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Tube Fitted Bulk Monolithic Catalyst as a Novel Concept for Hydrogen Production for Fuel Cell Application

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A novel fixed bed reactor for natural gas steam reforming reaction using bulk monolithic catalyst (BMC), the so-called tube fitted bulk monolithic catalyst (TFBMC), is presented. The physical parameters of various TFBMC shapes have been analysed. Using modelling analysis, the performance of the selected TFBMC configuration as compared with the other BMC configuration and commercial pellet shape have been studied and analysed for hydrogen production by natural gas reforming reaction. It was indicated that the intraparticle mass transfer limitation can be eliminated and the size of rector can decrease considerably which are necessary for fuel cell application.

1. Introduction

Methane steam reforming is still the most economical routes for hydrogen production. It generates hydrogen for refining processes, food industry, and recently for fuel cell application.The rate of the methane steam reforming reactions is controlled by the intraparticle mass transfer limitations. Studies show that the effectiveness factor is very small and in the order of 10^{-2} (Xu and Froment, 1989). Therefore, this is an important challenge from economical point of view because about 95 % of the catalyst loaded into the conventional reactor tubes, is not utilized (Soltan M. and Zamaniyan, 2002). For fuel cell applications, especially portable applications, this is more important parameter. Thus many researches have been performed to develop new more active catalyst and or compact reactors (Palma et al., 2011 and Liang et al., 2011).

For strongly diffusion limited reactions, such as reforming reaction, the effective reaction rate is proportion to the geometric surface area per pellet volume (Bruno et al. 1988) and the catalyst activity may be improved by providing high value of this parameter. Since the size and shape of the catalyst is constrained by the need to maintain a low pressure drop in the bed and proper mechanical strength, manufacturers have introduced new multi holed-cylinders so as to increase external surface area of the pellets. Recently the cylindrical pellet shape with four, five, seven and ten holes and also spoke wheel pellet shape have been proposed and applied in industrial reformer. A number of studies have investigated the effect of catalyst shape on the performance of reforming reaction, but the results show that even using these catalyst shapes, the effectiveness factor is low and still about 85% of the catalyst doesn’t utilize in the reaction.

Recently researches have focused on monolithic catalyst, as structured catalyst, to be used in mass transfer limited-reactions (Zamaniyan et al., 2010; Kolb et al. 2011). The studies indicate that there are potentially several advantages for monolithic reactor as compared to the packed reactors such as: lower pressure drop, better mass transfer performance, higher specific surface area, lower investment and operation costs, higher productivity, higher mechanical strength, milder operating conditions, evenly distributed flow, better heat transfer, and larger degrees of freedom in flow type, e.g. down, up

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and horizontal flow (Zamaniyan et al., 2010). The reforming reaction, as a mass transfer limited gas solid reaction, has potentially attractive to apply monolithic catalyst especially for fuel cell applications. Some studies have investigated reforming reaction using monolithic catalyst (Kolb et al., 2011).

It must be noted that there are two types of monolithic catalysts, washcoated monolithic catalyst (WMC), and bulk monolithic catalyst (BMC). For the WMC, the active phase is somehow coated on a structured support. For the second type the whole monolithic body is made out of the catalytic material. Zamaniyan et al. (2010) have discussed the advantages and disadvantages of the two mentioned type. It was demonstrated that there are some disadvantages for WMC as compared to the pellet and BMC types. Also WMC make more volume as compared to BMC type, due to need an inert support for washcoat of the active phase, which is important parameter for fuel cell applications. These disadvantages prevent extensive use of the WMC and so far have found very limited commercial use.

In this study a new concept for packaging of BMC and reactor loading, the so-called tube fitted bulk monolithic catalyst (TFBMC) that has been introduced and described by Zamaniyan et al. (2010), has been selected. A detailed investigation for selecting of the best shape has been performed. The performance of the selected BMC configuration as compared with the other BMC configuration and commercial pellet shape have been studied and analysed for natural gas steam reforming reaction.

2. Investigation and modelling

The monoliths are characterized by the size and geometry of the channel diameter (d_{ch}), the void fraction (ε) or open frontal area (OFA), and the cell density usually designated by number of cells per square inch (cpsi). The cpsi coupled with wall thickness, dictates the geometric surface area (GSA), a key factor for mass transfer-controlled reactions and also for pressure drop. The optimum design is based on the intrinsic kinetics of the reactions and transport phenomena on one hand, and the physical shape on the other hand. Various channel shapes such as hexagonal, trigonal, square and circular can be made. For circular shape, the triangular, square and circular arrangements are possible too (Figure 1). The size of the channels and the wall thickness may be varied independently.

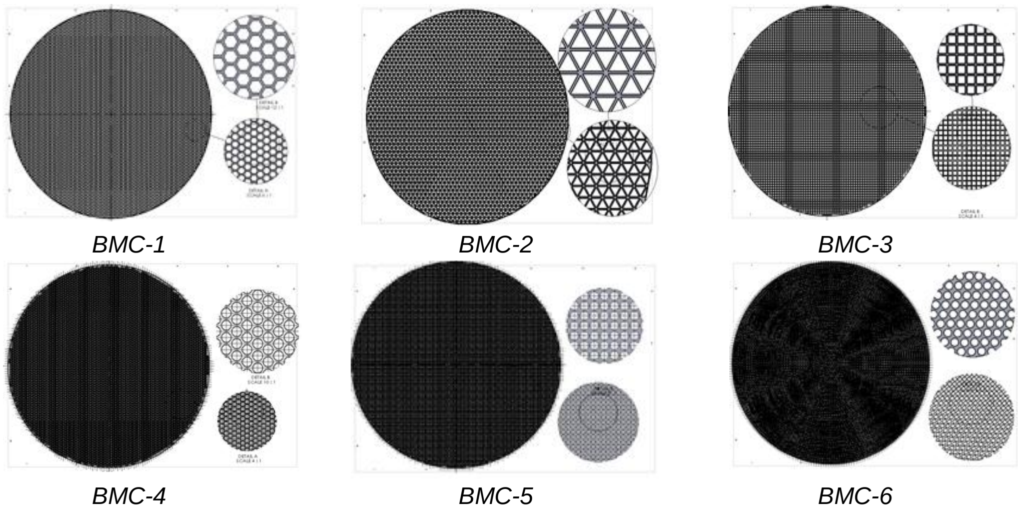

Figure 1: Various channel shapes and arrangements for bulk monolithic catalyst preparation BMC-1: hexagonal, BMC-2: trigonal, BMC-3: square, BMC-4: circular-triangular arrangement, BMC-5: circular-square arrangement, BMC-6: circular-circular arrangement.

Details of the model have been described by Zamaniyan et al. (2011). Here the main equations are presented. A one-dimensional heterogeneous model is used for chemical reaction in the tubes. The main reactions occurring in the reactor in the course of methane reforming are methane-steam reforming (r_1), water gas shift (r_2) and methanation (r_3) as following:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (r_1)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (r_2) \qquad (1)$$
$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (r_3)$$

The kinetics of the reforming reaction is well known and has been widely investigated. The intrinsic kinetic and reaction rates have been introduced by Xu et al. (1989a). As only thin layer of the catalyst contribute for reaction, to find the profile of partial pressure of each component in the catalyst pores, planar geometry can be used for solving continuity equations in the model. Thus the mass balance equations for different catalyst shape are similar. The equations governing partial pressures of CH_4 and CO_2 are derived as sample for reactant and product respectively:

$$D_{e,CH_4} \frac{d^2 P_{s,CH_4}}{d\xi^2} = 10^{-2} RT.\chi^2.r_{CH_4}.\rho_s \qquad (2)$$

$$D_{e,CO_2} \frac{d^2 P_{s,CO_2}}{d\xi^2} = 10^{-2} RT.\chi^2.r_{CO_2}.\rho_s \qquad (3)$$

Which for Pellet: $\xi = \frac{r}{R_p}$, $\chi = R_p$ (4)

for TFBMC (Fig. 3): $\xi = \frac{r}{w}$, $\chi = w$ (5)

The boundary conditions are:

$$\frac{dP_{s,CH_4}}{d\xi} = \frac{dP_{s,CO_2}}{d\xi} = 0 \quad \text{at} \quad \xi = \infty \qquad (6)$$

$$P_{s,CH_4} = P_{CH_4} \text{ , } P_{s,CO_2} = P_{CO_2} \text{ at } \xi = 1 \qquad (7)$$

Parallel cross-linked pore model with uncorrelated pore size distribution and orientation have been used for evaluation of components effective diffusivity in the catalyst side (Zamaniyan et al. 2008). The concentration of CH_4 and CO_2 may be fitted by polynomial equation of order n:

$$P_{s,CH_4} = a_1 x^n + a_2 x^{n-1} + a_3 x^{n-2} + ... + a^n x + a_{n+1} \qquad (8)$$

$$P_{s,CO_2} = b_1 x^n + b_2 x^{n-1} + b_3 x^{n-2} + ... + b^n x + b_{n+1} \qquad (9)$$

D_e, P_s, R, T, r_i, ρ_s and R_p denominated to the effective diffusion coefficient (m^2s^{-1}), catalyst surface pressure (bar), universal gas constant ($kJkmol^{-1}K^{-1}$), temperature (K), rate of reaction for component i ($kmolkgcat^{-1}h^{-1}$), solid density ($kg_{cat}m^{-3}{}_{cat}$) and particle radius (m) respectively.

3. Results and discussion

The value of desired parameters can be obtained by solving the governing equations (nonlinear) using finite difference and orthogonal collocation methods. Figures 2 and 3 show the rate of reactions and the profile of the components concentration inside the catalyst pore, respectively. As Figure 2 shows the reforming reactions take place in a thin layer close to the catalyst surface. Figure 3 shows that concentration profile of the reactants on catalyst layer is quite steep. In fact about 93 % of variations in the reactant concentration occur within only 100 μm of thickness.

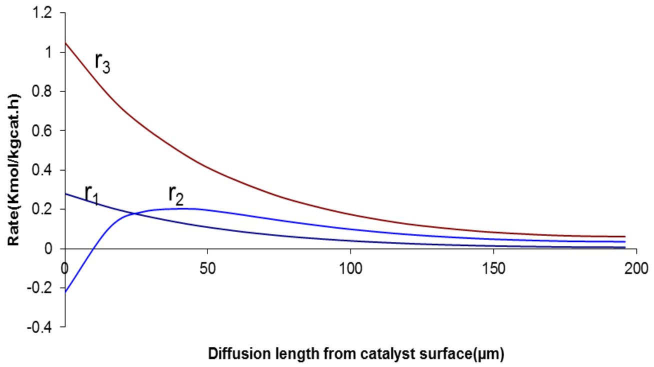

Figure 2: Rate of reforming reactions at catalyst layer

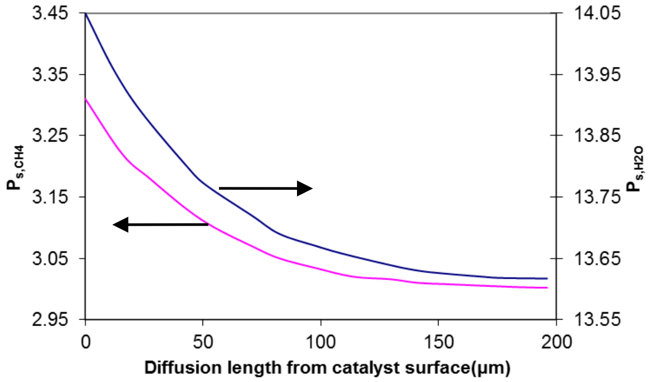

Figure 3: Partial pressure of reactants at catalyst layer

These results show clearly that only the outer layer of the catalyst contributes to the reactions and the effectiveness factor is a function of the catalyst shape. The size of this layer is sometimes described as the effectiveness factor. Therefore it may be concluded that proper design of the catalyst shape can increase the external surface area, improves the effectiveness factor and furthermore the catalyst usage. The special consideration must be applied to find the optimum catalyst layer and design the structured catalyst. Here the wall thickness of 200 μm has been selected for all configurations in Fig.1. Table 1 gives the value of the physical parameters for the mentioned structures in Fig. 1, calculated by the Solid Work software.

Table 1: The characteristics of various types of bulk monolithic catalyst.

Channel type	Solid Volume (cm^3)	Exposed surface area (cm^2)	cpsi	OFA (cm^2) / %
hexagonal	2410.7	217,778	516	54.4 / 69.3
trigonal	2244.9	224,405	355	56.1 / 71.4
square	2410.7	217,778	447	54.4 / 69.3
Circular: (triangular arrangement)	2917.5	197,518	516	49.4 / 62.8
Circular: (square arrangement)	3578.9	171,076	447	42.7 / 54.4
Circular: (circular arrangement)	3527.4	173,134	443	43.3 / 55.1

The data for various types are reported for the same outer monolith diameter (10 cm), the same channel hydraulic diameter (1 mm), the same wall thickness 200 μm and the same length of reactor (100 cm). As is observed in Table 1, the characteristics of monolith depend strongly on the channel shape and arrangement. The square and hexagonal types have the best characteristics. Figure 4 show the weight of total catalyst applied and the weight of used catalyst in reaction for various shapes of Fig. 1. Although the BMC-5 and BMC- 6 indicate the maximum applied catalyst weight, but they appropriate lowest weight of used catalyst in the reaction. In fact the BMC-1 and BMC-3 show the best results in this field due to almost all applied catalyst has been contributed in the reaction

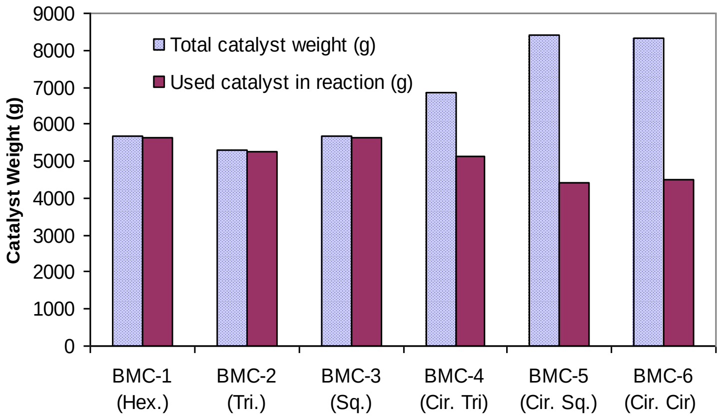

Figure 4: Weight of total catalyst applied and used catalyst in reaction for various shapes of Fig. 1

Figure 5 illustrates the percent of catalyst usage and the percent of used catalyst per reactor volume for various shapes of Fig. 1. The BMC-1, BMC-2 and BMC-3 indicate maximum value of catalyst usage percent close to 100 %. Also the BMC-1 and BMC-2 reveal the highest value and the BMC-5 and BMC-6 reveal the lowest value for percent of use catalyst in reaction.

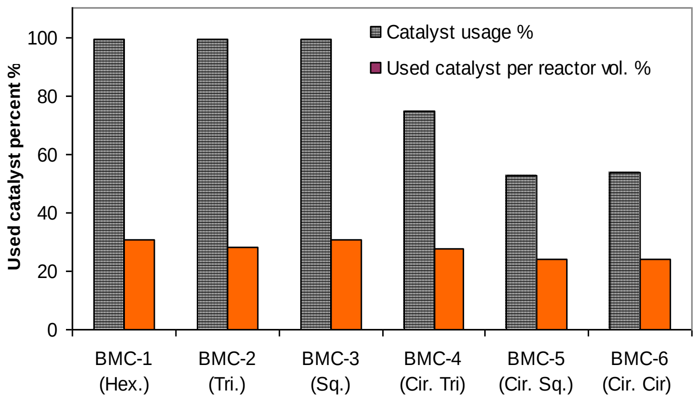

Figure 5: Percent of catalyst usage and used catalyst per reactor volume for various shapes of Fig. 1

From Figures 5 and 6 it can be concluded that the BMC-1 and BMC-3 show the best results. These catalysts indicate that almost all applied catalyst contribute in the reaction and appropriate the highest value for the used catalyst per rector volume. Table 2 presents the performance of the BMC-3 as compared with some commercial pellets of cylinder shape, single channel shape (ICI 57-3), four channel cylinder pellet (ICI 57-4M) and seven channel cylinder pellet (Sud Chemie). As Table 2 indicates the BMC-3 shows the highest value of reactor bed void fraction that in turn means the lowest pressure drop. The weight of catalyst usage for the BMC-3 is 6-15 folds of that for the pellet shapes.

Although the BMC-3 appropriates the lowest value of catalyst weight but this not the key parameter. The maximum value of the catalyst usage, in turn catalyst effectiveness factor, for the pellet shapes is about 12 %, while this value for the BMC-3 close to 100 %. This means that using BMC-3, the intraparticle mass transfer limitation can be eliminated.

Table 2: The characteristics of various types of bulk monolithic catalyst.

Catalyst type	**Cylinder pellet**	**Single channel cylinder pellet**	**Four channel cylinder pellet**	**Seven channel Cylinder pellet**	**BMC-3**
Reactor bed void fraction	0.43	0.57	0.61	0.62	0.69
Total catalyst weight (kg)	10.53	7.85	7.12	7.03	5.68
Used catalyst based on total loaded catalyst (%)	3.48	4.77	12.33	9.47	99.3
Total exposed ext. surface area in reaction (cm^2)	15786	16037	37375	28322	217778
Weight of used catalyst in reaction (kg)	0.36	0.37	0.88	0.67	5.64
Effectiveness factor	0.04	0.05	0.12	0.1	~ 1

4. Conclusion

The results indicate how the TFBMC can apply for hydrogen generator for fuel cell application that need to small scale device at the same time proper production rate. With proper design, reactor with TFBMC indicates superior advantages such as lower pressure drop, more used catalyst per reactor volume, higher value of external surface area and 100 % usage of the loaded catalyst. Also TFBMC can be adopted for vertical and horizontal reactors which make it applicable for special cases.

For TFBMC, the effectiveness factor and catalyst usage close to one and 100 % respectively that means the intraparticle mass transfer limitation can be eliminated. This leads to minimize the reactor volume with the same catalyst weight or larger amount of the products at the same reactor volume.

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