

Catalysis, Kinetics and Reaction Engineering

Numerical simulation of fixed bed reactor for oxidative coupling of methane over monolithic catalyst[☆]

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ABSTRACT

A three-dimensional geometric model was set up for the oxidative coupling of methane (OCM) fixed bed reactor loaded with $\text{Na}_3\text{PO}_4\text{-Mn/SiO}_2$ /cordierite monolithic catalyst, and an improved Stansch kinetic model was established to calculate the OCM reactions using the computational fluid dynamics method and Fluent software. The simulation conditions were completely the same with the experimental conditions that the volume velocity of the reactant is $80 \text{ ml} \cdot \text{min}^{-1}$ under standard state, the CH_4/O_2 ratio is 3 and the temperature and pressure is $800 \text{ }^\circ\text{C}$ and 1 atm, respectively. The contour of the characteristic parameters in the catalyst bed was analyzed, such as the species mass fractions, temperature, the heat flux on side wall surface, pressure, fluid density and velocity. The results showed that the calculated values matched well with the experimental values on the conversion of CH_4 and the selectivity of products (C_2H_6 , C_2H_4 , CO , CO_2 and H_2) in the reactor outlet with an error range of $\pm 4\%$. The mass fractions of CH_4 and O_2 decreased from 0.600 and 0.400 at the catalyst bed inlet to 0.445 and 0.120 at the outlet, where the mass fractions of C_2H_6 , C_2H_4 , CO and CO_2 were 0.0245, 0.0460, 0.0537 and 0.116, respectively. Due to the existence of laminar boundary layer, the mass fraction contours of each species bent upwards in the vicinity of the boundary layer. The volume of OCM reaction was changing with the proceeding of reaction, and the total moles of products were greater than reactants. The flow field in the catalyst bed maintained constant temperature and pressure. The fluid density decreased gradually from $2.28 \text{ kg} \cdot \text{m}^{-3}$ at the inlet of the catalyst bed to $2.18 \text{ kg} \cdot \text{m}^{-3}$ at the outlet of the catalyst bed, while the average velocity magnitude increased from $0.108 \text{ m} \cdot \text{s}^{-1}$ to $0.120 \text{ m} \cdot \text{s}^{-1}$.

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1. Introduction

The conversion of methane to chemicals and liquid fuels is achieved mainly by direct methods and indirect methods. The direct methods are more potential since they can avoid the syngas step [1]. Oxidative coupling of methane (OCM) is one of the direct methods and regarded as a promising way for methane conversion [2]. Various catalysts have been investigated by researchers for OCM reaction [3]. Among these, $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ particle, invented by Fang *et al.* in 1992 [4], is believed to be one of the most effective catalysts over the past thirty years. Jiang *et al.* [5] report that the existence of Na_2WO_4 can decrease the phase transition temperature of SiO_2 from amorphous to cristobalite, which plays an important role in the activity of $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst. Ji *et al.* [6,7] studies the effect of Na, W, Mn and other alkali metals on the structure and reaction performance of $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst. They confirm that WO_4 , which is apt to form transition state compounds with CH_4 , works as the active center of $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst. Some other studies [8,9] also find that

the presence of La and Li has positive effect on the activity and selectivity of $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ catalyst.

The OCM reaction is known to be highly exothermic, so it is easy to form hot spots in reactor. No less than $100 \text{ }^\circ\text{C}$ of temperature gap is measured by researchers during OCM reaction over $\text{La}_2\text{O}_3/\text{CaO}$ [10], Li/MgO [11], $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ and $\text{Mn-Na}_2\text{WO}_4/\text{MgO}$ [12] catalysts. The hot spot is a decisive factor in the performance of reactor, which may lead to temperature runaway, catalyst deactivation and even thermal cracking of the main products [13]. To inhibit the formation of hot spots and improve the selectivity of product, the selection of reactor and the alteration of contact mode between reactant and catalysts function a lot apart from the exploration of highly selective catalysts. Taniewski *et al.* [11] show that successive active catalyst layers can be involved and a nearly unchanged overall selectivity is given during the process of CH_4 transformation over the bed by changing the feed inlet locations. Talebizadeh *et al.* [13] study the OCM in a two-zone fluidized-bed reactor (TZFBR). In their work, diluted oxygen in argon is introduced into the bottom of the TZFBR, while methane is entered at higher positions along the fluidized bed. They find that the TZFBR gives a higher C_2 (both C_2H_6 and C_2H_4) selectivity than that obtained in the fluidized-bed reactor, since the CH_4 introduced in medium height decreases the concentration of O_2 , inhibiting the oxidation reaction occurred in gas

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phase. Pan *et al.* [14] study the OCM reaction in a dual-bed reactor loaded with $\text{Na}_2\text{WO}_4\text{-Mn/SiO}_2$ particle catalyst and $\text{Ce-Na}_2\text{WO}_4\text{-Mn/SiO}_2$ /cordierite monolithic catalyst. A maximum C_2 yield of 23.6% is obtained when the bed height of particle catalyst and monolithic catalyst are 10 mm and 50 mm respectively. It is noted that the raw gas must go through the particle catalyst first. Wang *et al.* [15] make extensive researches about OCM reaction in the above reactor. They confirm that similar results can be obtained if the monolithic catalyst is replaced by $\text{Na}_3\text{PO}_4\text{-Mn/SiO}_2$ /cordierite monolithic catalyst. They also claim that the OCM reaction is restrained by the low concentration of O_2 in monolithic catalyst bed since the raw gases first go through the particle catalyst layer. Therefore, a supplement of O_2 between the two beds is necessary [16]. After a series of researches, they improve the C_2 yield to 24.3% when the flow of extra O_2 is 15% of the inlet flow.

However, the experimental researches involve many disadvantages, such as high cost and long research cycle. By contrast, the simulation method can rapidly and accurately predict the reaction characteristics of OCM reactor, and provide basic data for the development of OCM technology [17–21]. The classic models of OCM fixed bed include 1D models [17,18] and 2D models [21], which discard the influence of three-dimensional flow field on heat transfer and chemical reaction. When reactor scale up, the three-dimensional effect is enhanced, so the classical model of OCM reactor will bring large error, unable to instruct the amplification of OCM process. Computational fluid dynamics (CFD) method is a simulation method based on flow field analysis. It can accurately predict the impact of three-dimensional flow field inside the reactor on heat transfer and chemical reaction. This method has been successfully applied to predict the reaction performance of the packed bed reactor loaded with SnBaTiO_3 catalyst [19,20]. However, the application of CFD on the fixed bed reactor filled with $\text{Na}_3\text{PO}_4\text{-Mn/SiO}_2$ /cordierite monolithic catalyst has not been seen in literature.

In this work, we improved the Stansch reaction kinetics model [22] using the existing experimental data [15], making it suitable to simulate the packed bed reactor filled with $\text{Na}_3\text{PO}_4\text{-Mn/SiO}_2$ /cordierite monolithic catalyst, and established a three-dimensional numerical model of OCM tubular packed bed reactor. The Fluent solver was used to solve the Navier–Stokes equations and species transport equations, and the reaction kinetics model added by the user-defined function (UDF) of Fluent software was adopted to estimate the actual reaction performance of reactor.

2. Model and Numerical Method

2.1. Geometric model and meshes

A fixed bed reactor with GHSV of 1920 h^{-1} was selected as the subject of study in this work. To diminish the error of model, we established a geometric model completely the same with the experimental apparatus [15] that is a tubular reactor with a diameter of 8 mm and a length of 600 mm. The catalyst bed with a height of 50 mm was settled in the middle of the tube, and two sections with a length of 75 mm were filled with quartz at its both ends (see Fig. 1(a)).

The meshes of cross-section, which was perpendicular to the symmetry axis of the reactor, were quadrilateral (see Fig. 1(b)), and all three dimensional meshes of the reactor were hexahedral for reducing numerical viscosity. To ensure the convergence of the numerical iteration and the independence of mesh, the aspect ratio of meshes in the bulk of the catalyst bed was about 1:1 and other sections were 1:3 respectively (see Fig. 1(c)). In order to accurately predict the laminar boundary layer effects on the flow and chemical reactions, the vicinity of reactor wall was portioned by inflation meshes of hexahedron (see Fig. 1(b)). The number of meshes in the reactor model was about 500,000.

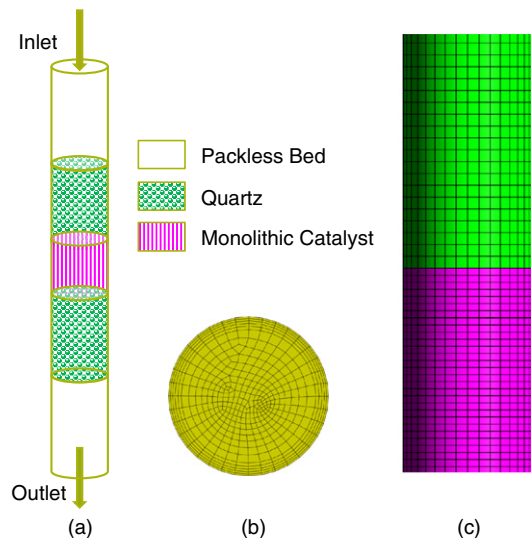


Fig. 1. Sketch (a), meshes and geometric model (b, c) of packed bed reactor of monolithic catalyst.

2.2. Governing equations

According to the operating conditions in literature [15], the flow in OCM packed bed reactor is laminar ($Re = 5.7$), which is suitable to be described by the Navier–Stokes equations [23]. The set of governing equations of flow is given as:

(1) Continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 \quad (1)$$

(2) Momentum equation

$$\rho \frac{\partial \mathbf{V}}{\partial t} + \rho \mathbf{V} \cdot \nabla \mathbf{V} = \nabla \cdot \mathbf{T} + \mathbf{S}_m \quad (2)$$

(3) Energy equation

$$\rho \frac{\partial H}{\partial t} + \rho \mathbf{V} \cdot \nabla H = \nabla \cdot (\mathbf{T} \cdot \mathbf{V}) + \nabla \cdot (k \nabla T) + S_h \quad (3)$$

where t is time, ρ is density, \mathbf{V} is velocity vector, \mathbf{S}_m is momentum equation source term, such as the drag caused by catalyst bed, T is temperature, S_h is energy equation source term, such as the energy released by chemical reaction, H is total energy, the sum of kinetic energy and internal energy, and \mathbf{T} is surface stress tensor.

The quartz particles and catalyst in the reactor can produce resistance to the flow. The drag can be calculated by porous medium model and added to the momentum equations in the form of source terms. For the isotropic porous medium, source terms of the momentum equations can be simplified as:

$$\mathbf{S}_{m,i} = - \left(\frac{\mu}{\alpha} u_i + c \frac{1}{2} \rho |\mathbf{V}_s| u_i \right) \quad (4)$$

where α is the permeability and c is the inertial resistance factor.

For the packed bed of quartz particles, the α and c can be obtained from empirical equations [24], which are expressed as:

$$\alpha = \frac{D_p^2}{150} \frac{\varepsilon^3}{(1-\varepsilon)^2} \quad (5)$$

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