



Modeling of a microreactor for propylene production by the catalytic dehydrogenation of propane



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ARTICLE INFO

Article history:

Received 2 October 2013

Received in revised form 22 March 2014

Accepted 27 March 2014

Available online 4 April 2014

Keywords:

Microreactor

Microreactor modeling

Catalytic dehydrogenation

Propane dehydrogenation

Propylene production

Vanadia-titania catalyst

ABSTRACT

A model of a microreactor was proposed to analyze the production of propylene by the propane dehydrogenation using a catalytic surface of V_2O_5/TiO_2 doped with Rb. The reactor is a 50 mm length tube of 2 mm diameter whose wall is a catalytic surface, modeled using finite volume method in cylindrical coordinates over a tangential plane. Dehydrogenation kinetics is reported by Grabowski (2004). First, a mesh independence analysis was done to assure the adequate cell size. Second, a parametric analysis changing Reynolds number at different temperatures and propane-oxygen relations was done to find the Reynolds range to effectively use the reactor length (Re from 1 to 10). Then at the later Reynolds interval a parametric analysis involving temperature and composition was done to create productivity surfaces to find the highest productivity operation conditions. Finally, an analysis varying pressure at the maximum productivity conditions ($Re = 1$, $T = 500$ K, $C_3H_8/O_2 = 2$) was developed.

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1. Introduction

Propylene is primarily produced by naphtha cracking. In this process the main products are ethylene and propylene. Since the demand of propylene has overcome that of ethylene, research on new technologies to produce propylene are a main concern to avoid a long term propylene shortage. Catalytic propane dehydrogenation is a promising route to produce propylene thanks to the occurrence of increasing natural sources which are reducing propane price (INTRATEC, 2013). Propane dehydrogenation is an equilibrium reaction, which has a higher dependency on selectivity and conversion caused by the effects of multiple side reactions and coke formation. These kind of chemical reactions are difficult to operate in packed bed reactors due to the occurrence of heat and mass transfer problems which are easily overcome in a micro-reactor system. Theoretically, micro-reactors are a suitable configuration for this kind of reactions (Ehrfeld et al., 2000).

Several types of heterogeneous catalysts have been studied to increase propylene productivity and selectivity increasing propane conversion. Sloczynski studied the mechanism of reduction and oxidation reactions of alkali metals promoted by vanadium–titanium catalysts (Sloczynski, 1996). Grabowski et al. considered propane dehydrogenation using a TiO_2/V_2O_5 catalytic

surface, they also described the mechanism of oxygen adsorption (Grabowski et al., 2002). Grabowski et al. examined propane dehydrogenation over catalytic surfaces with Li, K and Rb (Grabowski et al., 1995). Khodakov et al. presented a comparative study of different catalyst alternatives, in which TiO_2/V_2O_5 doped with Rb had a higher selectivity in comparison to other materials (Khodakov et al., 1999). Grabowski fitted a SSAM-Eley-Rideal model for propane dehydrogenation using a catalytic surface of TiO_2/V_2O_5 doped with Rb (Grabowski, 2004). However, heat and mass transfer problems as hot spots, intra-particle mass transfer and axial effects are still a challenge to obtain a higher productivity (Levenspiel, 1999).

Different reactor alternatives have been proposed to overcome these difficulties. Sugiyama et al. used a microreactor with a calcium hydroxyapatite and magnesium ortho-vanadate catalysts for propane dehydrogenation, to suppress the oxidation of the resultant propylene to CO and CO_2 (Sugiyama et al., 2010). Genser et al. studied a mechanism based on the proposition of Oyama for propane dehydrogenation using a packed bed reactor (Genser and Pietrzyk, 1999). Grabowski fitted a SSAM-Eley-Rideal model from data obtained using a packed bed reactor (Grabowski, 2004). Due to its control, manipulation, and predictability, capillary reactors are used to make kinetic analysis. An example is presented by Zamaniyan et al. for syngas production (Zamaniyan et al., 2010).

In the present work, a model of a microreactor for propylene production by propane dehydrogenation, carried out over a titanium–vanadium doped with Rb catalysts is proposed in Fluent®

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using a SSAM-Eley-Rideal model adjusted by Grabowski (2004). Once a mesh independence analysis has been done, the model is used to examine in detail the behavior of conversion, selectivity and productivity by a comprehensive parametric analysis in which wall temperature, inlet composition and pressure conditions are changed to obtain the highest productivity operation condition.

2. Materials and methods

The micro reactor is modeled using the finite volume method (Fluent®) over a 2D axisymmetric tube. It is supposed that the reactor is at a steady state, and that the flow is in laminar regimen. Transport coefficients and the specific heat capacities are evaluated using kinetic theory models. The gas pressure–volume–temperature behavior is calculated using the ideal gas law. As the model is run at low wall temperatures (lower than 700 K), volumetric reactions do not have an appreciable

$$\theta = \frac{-C_{C_3H_8} r_1 - 2\sqrt{C_{O_2} r_{O_s}} + \sqrt{(C_{C_3H_8} r_1 + 2\sqrt{C_{O_2} r_{O_s}})(C_{C_3H_8} r_1 + 2\sqrt{C_{O_2} r_{O_s}}) + 8\sqrt{C_{O_2} r_{O_s}}(3C_{C_3H_6} r_2(1+x) + C_{C_3H_8} r_4(4+3x))}{6C_{C_3H_6} r_2(1+x) + 2C_{C_3H_8} r_4(4+3x)} \quad (1)$$

$$x = p + 2(1 - p) \quad (2)$$

$$p = \frac{6C_{C_3H_8} + 7C_{C_3H_6}}{15C_{C_3H_8} + 17C_{C_3H_6}} \quad (3)$$

rate and it is supposed that only surface reactions are occurring at a significant rate. Aspen properties was used to calculate density at inlet conditions. For all models inlet temperature is fixed at 280 K, and pressure is set at 1 bar except in the pressure analysis. Table 1 shows inlet conditions imposed to obtain the highest productivity.

2.1. Geometry of the reactor

The reactor is a 50 mm length tube of 2 mm diameter whose wall is a catalytic surface, similar to the reactor of Zamaniyan et al. (2010) used to produce syngas. The reactor is modeled in cylindrical coordinates over a tangential region of the reactor, and consists of an inlet (left side), an outlet (right side), a catalytic fixed temperature wall condition on the upper side, and a symmetry condition on the opposite side. A parallel quadrilateral mesh is used as velocity, temperature, pressure and concentration variations are uniform over the transversal section.

3. Theory

In this section the implemented equations for a system in laminar conditions are described, based on a kinetic proposed by Grabowski (2004). The chemical reactions were separated to represent the combustion phenomena in a set of four chemical reactions.

Table 1
Summary of inlet conditions for the highest productivity condition.

T_{in} (K)	280
T_w (K)	500
C_3H_8/O_2	2
D (m)	0.002
L (m)	0.05
v (m/s)	0.0024
ρ (Kg/m ³)	2.2080
q (m ³ /s)	7.44E–09
μ (Kg/s m)	1.05E–05
D_{ab} (m ² /s)	1.08E–05
Re	1.000
Sc	0.441
Sh	0.484

3.1. Conservation equations

Continuity, momentum, energy, and mass conservation equations were solved for all variables except pressure using Flexible-cycle (including the effects of concentration gradient and thermal diffusion); pressure was solved using v-cycle in radial and axial directions (Bird et al., 2006).

3.2. Surface chemistry model

The mechanism includes 6 chemical reactions, it was deduced from the SSAM-Eley-Rideal model for the propane dehydrogenation process adjusted by Grabowski (2004). The later model just involves surface chemical reactions. In our model we assume that an equilibrium steady state occurs in the catalytic surface, and so, the surface oxygen concentration does not change with time. This assumption is used to deduce an equation for superficial oxygen concentration θ .

where r_{O_s} is the rate of oxygen adsorption, and x is the stoichiometric coefficient of the theoretical compound CO_x which represents a mixture of CO_2 and CO produced by combustion reactions (Grabowski, 2004). The stoichiometric coefficient x is calculated by the addition of each of the fractional productions of CO_2 and CO multiplied by the oxygen content of each compound. Defining p as the fractional production of CO in a mixture of CO_2 and CO , the fractional production of CO_2 is calculated as $(1 - p)$. Then, the stoichiometric coefficient x is calculated using Eq. (2).

Fractional production p , is calculated using Eq. (3); fractional production p is expressed as the amount of atomic oxygen required for the combustion of one mole of C_3H_8 and one of C_3H_6 to produce CO and H_2O (reactions 2 and 4), divided by the addition of the oxygen required for the combustion of one mole of C_3H_8 and one of C_3H_6 to produce CO and H_2O (reactions 2 and 4) and the oxygen required for the combustion of one mole of C_3H_8 and one of C_3H_6 to produce CO_2 and H_2O (reactions 3 and 5).

3.3. Convective and diffusive mass transfer comparison

For multicomponent systems Sherwood number can be used to compare convective and diffusive mass transfer. Sherwood number can be calculated using mathematical expression as a function of Reynolds, Schmidt numbers and the geometry of the region where mass transfer occurs. Sherwood number equations for a pipe is suitable to compare mass transfer mechanisms in a tubular micro-reactor (Welty et al., 2007).

$$Re = \frac{D\rho v}{\mu} \quad (4)$$

$$Sc = \frac{\mu}{D_{a,b}\rho} \quad (5)$$

$$Sh = 1.86 \left(\frac{D}{L} Re Sc \right)^{1/3} = 1.86 \left(\frac{D^2}{L} \frac{v}{D_{a,b}} \right)^{1/3} \quad (6)$$

where Re is the Reynolds number, Sc is the Schmidt number, Sh is the Sherwood number, D is the diameter and L the length of the microreactor. v is the fluid mean velocity, ρ the density, μ the viscosity, and $D_{a,b}$ the diffusivity of the inlet mixture. Sherwood

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