Chemical Engineering Journal 176–177 (2011) 151–157

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Mathematical modeling of the propane dehydrogenation process in the catalytic membrane reactor

E.V. Shelepova*, A.A. Vedyagin, I.V. Mishakov, A.S. Noskov

Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Science, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russian Federation

ARTICLE INFO

Article history:
Received 1 December 2010
Received in revised form 25 April 2011
Accepted 17 June 2011

Keywords:
Catalytic membrane reactor
Mathematical modeling
Propane dehydrogenation
Hydrogen oxidation

ABSTRACT

The two-dimensional non-isothermal stationary mathematical model of the catalytic membrane reactor for the process of propane dehydrogenation has been developed. The made calculations have shown the higher efficiency of the membrane reactor in comparison with the tubular one which is achieved due to removal of hydrogen from reactionary zone through the membrane to shift the reaction equilibrium towards formation of products. The use of membrane was found to cause the propane conversion increase from 41% to 67%. The highest value of propane conversion (X = 96%) was reached in case of additional oxidation of the removed hydrogen (conjugated dehydrogenation). The maximum value of propylene selectivity S = 98% can be as well reached in case of conjugated dehydrogenation in the membrane reactor at the reaction temperature of 500 °C. The oxidation of hydrogen in conjugated dehydrogenation process gives the increase of propylene yield from 65% (the tubular reactor) to 95%. The maximum propylene yield corresponds to T = 525 °C. It was also established that the gas space velocity in both internal and external parts of the membrane reactor is to be the one of the most important factors defining efficiency of the conjugated dehydrogenation process.

1. Introduction

Olefinic hydrocarbons, such as ethylene, propylene, butene, and isobutene, are critical intermediates in the petrochemical industry. In order to satisfy market demand, substantial efforts have been invested in the production of such compounds by conventional thermal steam cracking of alkanes and naphtha and by catalytic dehydrogenation methods [1]. Conventional catalytic dehydrogenation is equilibrium limited and requires very high temperatures (over 700 °C) to achieve a high enough conversion of propane to be economically viable. In addition, it has such disadvantages as the deactivation of the catalyst by coke formation, and the consequent need for continuous or periodic catalyst regeneration at frequent intervals throughout the process. As a result of these substantial drawbacks, the petroleum industry has sought a solution to the demand for olefinic hydrocarbons in the use of oxidative dehydrogenation (ODH) methods. ODH uses oxygen to react with the hydrogen released from the hydrocarbon, in situ, so that the aforementioned equilibrium limitation is removed, and high single pass yields can be achieved. The reaction is exothermic overall and does not require a supply of heat as in endothermic dehydrogenation reactions. However it always faces the main problem associated with combustion of principle reaction product. The mentioned alternative reaction pathway limits the selectivity towards propylene, especially at high conversions.

The use of the catalytic membrane reactor (CMR) permits one to combine the advantages of conventional dehydrogenation and oxidative dehydrogenation processes. In this case the propane undergoes the dehydrogenation reaction over the catalyst in the tube side. Hydrogen permeates through the membrane to the shell compartment where has been oxidized by oxygen. Selective hydrogen removal through the membrane allows one to shift the reaction equilibrium towards the desired products. Further oxidation of hydrogen in shell side of the reactor leads to the increase of hydrogen amount permeated through the membrane and to additional shift of the reaction equilibrium [2].

The catalytic membrane reactor model and the analysis of reasonability of the suggested approach are presented in this report.

There are significant amount of works devoted to mathematical modeling of different processes in the catalytic membrane reactors. However, in most cases the existing models are not capable to describe in full the diversity of heat- and mass-transfer processes taking place in real reactors. So, for example, one-dimensional mathematical models cannot allow one to study the influence of structural and textural properties of a material of which the membrane reactor is made on key process characteristics, which in whole substantially reduces the reliability and importance of calculations made [3–6]. Two-dimensional models are known to assume the isothermality of occurring processes that does not allow one to study the effect of released exothermal heat upon the indicators

* Corresponding author. Tel.: +7 383 3269406; fax: +7 383 3306878.
E-mail address: shev@catalysis.ru (E.V. Shelepova).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.06.048

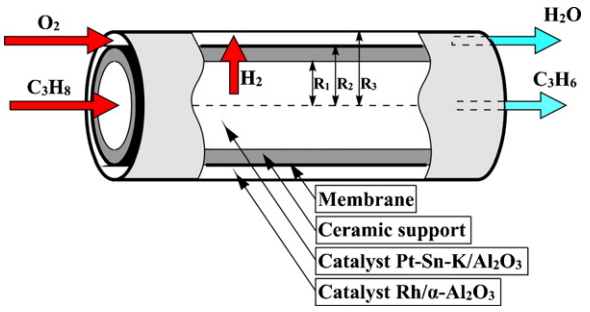

Fig. 1. The principle scheme of membrane reactor.

of endothermic process [7–9]. They also do not take into consideration the diffusion transfer throughout the support [10–15]. The detailed modeling of transport through the multilayered porous support was also described [16]. However, as a rule, in such works there is no complete description of heat and mass transfer processes within both tube and shell sides. Under these circumstances the development of two-dimensional non-isothermal reactor model taking into account the hydrogen flux across the membrane, diffusion and thermal conductivity in the radial direction for tube side and ceramic support is considered as quite actual.

2. Mathematical model

A mathematical model was developed to evaluate the performance of the dehydrogenation of propane in the catalytic membrane reactor. The isothermal mathematical model, presented in [7] was improved by energy balance equations.

Some modifications were used for mass balance equations: variable gas mixture space velocity in the tube and shell sides and the catalytic hydrogen oxidation in the shell side including the equations for the oxygen and water mass transfer.

The configuration of membrane reactor is depicted in Fig. 1. The membrane reactor consists of two concentric tubes, where the interior ceramic tube with catalyst bed is placed in the exterior one. A very thin layer of palladium-silver membrane is deposited as a continuous layer on the outer surface of thermostable ceramic tube.

The several simplifying assumptions are used:

1. Steady-state conditions.
2. Negligible convective radial dispersion and axial diffusion.
3. High heat conduction of the membrane material.
4. Negligible pressure drop.
5. Negligible internal mass- and energy-transport limitations inside the catalyst pellets (tube side) and negligible external mass and heat transfer resistances at the surface of the pellets (tube, shell side).

The two-dimensional non-isothermal stationary reactor model includes the mass and energy balance equations with the appropriate boundary conditions for tube and shell sides and for the ceramic support.

2.1. Mass balances

Tube side: $0 < r_1 < R_1$

To describe the mass transfer processes in the tube side the convective mass transfer in the axial direction, diffusion in the radial direction and chemical reactions were taken into account.

$$\frac{\partial(u_l^t C_i^t)}{\partial l} = \varepsilon^t \frac{1}{r_1}\frac{\partial}{\partial r_1}\left(r_1 D_{e_i}^t \frac{\partial C_i^t}{\partial r_1}\right) + \rho_k^t(1-\varepsilon^t)\times\sum_{j=1}^{N_R}\gamma_{ij}w_j, \quad \forall i$$

The following boundary conditions are used together with equations:

Boundary conditions:

$$l = 0 : C_i^t = C_{in}^t$$

Symmetry condition at the tube center line:

$$r_1 = 0 : (\partial C_i^t/\partial r_1) = 0$$

At the boundary *tube/ceramic support*:

$r_1 = R_1 : C_i^t = C_i^c$ for each substances

$$D_{e_i}^t \varepsilon^t \left.\frac{\partial C_i^t}{\partial r_1}\right|_{r_1=R_1} = D_{e_i}^c \varepsilon^c \left.\frac{\partial C_i^c}{\partial r_2}\right|_{r_2=R_1}, \quad \forall i$$

Ceramic support: $R_1 < r_2 < R_2$

The diffusion of all substances in the radial direction was considered for ceramic support layer.

$$\frac{\varepsilon^c}{r_2}\frac{\partial}{\partial r_2}\left(r_2 D_{e_i}^c \frac{\partial C_i^c}{\partial r_2}\right) = 0, \quad \forall i$$

Boundary conditions:

The boundary conditions for *ceramic support/tube* are the same as for *tube/ceramic support.*

At the boundary *ceramic support/shell*:

$$r_2 = R_2 : \left.\frac{\partial C_i^c}{\partial r_2}\right|_{r_2=R_2} = 0, \quad \forall i \neq H_2$$

Hydrogen flux through the membrane has been proportional to the difference of the square roots of the hydrogen partial pressures across the membrane.

$$D_{e_{H_2}}^c \varepsilon^c \left.\frac{\partial C_{H_2}^c}{\partial r_2}\right|_{r_2=R_2} = \left(\frac{Q_0}{\delta}\right)\left[\sqrt{P_{H_2}^c} - \sqrt{P_{H_2}^s}\right]$$

Shell side:

The convective mass transfer in the axial direction, flux of the hydrogen across the membrane and the catalytic reaction of the hydrogen oxidation were taken into consideration with appropriate boundary conditions.

$$\frac{\partial(u_l^s C_{H_2}^s)}{\partial l} = \frac{Q'_{H_2} P_w}{S_{cr.s.}} + \rho_k^s(1-\varepsilon^s)\times\gamma_i w^s$$

$$\frac{\partial(u_l^s C_i^s)}{\partial l} = \rho_k^s(1-\varepsilon^s)\times\gamma_i w^s, \quad i = O_2, H_2O$$

where $Q'_{H_2} = Q_{H_2}/A_m$.

The permeation rate of hydrogen through the membrane is determined by relation [7]:

$$Q_{H_2} = Q_0\left(\frac{A_m}{\delta}\right)\left[\sqrt{P_{H_2}^c} - \sqrt{P_{H_2}^s}\right]$$

Boundary conditions:

$$l = 0 : C_{H_2}^s = C_{H_2O}^s = 0, \quad C_{O_2}^s = C_{O_2,in}^s$$

2.2. Energy balance

Tube side: $0 < r_1 < R_1$

To describe the heat transfer processes in the tube side the convective heat transfer in the axial direction, thermal conductivity in