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Numerical simulation of particle/monolithic two-stage catalyst bed reactor for oxidative coupling of methane

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ABSTRACT

Three-dimensional models were set up for the oxidative coupling of methane (OCM) two-stage packed bed reactors loaded with Na_2WO_4–Mn/SiO_2 particle catalyst and Na_3PO_4–Mn/SiO_2/cordierite monolithic catalyst using the computational fluid dynamics simulation. Firstly, the reactor with particle and monolithic catalyst bed heights of 10 mm and 50 mm was simulated. Secondly, the effects of particle and monolithic catalyst bed heights on reactor performance were investigated. The results showed that the simulation 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) in the reactor outlet with an error range of ±10%. The monolithic catalyst bed had a higher C_2 (C_2H_4 and C_2H_6) selectivity and less O_2 consumed than the particle catalyst bed did. When the heights of particle and monolithic catalyst bed were 10 mm and 50 mm, respectively, the best values of C_2 yield were 21.8% obtained due to the effects of residence time and the CO_2 blocking in the oxidation reaction.

1. Introduction

The oxidative coupling of methane (OCM) is a promising way for the conversion of methane to C_2 hydrocarbons (ethylene and ethane) and is considered to be the most concise way of natural gas utilization because that OCM is a direct conversion methods and it can avoid the syngas step (Gesser and Hunter, 1998; Lunsford, 2000). A large number of catalysts, mainly metal oxide based catalysts, have been reviewed by Khammona et al. (2012). Over the past thirty years, one of the most effective catalysts is believed to be Na–W–Mn/SiO_2 catalyst which was first reported by Fang et al. (1992). Then, its structure, property for OCM reaction and addition of rare earth oxides were reported by substantial researchers in the literatures (Ji et al., 2003; Jiang et al., 1992; Malekzadeh et al., 2007; Wu et al., 2007). However, one major challenge of the commercialization of the OCM process is that the C_2 yield is still not high enough.

Another challenge of commercialization is that the OCM reaction is highly exothermic and hot spots are easily formed in the reactor (Pak and Lunsford, 1998; Schweer et al., 1994; Taniewski et al., 1997). Apart from the exploration of highly selective catalysts, the reactor type and alternated the contact mode between reactant and catalysts to inhibit the formation of hot spots and improve the selectivity of reactant was been researched (Liu et al., 2008a,b; Talebizadeh et al., 2009; Taniewski et al., 1997).

Monolithic catalyst, which is prepared by coating the active components onto a regular structure support with appropriate channels, has lower pressure drop, smaller diffusion resistance, and more excellent mass and heat transfer than the traditional catalyst mode, i.e. in the particle form (Groppi et al., 2001). Liu et al. (2008b) and Tang et al. (2009) reported that the hot spot effect was effectively depressed and the selectivity of C_2 was improved over the monolithic catalyst. However, the monolithic catalyst channels are relatively large, leading to

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a low methane conversion because of the very short contact time between the reactants and active component.

It is probably favorable to construct a two-stage reactor by combination of particle and monolithic catalysts in view of their disadvantages and advantages for OCM reaction. Pan et al. (2010) study the OCM reaction in a two-stage reactor which is filled with Na_2WO_4–Mn/SiO_2 particle catalyst and Ce–Na_2WO_4–Mn/SiO_2/cordierite monolithic catalyst. When particle and monolithic catalyst bed heights are 10 mm and 50 mm, respectively, and the raw gas goes through the particle catalyst first, C_2 yield reaches its maximum value of 23.6%. Wang et al. (2011) confirm that similar results can be obtained if the monolithic catalyst is replaced by Na_3PO_4–Mn/SiO_2/cordierite. Since the raw gases first go through the particle catalyst bed, the OCM reaction in monolithic catalyst bed is depressed by the low partial pressure of O_2. A flow of supplementary O_2 between the two beds is better to activate the monolithic catalyst (Ji and Wang, 2012). Finally, they improve the C_2 yield to 24.3% when the flow rate of supplementary O_2 is 3 ml/min. Meanwhile, the flow rate of CH_4 and O_2 in raw gas is 60 ml/min and 20 ml/min.

Computational fluid dynamics (CFD) can accurately predict the effect of reactor flow field on heat transfer and chemical reaction. It has been applied to simulate the OCM reactor performance (Nakisa and Reza, 2008, 2009; Zhang et al., 2015a,b). Reaction kinetic model is the main accuracy factor of reactor model for CFD simulation. The blocking effect of CO_2 and computational time must be considered if we plan to select a suitable reaction kinetics model. A kinetic model is built by Stansch et al. (1997), includes 10 step reactions and 8 species, is applied to the OCM reaction catalyzed by La_2O_3/CaO particles first and meet with our selected subjects. The model has been improved for simulation of reactors filled with Na_2WO_4–Mn/SiO_2 particle catalyst (Zhang et al., 2015b) and Na_3PO_4–Mn/SiO_2/cordierite monolithic catalyst (Zhang et al., 2015a) in our previous work.

In this work, the improved Stansch reaction kinetics models were used again and three-dimensional numerical models were established for the OCM tubular packed two-stage reactors filled with Na_2WO_4–Mn/SiO_2 particle catalyst and Na_3PO_4–Mn/SiO_2/cordierite monolithic catalyst. The FLUENT commercial code was used to solve the Navier–Stokes equations and species transport equations. The reaction kinetics models were added by the user-defined function (UDF) of FLUENT software. The advantages of two-stage reactor were illustrated using the simulation results, such as the contour of the species mass fractions, fluid density and velocity. The effect of catalyst bed heights on reactor performance was also investigated using these models. These models were adopted to provide guidance for the reactor scaling up in the future.

2. Models and numerical method

2.1. Geometric model and meshes

To diminish the error of model, we established geometric models for two-stage reactors completely same with the experimental apparatus (Wang et al., 2011). The particle catalyst and the cordierite monolithic catalyst were placed in a quartz tube (inner diameter 8 mm, length 600 mm) and separated with quartz wool between the two catalyst beds to construct a two-stage reactor as shown in Fig. 1(a). Two sections of 75 mm length were filled with quartz clips above the particle catalyst and under the cordierite monolithic catalyst (see Fig. 1(a)).

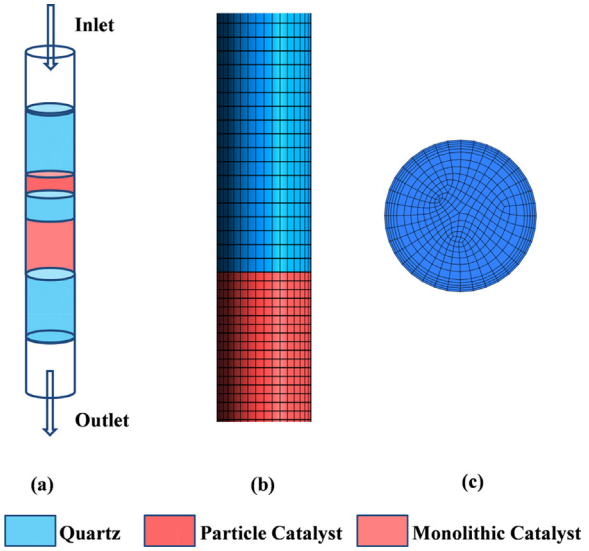

Fig. 1 – Sketch (a), meshes and geometric model (b and c) of packed bed reactor of monolithic catalyst.

For convenience, the particle catalyst bed was denoted as P and the monolithic catalyst bed was denoted as M. When the raw gas was fed from reactor top through the particle catalyst bed firstly and then through the monolithic catalyst bed, the reactor can be denoted as P_xM_y (x, y, the height of particle catalyst bed and monolithic catalyst bed, respectively). In order to study the effect of catalyst heights on the performance of the reactor, a set of reactors, which were denoted as $P_{10}M_{25}$, $P_{10}M_{50}$, $P_{10}M_{75}$, P_5M_{50} and $P_{15}M_{50}$, was simulated in this work. The geometry models were portioned by meshes was similar with the model mentioned in previous work (Zhang et al., 2015b) and meshes of cross section and catalyst bed were shown in Fig. 1(b) and (c). The numbers of meshes in the reactor models were about 400 000, 650 000, 900 000, 600 000, 700 000 and 750 000, respectively.

2.2. Governing equations

The simulation of packed bed reactor includes two kind of model: pseudo homogeneous model and heterogeneous model. The heterogeneous model (Kočí et al., 2004; Starý et al., 2006) is an excellent model for monolith bed simulation and can give accuracy results with short time. But heterogeneous model for particle bed simulation is a time consuming work (Wehinger et al., 2015). In this work, the reactor has two catalyst beds and heterogeneous model is not suitable to simulate the particle bed. We chose a pseudo homogeneous phase model (porous medium model) to save the computational time when the error was limited in an acceptable range.

According to the operating conditions in literature (Wang et al., 2011), the flow in OCM packed bed reactor is laminar (Re = 5.7), which is suitable to be described by the Navier–Stokes equations (Batchelor, 2000). The porous medium model was used to estimate drag of catalyst bed on reaction gas flow. The temperature gradient from gas to catalyst was estimated by non-equilibrium thermal model in FLUENT software. In the reactor, the presence of molecular diffusion and convection diffusion between species made it necessary to use species transport equation. The set of governing equations was given in previous work (Zhang et al., 2015b).