p^2}u_s^2 - \frac{\mu_{eff}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_s}{\partial r}\right) \qquad \text{Eq. 6}$$

where μ is the mixture viscosity (Pa-sec), d_p the equivalent particle diameter (m) and μ_{eff} is the effective viscosity, an empirical parameter adjusted to better fit the predictions of Eq. 6 to experimental isothermal velocity profiles. In this work μ_{eff} is set equal to the mixture viscosity (μ).

It is further assumed that the pressure drop through the reactor is negligible so that the reactor is isobaric. Eq. 6 is solved by determining $-dP/dz$ so that overall conservation of mass is satisfied,

$$\dot{m}_{inlet} = \int 2\pi r \rho u_s \, dr \qquad \text{Eq. 7}$$

where $\dot{m}_{inlet}$ is the total mass flow into (and through) the reactor (kg-sec^{-1}). Also needed in Eq. 6 is the porosity profile, $\varepsilon(r)$. For cylindrical catalyst pellets, the correlations developed by Bey and Eigenberger [14] (oscillatory void profile) are used. The density ρ is calculated from the ideal gas law. The bulk density of the catalyst (ρ_{cat}) is 1.2 kg-m^{-3} while the BET surface area for fresh catalyst is 73 m^2-kg^{-1} [15].

5.2 Correlations for Effective Transport Properties

The effective thermal conductivity is computed from the standard correlation:

$$\frac{k_{eff}}{k_{gas}} = \frac{k_{eff}^0}{k_{gas}} + \frac{1}{Pe_h} \cdot PrRe \qquad \text{Eq. 8}$$

where k_{eff}^0 is the stagnant effective thermal conductivity and Pe_h the Peclet Number for radial heat transfer. In applying this correlation, we have assumed $Pe_h = 8$ and $k_{eff}/k_{eff}^0 = 5$, both standard values [16, 17]

We further assume that the complete analogy between heat and mass transfer holds in the packed-bed so that $Pe_m = 8$. The effective mass diffusivity then follows from the definition of Pe_m:

$$D_{eff} = \frac{d_p u_s}{Pe_m} \qquad \text{Eq. 9}$$

5.3 Boundary Conditions

At the centre of the packed-bed, since it is a line of symmetry, all gradients are zero. At the wall of the reactor, the gradient of any species (mass fraction) again must be zero.

Since the effective thermal conductivity is computed up to the reactor wall, the bed temperature must be equal to the wall temperature:

$$T(z, R) = T_{wall} \qquad \text{Eq. 10}$$

At the bed inlet, temperature and mass fractions are set equal to the inlet values:

$$T(0, r) = T_{inlet}$$
$$\varpi_i(0, r) = \varpi_{i, inlet}$$

6 Foam Reactor Model

6.1 Description of Model

The pseudo-homogenous methodology is used to formulate the governing equations for the Foam Reactor. The equations for the temperature and species fields are given by equation 4 and 5.

These equations undergo two simplifications when used to simulate the Foam Reactor. First the porosity is constant for the foam so that $\varepsilon = \bar{\varepsilon}$. Second, as discussed above, the effectiveness factor (η) is one.

We further assume that the superficial velocity is uniform in the radial direction (i.e. plug flow assumption), consistent with the uniform porosity of the foam. The superficial velocity is computed from an overall mass balance:

$$\dot{m}_{inlet} = u_s \int 2\pi r \rho dr$$

Eq. 11

The pressure drop through the foam is small and it is reasonable to assume that the reactor is isobaric.

The reactions and rate expressions for the Foam Reactor are the same as those for the Packed-bed reactor (equations 1–3) with the notable exception of the catalyst surface area (S_A). For the foam, we assume a value of 20m^2-g^{-1}. The values of the site concentrations ($C_{S_1}^T$, $C_{S_{1a}}^T$, $C_{S_2}^T$ & $C_{S_{2a}}^T$) are the same for the Foam Reactor and the Packed-bed.

6.2 Correlations for Effective Transport Properties

The effective thermal conductivity is computed from a correlation developed by Peng & Richardson [12]:

$$\frac{k_{eff}}{k_{gas}} = \frac{6.84 \times 10^{-5} (1/S_V) T^3}{k_{gas}} + 42.2 Re_s$$

Eq. 12

where S_V is the external surface area of the foam per unit volume of foam (m^2-m^{-3}) and Re_S is the Reynolds Number for the foam, $\rho u_s (1/S_V)/\mu$. The above correlation summarizes measurements by Peng & Richardson for 30 PPI ceramic foam without a washcoat. The addition of washcoat roughens the external surface so that the dynamic term becomes larger at a given Re_S (i.e. coefficient of Re_S increases with the addition of washcoat; see Peng & Richardson [12], equations (21) – (23)). In our work, no adjustment to the above correlation is made to account for the presence of the washcoat.

Peng & Robinson didn't measure the effective mass diffusivity (D_{eff}) for the 30 PPI foam. We will assume, as with the packed-bed model, the complete analogy between heat and mass transfer holds $(Pe_m = Pe_h)$ and obtain the Peclet Number for heat from Equation 12.

If Equation 12 is written in the same manner as Equations 9 then we have:

$$\frac{k_{eff}}{k_{gas}} = \frac{6.84 \times 10^{-5} (1/S_V) T^3}{k_{gas}} + 70.3 Re_s Pr$$

Eq. 13

which implies that $Pe_m = Pe_h = 1/70.3 = 0.0142$ (with $Pr = 0.6$), about 550 times smaller than the Peclet Number for packed-beds.

6.3 Boundary Conditions

Boundary conditions are the same as the packed bed except for temperature at the reactor wall. At the centre of the foam, since it is a line of symmetry, all gradients are zero. At the wall of the reactor, the gradient of any species (mass fraction) again must be zero.

At the reactor wall, the temperature satisfies a mixed (Robin) boundary condition:

$$\alpha_W (T_{wall} - T(z, R)) = -k_{eff} \left. \frac{dT}{dr} \right|_{r=R}$$

Eq. 14

where α_W is the wall heat transfer coefficient and given by Equation 26 in Peng & Richardson [12].

At the reactor inlet, temperature and mass fractions are set equal to the inlet values:

$$T(0, r) = T_{inlet}$$
$$\varpi_i(0, r) = \varpi_{i, inlet}$$

7   Results

The reformer geometry mimics the semi-commercial reformer described above. The inner diameter of the reactor is 5.715 cm, length is 47 cm so that the reactor volume is about 1.2 L. The feed is 35 cm^3/min of a 54% by weight methanol-water solution. The wall temperature is constant at 300ºC and the inlet temperature is equal to the wall temperature.

The key parameters for the packed-bed are a bulk density (ρ_{cat}) of 1.2 g-cm^{-3} and the BET surface area of 73 m^2-g^{-1}. The total mass of catalyst in the reformer is about 1447 grams.

The key parameters for the catalytic ceramic foam are taken from Peng and Richardson [12] (Table 2, 30PPI foam, external surface area (S_V) of 3.24 x 104 m^2-m^{-3}, bulk density of 0.498 g-cm^{-3}). The bulk density of the catalyst is 0.055 g-cm^{-3} assuming an 11% by weight loading of washcoat. The internal (BET) surface of the washcoat is conservatively set at 20 m^2-g^{-1}. The total mass of catalyst in the reformer is about 66 grams.

Both models are implemented and solved in Femlab® 3.1i with calls to MATLAB® subroutines to compute molecular properties (viscosity, thermal conductivity, etc) and kinetics.

Two categories of metrics are used to compare performance of two different reformers. The first category is traditional metrics of methanol conversion, reformate flowrate (SLPM) and reformate composition.

The carbon monoxide concentration is an important criterion. It is well known that PEM fuel cells require very low levels of carbon monoxide (< 20 ppm) in the feed in order to avoid poisoning the platinum electrocatalyst in the anode. As the concentration of carbon monoxide in the reformate increases, the size of the Water-Gas Shift reactors must also increase in order to reduce the carbon monoxide level to less than 20 ppm.

The second category of metrics is gross measures of hydrogen productivity on a volume or mass basis. They are computed as the flow of hydrogen in the reformate (moles/min) divided by the volume of the reactor or the mass of catalyst. In the case of the catalytic ceramic foam, only the washcoat is considered catalyst while the supporting ceramic foam is excluded.

A summary of the simulations is presented in Table 1.

The first results (A) are for the base case for the packed-bed reformer. A high conversion of methanol is observed which leads to a reformate flowrate of ~44 SLPM. The reformate composition is about 74% hydrogen, 22% carbon dioxide and 3.4% carbon monoxide. It would be possible to reduce the CO level by lowering the wall temperature thereby lowering the temperatures in the reformer but this would also reduce the conversion and the production of hydrogen.

The second case (B) is for the base case for the catalytic ceramic foam. The conversion is about 62%, roughly two-thirds the conversion computed for the packed-bed. The reformate flowrate is also reduced by almost two-thirds and the carbon monoxide concentration is slightly larger than the packed-bed at 3.8%.

Comments	Methanol Conversion	Reformate Flowrate	Reformate Composition		Relative Volumetric Productivity	Relative Mass Productivity
			Hydrogen	Carbon Monoxide		
		SLPM				
A. Pellets – base case	94.7	43.90	0.7414	0.0343	1.53	0.07
B. Foam - base case	62.1	28.69	0.7404	0.0383	1.00	1.00
B1. Bulk density (2X)	78.6	36.31	0.7403	0.0387	1.27	0.63
B2. BET surface area (2X)	78.6	36.31	0.7403	0.0387	1.27	1.27
B3. Wall heat transfer coefficient (2X)	70.7	32.25	0.7371	0.0514	1.12	1.12
B4. External surface area (2.11X)	66.8	30.70	0.7390	0.0441	1.07	1.07
B5. Double BET & wall heat transfer	88.5	40.33	0.7368	0.0529	1.40	1.40
B6. Reactor length (2X)	89.7	40.91	0.7369	0.0523	0.71	0.71

Table 1 Reactor Metrics obtained from simulations of packed-bed reformer ('Pellet') and catalytic ceramic foam reformer ('Foam'). The Relative Productivities are computed by taking the 'Foam - base case' predictions as unity.

A notable difference between the 'Foam – base case' & 'Pellet – base case' simulations are the temperature profiles. For the Foam the temperature (and species concentration) profiles vary in the axial direction but are flat in the radial direction. The catalytic ceramic foam has exceptional radial mixing leading to uniform temperatures and concentrations in the radial direction. In contrast, the 'Pellet – base case' has large variations in temperature from wall to centerline. At one point, the wall – centerline temperature difference exceeds 100°C, consistent with experimental data [10].

The packed-bed is clearly greater in its production of hydrogen. The volumetric productivity metric shows that the packed-bed has about 1.5 times greater productivity per unit volume than the catalytic ceramic foam. However, examination of the mass productivity shows the opposite: the catalytic ceramic foam is an order of magnitude more productive than the packed-bed.

The opposition of the metrics is due to the utilization of the catalyst in the reformer. In the packed-bed, there is a large amount of catalyst (1447 grams) but due to the limitations of mass transfer (effectiveness factor < 1) not all the catalyst is exposed to the bulk concentrations (i.e. poorly or modestly utilized). In the catalytic ceramic foam, the amount of catalyst is only 66 grams – about 20 times less catalyst compared to the packed-bed. However, since the rate of reaction is kinetically controlled (i.e. mass transfer limitations are small) the catalyst is fully utilized. So on a volume basis the packed bed reactor is superior in terms of productivity but on a mass basis, it is inferior.

We now investigate ways to increase the productivity of the catalytic ceramic foam reformer without changing the reactor geometry. Four factors are examined: bulk density of the catalyst (ρ_{cat}), internal (BET) surface area (S_A), wall heat transfer coefficient (α_W), and external surface area (S_V). Results of the simulations are presented in Table 1, Cases B1-B5.

In the first case (B1), the bulk density of catalyst is doubled. The methanol conversion is increased from 62% to about 79% and the volumetric productivity is increased by 27%. However, the mass productivity drops as the increase in hydrogen flow (27%) is less than doubling of the catalyst mass. The CO concentration is only slightly more than then base case.

The internal (BET) surface is now doubled to 40 m^2-g^{-1}. The methanol conversion is again increased from 62% to 79% and the volumetric productivity increases by 27%. There is an equal increase in the mass productivity as the catalyst mass has not changed. The CO concentration is again only slightly more than the base case.

Although not immediately apparent in the governing equations, these two factors are multiplied to obtain the total rate of production or consumption of a species. Doubling either the BET surface area or the catalyst mass is equivalent to doubling the rate of reaction so that each has the same effect on reformer performance.

For the third case (B3), the wall heat coefficient is doubled so that the heat flow at the wall is improved. The methanol conversion increases from 62% to 71% with a 12% increase in hydrogen flow compared to the base case. Similar to increasing the internal surface area, both the mass and volume productivity increase by equal amounts.

However, the CO level in the reformate increases significantly from 3.8% to 5.1%. This is caused by the higher temperatures in the reformer associated with faster kinetics and greater production of hydrogen.

The last factor is increasing the external surface area (B4). For this case, the 30 PPI foam is replaced with a 65 PPI foam [18, Table 4] with a external surface are of 6.84 x 10^4 m^2-m^{-3}, an increase of 2.11 times. The increased external surface area increases the Reynolds Number (Re_S), which improves both the wall heat transfer coefficient and the effective thermal conductivity through the respective correlations. No other factor is altered compared to the base case.

The methanol conversion is modestly increased to 67% and the volume and mass productivity both increase by 7% (due to a 7% increase in the hydrogen flow). The CO concentration is 4.4% higher than the base case but less than the CO level computed when the wall heat transfer coefficient is doubled.

In the next case (B5), both the BET surface area and the wall heat transfer coefficient are doubled. The methanol conversion increases from 62% to 88.5% and the productivity metrics increase by 40%. The CO concentration also increases significantly to 5.3% reflecting the higher reactor temperatures due to the improved heat transfer at the wall.

It is worth noting, for this case, that the catalytic ceramic foam produces about 93% of the hydrogen flow of the 'Packed-bed – base case' scenario with less than 5% of the mass of the catalyst.

The last case (B6) involves doubling the length of the reactor by a factor of 2. The methanol conversion and hydrogen flow are comparable to the last scenario (B5) and again modestly less than that of the packed-bed (A). The performance metrics drop due to the increased volume and mass of catalyst.

In doubling the reactor length two factors are altered. First, the mass of catalyst is doubled. Second, the surface area for heat transfer to the reformer is also increased. So comparing this case (B6) to B1, there is seen a significant increase in methanol conversion (79% versus 90%) and a similar increase in the hydrogen flow.

The above cases show the sensitivities of the catalytic foam reactor to significant improvements in the properties of the catalyst (i.e. doubling the loading, doubling wall heat transfer, etc). The best method of improving the performance is to increase the internal (BET) surface area, followed by increase the catalyst loading with third best method improve the wall heat transfer coefficient. Of course, it is tacitly assumed that improving one factor doesn't degrade any other factor. So, for example, increasing the internal surface area doesn't cause a loss in catalyst loading or a reduction in wall heat transfer coefficient.

Increasing reactor length is perhaps not the most advantageous method for increasing hydrogen flow, but, when other methods are not possible, it remains as an option.

8 Summary

The key characteristic of catalytic ceramic foams is the improvement in both external and internal mass transfer. The mixing induced by the open cells and connecting struts leads to very small radial Peclet numbers compared to packed-beds. A consequence is that temperature and species profiles are uniform in the radial direction and the mass transfer to the surface of the washcoat is excellent.

Since the washcoat is thin, mass transfer limitations due to diffusion in the pores is not significant so that the effectiveness factor is close to unity.

The improvement in mass transfer is obtained at a price, however. The bulk density of the catalyst is very low due to the thinness of the washcoat and the high porosity of the foam. In the case of methanol-steam reforming, this limits the productivity of the reformer. Clearly, one way to compensate for the low bulk density is to advance the formulation of the washcoat so that it generates a large internal (BET) surface area without adversely affecting other properties of the washcoat.

9 Acknowledgements

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