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Numerical simulation of packed-bed reactor for oxidative coupling of methane

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Abstract

A three-dimensional geometric model of the oxidative coupling of methane (OCM) packed-bed reactor loaded with Na_2WO_4-Mn/SiO_2 particulate catalyst was set up, 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 was 80 mL/min under standard state, the ratio of CH_4/O_2 was 3, the temperature and pressure were 800 °C and 1 atm, respectively. The contour of the characteristics 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 to products (C_2H_6, C_2H_4, CO_2, CO) in the reactor outlet with an error range of ±2%. The mass fractions of CH_4 and O_2 decreased from 0.6 and 0.4 in the catalyst bed inlet to 0.436 and 0.142 in the outlet, where the mass fractions of C_2H_6, C_2H_4, CO and CO_2 were 0.035, 0.061, 0.032 and 0.106, respectively. Due to the existence of laminar boundary layer, the contours of each component bent upwards in the vicinity of the boundary layer. This OCM reaction was volume increase reaction and the total moles of products were greater than those of reactants. The flow field in the catalyst bed maintained constant temperature and pressure. The fluid density decreased gradually from 2.28 kg/m^3 in the inlet of the catalyst bed to 2.22 kg/m^3 in the outlet of the catalyst bed, while the velocity increased from 0.108 m/s to 0.115 m/s.

Key words

oxidative coupling of methane; packed-bed reactor; computational fluid dynamics; numerical simulation

1. Introduction

The conversions of methane to chemicals and liquid fuels are achieved mainly by indirect methods and direct 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, Na_2WO_4-Mn/SiO_2 particle, invented by Fang et al. in 1992 [4], is believed to be one of the most effective catalyst over the past thirty years. Jiang et al. [5] reports 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 Na_2WO_4-Mn/SiO_2 catalyst. Ji et al. [6,7] studies the effects of Na, W, Mn and other alkali metals on the structure and reaction performance of Na_2WO_4-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 Na_2WO_4-Mn/SiO_2 catalyst. Some other studies [8,9] also find that the presence of La and Li has positive effect on activity and selectivity of Na_2WO_4-Mn/SiO_2 catalyst.

The OCM reaction is known to be highly exothermic, so it is easy to form hot spots in a reactor. No less than 100 °C of temperature gap is measured by researchers during OCM reaction over La_2O_3/CaO [10], Li/MgO [11], Mn-Na_2WO_4/SiO_2 and Mn-Na_2WO_4/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 reactant, 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

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and a nearly unchanged overall selectivity is obtained 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 introduced CH_4 in medium height decrease the concentration of O_2, inhibiting the oxidation reaction occurred in gas phase. Pan et al. [14] study the OCM reaction in a dual-bed reactor comprising of Na_2WO_4-Mn/SiO_2 particle catalyst and Ce-Na_2WO_4-Mn/SiO_2/cordierite monolithic catalyst. A maximum C_2 yield of 23.6% is obtained when the bed heights 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 Na_3PO_4-Mn/SiO_2/cordierite monolithic catalyst. They also claim that the OCM reaction is restrained by low concentration of O_2 in monolithic catalyst bed since the raw gases firstly go through the particle catalyst layer. Therefore, an extra addition 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 the reactor is scaled up, the three-dimensional effect is enhanced, so the classical model of OCM reactor will bring large error, which is 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 for 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 packed-bed reactor filled with Na_2WO_4-Mn/SiO_2 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 Na_2WO_4-Mn/SiO_2 particle catalysts, 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 packed-bed reactor with GHSV of 9600 h^{-1} was selected as the subject of study in this work. To diminish the error, the established geometric model was completely the same with the experimental device [15] that is a circular tube with a diameter of 8 mm and a length of 600 mm. The height of catalyst bed was 10 mm and two sections with a length of 95 mm were filled with quartz at both ends (see Figure 1a).

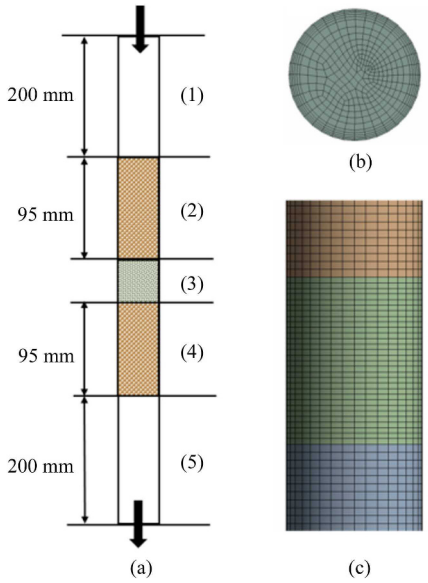

Figure 1. Sketch (a), meshes (b) and geometric model (c) of packed-bed reactor. (1) Preheating section, (2) quartz section, (3) catalyst section, (4) quartz section, (5) adiabatic section

The meshes of cross-section, which was perpendicular to the symmetry axis of the reactor, were quadrilateral (see Figure 1b), 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 Figure 1c). In order to accurately predict the laminar boundary layer effects on flow and chemical reactions, the vicinity of reactor wall was portioned by inflation meshes of hexahedron (see Figure 1b). The number of meshes in the reactor model was about 410000.

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-Stocks equations [23]. The set of governing equations of flow is given as:

(1) Continuity equation

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