



ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Effect of the catalyst pore structure on fixed-bed reactor performance of partial oxidation of n-butane: A simulation study



Ying Dong^a, Frerich J. Keil^a, Oliver Korup^a, Frank Rosowski^{b,c}, Raimund Horn^{a,*}

^a Institute of Chemical Reaction Engineering, Hamburg University of Technology, Eißendorfer Str. 38, D-21073 Hamburg, Germany

^b BASF SE, Chemicals Research and Engineering, Carl-Bosch-Straße 38, D-67056 Ludwigshafen, Germany

^c BasCat-UniCat BASF Joint Lab, Hardenbergstraße 36, D-10623 Berlin, Germany

HIGHLIGHTS

- n-Butane oxidation to maleic anhydride in a fixed-bed reactor was simulated.
- A two-dimensional pseudo-heterogeneous model was developed.
- Macro- and micro-pore model of Wakao and Smith was adopted.
- Pore structure parameters of the pellet have impacts on the reactor performance.
- Catalyst pellet with optimal pore structure can improve the yield by several percent.

ARTICLE INFO

Article history:

Received 3 November 2015

Received in revised form

9 December 2015

Accepted 11 December 2015

Available online 19 December 2015

Keywords:

Fixed-bed reactor

n-Butane oxidation

VPP catalyst

Heterogeneous model

Pore structure

Model of Wakao and Smith

ABSTRACT

The effect of catalyst pore structure on n-butane oxidation to maleic anhydride in a fixed-bed reactor was investigated by numerical simulations. The micro- and macro-pore model of Wakao and Smith was applied to model the diffusion–reaction inside the catalyst pellet. The studied pore structure parameters were macro-pore porosity, mean macro-pore diameter and mean micro-pore diameter. A fixed-bed reactor was simulated with a detailed two-dimensional heterogeneous model under typical industrial conditions. Simulation results have demonstrated that the reactor performance is sensitive to the chosen pore structure parameters especially macro-pore porosity and mean micro-pore diameter. A bi-modal catalyst pellet with bigger macro-pores and smaller micro-pores is favored to achieve higher yields of maleic anhydride. This work highlights the potential of improving this process by pore structure optimization.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Maleic anhydride (MAN) is an important intermediate in chemical industry with an annual worldwide consumption of 2.7 Mt (Trifirò and Grasselli, 2014). Since 2006, over 70% of the MAN is produced by selective oxidation of n-butane catalyzed by a vanadyl pyrophosphate (VPP) catalyst. Processes employ either multi-tubular fixed bed reactors immersed in a molten salt bath or fluidized bed reactors (Schunk, 2008; Gulians et al., 2000). The fixed-bed process, which we will focus on in this work, runs typically at 80–85% n-butane conversion and the non-converted butane is not recycled. The overall yield of MAN reported is 57–65% which is not optimal for selective oxidation processes (Trifirò

and Grasselli, 2014). Therefore, there is still room for improving the fixed-bed process and maximizing the yield of MAN.

Nowadays, reactor simulation plays a key role in process optimizations as it offers a cost-effective approach compared to experimentation (Stitt et al., 2015). For modeling fixed-bed reactors, the pseudo-homogeneous and heterogeneous models are the most popular ones due to their high accuracy and low computational cost (Jakobsen, 2014). In those models, the fixed-bed reactors are modeled as a porous media and effective parameters for heat and mass transfer have to be used (Tsotsas and Jecser, 2010). The pseudo-homogeneous and heterogeneous models have been applied to simulate the n-butane oxidation in fixed-bed reactors (Sharma et al., 1991; Ali and Al-Humaizi, 2014; Diedenhoven et al., 2012; Brandstädter and Kraushaar-Czarnetzki, 2007; Guettel and Turek, 2010) and membrane reactors (Marín et al., 2010; Alonso et al., 2001). The main difference between the pseudo-

* Corresponding author. Tel.: +49 40 42878 3042; fax: +49 40 42878 2145.

E-mail address: horn@tuhh.de (R. Horn).

homogeneous and heterogeneous model is that the heterogeneous model considers explicitly the presence of the catalyst phase. Therefore, two sets of conservation equations are applied for the interstitial fluid and the catalyst phase, respectively (Jakobsen, 2014). The resolved concentration and temperature profiles inside the catalyst pellets are coupled to the bulk fluid phase gradients via the boundary conditions applied on the pellet surface. Therefore, the heterogeneous model can be a useful tool for studying the catalyst scale parameters to the reactor performance.

The most applied VPP catalysts in industrial fixed-bed reactors are bulk catalysts typically made by pressing the active powder into a pellet with the desired dimensions (Cavani et al., 2006). The resulting catalyst pellets therefore have a bimodal pore structure, i.e. the micro-porous structure from the chemical synthesis of the active powder and the macro-porous region between the powder formed by the pelleting process. Due to diffusion limitation, the global reaction rate of the catalyst pellet in the reactor can be different from the intrinsic reaction rate measured for the active powder (Sharma et al., 1991). Hence, the real performance of the VPP catalyst pellet in a technical fixed-bed reactor is an overall result of the chemistry nature of the active component and the pore structure of the pellet. Most of current research on n-butane oxidation focusses on improving the catalytic chemistry of the VPP catalyst (Benziger et al., 1997; Centi, 1993; Trifirò and Grasselli, 2014). New synthesis methods are continuously proposed to increase the intrinsic activity of the VPP precursors (Glaum et al., 2012; Hutchings, 2004). To the best of our knowledge, the pore structure optimization of the VPP catalyst for n-butane oxidation is not explored yet.

Early studies have shown that an optimal pore structure of the catalyst pellet can be of great importance (Keil, 1999; Wei, 2011; Coppens et al., 2001). With the development of experimental techniques, rational design and synthesis of catalyst pellets with desired pore structure for better performance is nowadays possible (Liu et al., 2013; Luss, 1990). The effect of the pore structure parameters of the VPP catalyst pellet on the reactor performance for n-butane oxidation in a fixed-bed reactor is investigated in this work by means of detailed mathematical modelling. If the overall yield of maleic anhydride can be improved by 1% with altering the catalyst pore structure, this may open up a new direction for research of this process. To solve the reaction–diffusion equation inside the catalyst pellet, a pore structure model and a diffusion model are needed. Often used pore structure models are the micro- and macro pore model of Wakao and Smith (1962), the random pore model of Johnson (1965), the grain model of Szekely and Evans (1971). More recently, a more detailed and realistic three-dimensional pore network model has been proposed by Rieckmann and Keil (1999). The diffusion fluxes are usually modelled with the dusty gas model, Maxwell–Stefan model, Wilke and Wilke-Bosanquet models (Solsvik and Jakobsen, 2013). One may refer to the works of Solsvik and Jakobsen (2012a) for a detailed summary of different diffusion models. For catalyst pellet containing bi-modal pore size distribution, the micro- and macro pore model of Wakao and Smith (1962) with the Wilke formula can be a good option for practical reaction engineering calculations (Hegedus, 1980).

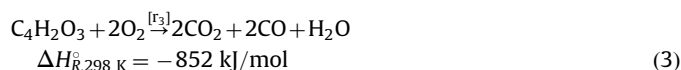
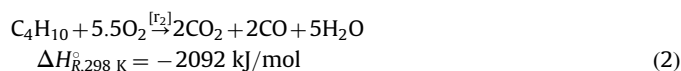
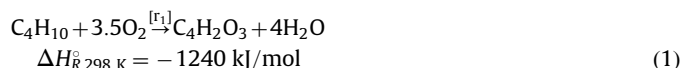
2. Mathematical modeling

2.1. Reaction kinetics

The triangle (three-reaction) network as shown in Fig. 1 was used in this work which includes the main reaction of n-butane to maleic anhydride, total oxidation of n-butane to carbon oxides (CO₂ and CO) and consecutive MAN oxidation to CO₂ and CO

(Wellauer et al., 1986). The formation of other by-products such as acetic acid, acrylic acid, phthalic and methacrylic acids is generally neglected in the reaction model because of observed low concentrations (lower than 2 %) (Alonso et al., 2001; Marín et al., 2010).

The stoichiometric equations used were as follows:



The intrinsic rate expressions and kinetic parameters were taken from Guettel and Turek (2010), and the parameters are given in Table 1:

$$k_j = A_j \cdot \exp\left(\frac{-E_{a,j}}{RT}\right) \quad (4)$$

$$r_1 = \frac{k_1 p_{\text{C}_4\text{H}_{10}} p_{\text{O}_2}^{0.5}}{1 + K_1 p_{\text{C}_4\text{H}_{10}} + K_2 p_{\text{H}_2\text{O}}} \quad (5)$$

$$r_2 = \frac{k_2 p_{\text{C}_4\text{H}_{10}} p_{\text{O}_2}^{0.5}}{1 + K_1 p_{\text{C}_4\text{H}_{10}} + K_2 p_{\text{H}_2\text{O}}} \quad (6)$$

$$r_3 = \frac{k_3 p_{\text{C}_4\text{H}_2\text{O}_3} p_{\text{O}_2}^{0.25}}{1 + K_1 p_{\text{C}_4\text{H}_{10}} + K_2 p_{\text{H}_2\text{O}}} \quad (7)$$

Since the aim of the present paper is to investigate the effect of the pore structure of the catalyst pellet on the reactor performance, the above-mentioned reaction rates r_j which are in units of mol/(kg_{cat} · s) were converted to the surface area based reaction rate $r_{j,s}$ which is in units of mol/(m² · s) with assumed active surface per catalyst mass S_g of $6.7 \cdot 10^5$ m²/kg.

2.2. Particle model

In this work, the micro- and macro pore model of Wakao and Smith (1964, 1962) was applied which was specifically developed

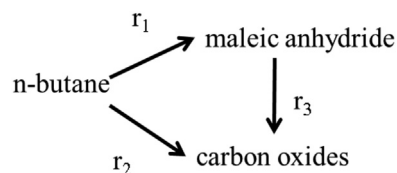


Fig. 1. Triangle reaction network for n-butane oxidation (Wellauer et al., 1986).

Table 1
Kinetic parameters for partial oxidation of n-butane taken from Guettel and Turek (2010).

Parameter	Value	Unit
A_1	1.28	mol/(s kg _{cat} Pa ^{1.5})
A_2	15.1	mol/(s kg _{cat} Pa ^{1.5})
A_3	0.26	mol/(s kg _{cat} Pa ^{1.25})
$E_{a,1}$	114	kJ/mol
$E_{a,2}$	132	kJ/mol
$E_{a,3}$	97	kJ/mol
K_1	$6.8 \cdot 10^{-4}$	1/Pa
K_2	$5.8 \cdot 10^{-4}$	1/Pa

Download English Version:

<https://daneshyari.com/en/article/154428>

Download Persian Version:

<https://daneshyari.com/article/154428>

[Daneshyari.com](https://daneshyari.com)