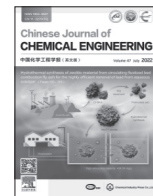




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Chinese Journal of Chemical Engineering

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

Full Length Article

Modeling of propane dehydrogenation combined with chemical looping combustion of hydrogen in a fixed bed reactor

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ARTICLE INFO

Article history:

Received 27 January 2021

Received in revised form 22 June 2021

Accepted 5 July 2021

Available online 1 September 2021

Keywords:

Propane dehydrogenation

Selective hydrogen combustion

Simulation

Optimization

Redox process

ABSTRACT

A redox process combining propane dehydrogenation (PDH) with selective hydrogen combustion (SHC) is proposed, modeled, simulated, and optimized. In this process, PDH and SHC catalysts are physically mixed in a fixed-bed reactor, so that the two reactions proceed simultaneously. The redox process can be up to 177.0% higher in propylene yield than the conventional process where only PDH catalysts are packed in the reactor. The reason is twofold: firstly, SHC reaction consumes hydrogen and then shifts PDH reaction equilibrium towards propylene; secondly, SHC reaction provides much heat to drive the highly endothermic PDH reaction. Considering propylene yield, operating time, and other factors, the preferable operating conditions for the redox process are a feed temperature of 973 K, a feed pressure of 0.1 MPa, and a mole ratio of H_2 to C_3H_8 of 0.15, and the optimal mass fraction of PDH catalyst is 0.5. This work should provide some useful guidance for the development of redox processes for propane dehydrogenation.

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1. Introduction

Propane dehydrogenation is one of the most important on-purpose techniques for producing propylene, a key intermediate for numerous products like polypropylene, propylene oxide, and acrylonitrile. Due to the large price gap between propane and propylene, propane dehydrogenation is very economically profitable. Driven by this, some commercial propane dehydrogenation processes have been developed, including Oleflex, Catofin, and STAR [1–3]. Although these processes have been widely applied in industry for many years, they still can be largely improved in some aspects.

Propane dehydrogenation to propylene is a reversible and highly endothermic reaction ($\Delta H_{298K} = +124 \text{ kJ}\cdot\text{mol}^{-1}$) [4]. To achieve a high propane conversion under the thermodynamic limitation, the reaction should take place under a high temperature ($>873 \text{ K}$) and a low pressure ($<0.2 \text{ MPa}$) [2], which largely reduces the efficiency of a commercial propane dehydrogenation process. To drive this endothermic reaction, much heat needs to be input into a propane dehydrogenation reactor. Besides, with the progression of propane dehydrogenation, hydrogen accumulates in the

reactor, which significantly reduces the equilibrium conversion of propane. To solve these problems, some approaches have been applied in the commercial processes. For instance, in the Oleflex process, preheaters are placed before propane dehydrogenation reactors to increase the temperature of reactants prior to the dehydrogenation reaction [5,6]. In the STAR process, a reformer-type dehydrogenation reactor is used to meet the high energy consumption by the dehydrogenation reaction [7]. These approaches can solve the problems of thermodynamic limitation and heat input, but at the great cost of capital investment and energy consumption. Some new approaches are still required to improve the propane dehydrogenation technique.

Propane dehydrogenation combined with selective hydrogen combustion is a very attractive approach [8–12]. The combustion of hydrogen shifts the reaction equilibrium to the desired product—propylene, and also supplies much heat to drive the dehydrogenation reaction. For a straightforward process of combining propane dehydrogenation and selective hydrogen combustion, gaseous oxygen can be co-fed with propane into the dehydrogenation reactor where a hydrogen combustion catalyst is mixed with a conventional dehydrogenation catalyst [13]. This “co-fed” process requires gaseous oxygen commonly obtained from cryogenic air separation, which is highly energy-intensive. Besides, it also has the safety issues related to the mixing of oxygen with hydrocarbons and hydrogen at high temperatures. To resolve these

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problems, solid oxygen carriers (also known as redox catalysts) with lattice oxygen can be used in the reactor [14,15]. The oxygen carriers donate lattice oxygen to convert hydrogen into water and then the reduced carriers are exposed to air to replenish the lattice oxygen, which is known as the chemical looping (or redox) process. A typical redox process for combining propane dehydrogenation with selective hydrogen combustion is illustrated in Fig. 1. Oxygen carrier and PDH catalyst are mixed and packed in a fixed bed reactor. The redox reactions ($\text{MeO}_{x-1} + \frac{1}{2}\text{O}_2 \rightarrow \text{MeO}_x$ and $\text{H}_2 + \text{MeO}_x \rightarrow \text{MeO}_{x-1} + \text{H}_2\text{O}$) occur in the reactor, and the feed is periodically switched between propane and air to achieve redox cycles. The chemical looping combustion of hydrogen avoids the direct contact of oxygen with the flammable mixture and the use of cryogenic air separation. Thus, propane dehydrogenation combined with chemical looping combustion of hydrogen is a safe and efficient approach to producing propylene.

To commercialize this technique of propane dehydrogenation combined with chemical looping combustion of hydrogen, it requires proper oxygen carriers, as well as reasonable designs of redox reactors and processes. The oxygen carriers are normally composed of metal oxides, and have been extensively investigated in the Refs. [16–26]. The representative oxides, like Sb_2O_4 , In_2O_3 , and Bi_2O_3 , show high hydrogen combustion selectivity (>90%), although they are normally unstable under high temperature redox cycling [18,22–26]. Ceria doped with W, Bi, Cr or Pb shows hydrogen combustion selectivity up to 98% and also good stability in the temperature range of 773–873 K [16,17,19–21]. However, few works have reported the designs of redox reactors and processes for propane dehydrogenation combined with chemical looping combustion of hydrogen. In order to aid these designs, we need a proper model for the reactor where propane dehydrogenation and chemical looping combustion of hydrogen occur simultaneously. The models for chemical looping combustion of fuels in fixed-bed and fluidized-bed reactors have been developed [27–32]. However, the model for propane dehydrogenation combined with chemical looping combustion of hydrogen in one reactor has not been reported in the literature to the best of our knowledge.

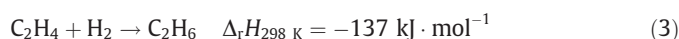
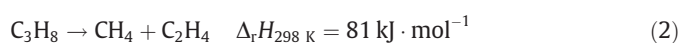
In this work, we develop a two-dimensional dynamic model for propane dehydrogenation and chemical looping combustion of hydrogen in a fixed-bed reactor, as fixed-bed reactors are widely used in commercial propane dehydrogenation processes [1,3,7]. In the fixed-bed reactor, the redox process is compared with a con-

ventional dehydrogenation process where only PDH catalysts are packed in the reactor. Besides, we investigate how operating conditions (i.e., feed temperature, pressure, and feed composition) and packing density of oxygen carrier affect this redox process.

2. Modeling

2.1. Reaction system

Two types of reactions take place in the fixed-bed reactor: (1) propane dehydrogenation and related side reactions; (2) combustion of hydrogen and hydrocarbons. A commercial Pt/ Al_2O_3 catalyst can be used as the propane dehydrogenation catalyst. Over this catalyst, propane dehydrogenation, propane cracking and ethylene hydrogenation occur simultaneously:



The reaction rates for propane dehydrogenation (r_1), propane cracking (r_2), and ethylene hydrogenation (r_3) are adopted from the Ref. [33]:

$$r_1 = \frac{k_1 \left(P_{\text{C}_3\text{H}_8} - \frac{P_{\text{C}_3\text{H}_6} P_{\text{H}_2}}{K_{\text{eq}}} \right)}{1 + \frac{P_{\text{C}_3\text{H}_6}}{K_{\text{C}_3\text{H}_6}}} \quad (4)$$

$$r_2 = k_2 P_{\text{C}_3\text{H}_8} \quad (5)$$

$$r_3 = k_3 P_{\text{C}_2\text{H}_4} P_{\text{H}_2} \quad (6)$$

Here, k_i ($i = 1, 2$, and 3) is the reaction rate constant of reaction i , P_j ($j = \text{C}_3\text{H}_8$, C_3H_6 , H_2 , and C_2H_4) is the partial pressure of component j , K_{eq} is the equilibrium constant, and $K_{\text{C}_3\text{H}_6}$ is the adsorption constant of propylene. These kinetics parameters can be found in the same Ref. [33].

Some metal oxides, e.g., Sb_2O_4 , In_2O_3 , Bi_2O_3 , and CeO_2 , could be the potential oxygen carriers for selective combustion of hydrogen, as they have excellent hydrogen combustion selectivity [13,14]. However, these oxides are still not stable enough under high temperature redox cycling, and they need to be largely improved

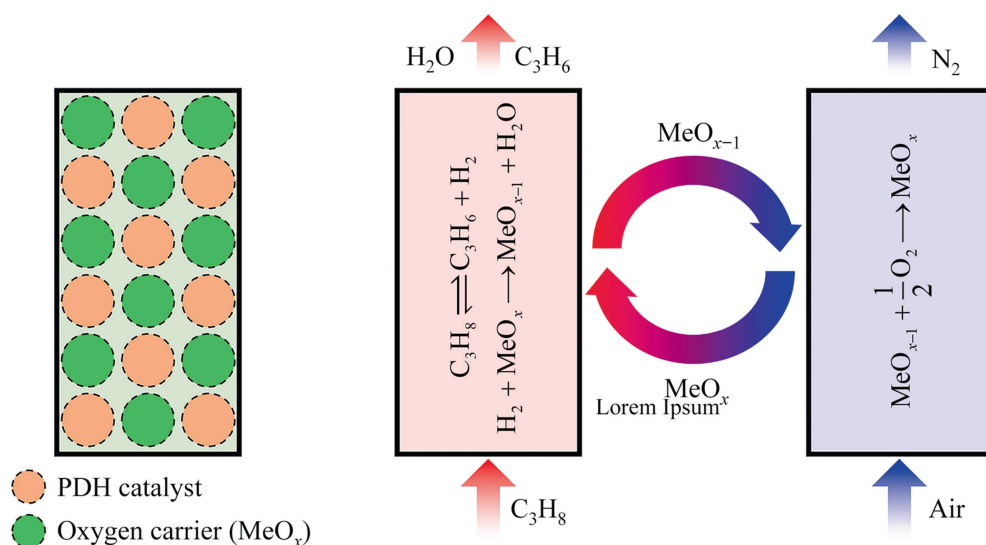


Fig. 1. A schematic illustration of the redox process for combining propane dehydrogenation with selective hydrogen combustion in a fixed-bed reactor.

before being used in industry [13,14]. Besides, systematic reaction kinetics of these oxides in the presence of hydrocarbons have not been reported in the literature. To build the reactor model, we define a pseudo-metal-oxide (i.e., MeO_x), and this pseudo-metal-oxide is assumed to be supported on alumina. Over this $\text{MeO}_x/\text{Al}_2\text{O}_3$ redox catalyst, we assume only combustion of hydrogen occurs (i.e., 100% hydrogen combustion selectivity), and the reaction enthalpy is assumed to be $-86 \text{ kJ} \cdot \text{mol}^{-1}$ (close to the one using copper oxide as the oxygen carrier) [34]:



The reaction rate equation for the combustion of hydrogen (r_4) is taken from the literature:

$$r_4 = k_4 c_{\text{H}_2} c_{\text{MeO}_x} \quad (8)$$

where k_4 is the reaction rate and c_j ($j = \text{H}_2$ and MeO_x) is the concentration of component j . The kinetic parameters can be found in the same work. When using different reaction enthalpies and kinetics for hydrogen combustion, the results should be quantitatively different but still qualitatively valid. It is also worth noting that this work focuses on modeling and simulation of propane dehydrogenation combined with hydrogen combustion and the cycle of the redox process is not investigated. The design and optimization of the process cycle is one of our objectives for future work.

2.2. Model equations

The propane dehydrogenation catalyst and oxygen carrier are uniformly mixed in the fixed-bed reactor, and the reactor can be assumed to be pseudo homogeneous. Besides, the reactor is assumed to be operated under adiabatic condition. The mass, energy and momentum conservation equations are employed to describe the coupled mass transfer, heat transfer, and chemical reactions in the adiabatic fixed-bed reactor. In this work, the fixed-bed reactor is assumed to have a cylindrical shape, and thus a two-dimensional axisymmetric model is adequate. It should be noted that a three-dimensional model is required when performing the reactor design where complex structures are involved.

The mass conservation equation for component i (excluding MeO_x and MeO_{x-1}) is given by:

$$\varepsilon \frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial z} = \varepsilon \frac{D_{e,i}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) + (1 - \varepsilon) y_{\text{PDH}} \rho_{\text{PDH}} R_{\text{PDH},i} + (1 - \varepsilon)(1 - y_{\text{PDH}}) \rho_{\text{SHC}} R_{\text{SHC},i} \quad (9)$$

Here, ε is the porosity of catalyst bed in the reactor, c_i is the molar concentration of component i , u is the apparent velocity of gas in the reactor, $D_{e,i}$ is the radial effective diffusion coefficient of component i , ρ_{PDH} is the density of the catalyst for propane dehydrogenation, ρ_{SHC} is the density of the redox catalyst for selective hydrogen combustion, y_{PDH} is the mass fraction of the PDH catalyst in the catalyst bed, $R_{\text{PDH},i}$ is the net reaction rate of component i determined from Eqs. (1)–(6), and $R_{\text{SHC},i}$ is the net reaction rate of component i determined from Eqs. (7) and (8). $D_{e,i}$ is calculated using the Wilke formula [35]:

$$D_{e,i} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^n x_j / D_{i,j}} \quad (10)$$

where x_i is the molar fraction of component i and $D_{i,j}$ is the binary diffusivity of component i in a mixture of i and j that is calculated from the Chapman-Enskog equation [36]. The mass conservation equation for MeO_x and MeO_{x-1} is:

$$\frac{\partial c_i}{\partial t} = R_{\text{SHC},i} \quad (11)$$

The initial condition for the mass conservation equations is:

$$c_i = c_{i,0} \quad \text{at } t = 0 \quad (12)$$

where $c_{i,0}$ is the molar concentration of component i at $t = 0$. The boundary conditions for the mass conservation equations are:

$$c_i|_{z=0} = c_{i,\text{in}}, \quad \frac{\partial c_i}{\partial z}|_{z=L} = 0 \quad (13)$$

$$\frac{\partial c_i}{\partial r}|_{r=0} = 0, \quad \frac{\partial c_i}{\partial r}|_{r=R_0} = 0 \quad (14)$$

where $c_{i,\text{in}}$ is the molar concentration of component i at the reactor inlet and L is the reactor length.

The energy conservation equation is given as follows:

$$\begin{aligned} & (\rho_b C_{p,s} + \varepsilon \rho_g C_{p,g}) \frac{\partial T}{\partial t} + u \rho_g C_{p,g} \frac{\partial T}{\partial z} = \frac{\lambda_{\text{eff}}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \\ & (1 - \varepsilon) y_{\text{PDH}} \rho_{\text{PDH}} \sum_{j=1}^3 r_j (-\Delta H_j) + (1 - \varepsilon)(1 - y_{\text{PDH}}) \rho_{\text{SHC}} r_4 (-\Delta H_4) \end{aligned} \quad (15)$$

Here, T is the temperature, ρ_b is the packing density of the reactor, $C_{p,s}$ is the heat capacity of the solid phase, ρ_g is the density of the gas mixture, $C_{p,g}$ is the heat capacity of the gas phase, λ_{eff} is the effective thermal conductivity, and ΔH_j is the reaction enthalpy of reaction j . λ_{eff} can be calculated by:

$$\lambda_{\text{eff}} = (1 - \varepsilon) \lambda_s + \varepsilon \lambda_g \quad (16)$$

where λ_s is the thermal conductivity of solid phase that is adopted from the Ref. [37] and λ_g is the thermal conductivity of gas mixture that is calculated using the Wassiljewa equation [36]. The initial condition for the energy conservation equation is:

$$T = T_0 \quad \text{at } t = 0 \quad (17)$$

where T_0 is the initial temperature. The boundary conditions for the energy conservation equation are:

$$T|_{z=0} = T_{\text{in}}, \quad \frac{\partial T}{\partial z}|_{z=L} = 0 \quad (18)$$

$$\frac{\partial T}{\partial r}|_{r=0} = 0, \quad \frac{\partial T}{\partial r}|_{r=R_0} = 0 \quad (19)$$

where T_{in} is the temperature at the reactor inlet.

The momentum balance equation is approximated by the Ergun equation [38]:

$$\frac{\partial P}{\partial z} = -150 \frac{(1 - \varepsilon)^2 \mu_g u}{\varepsilon^3 d_p^2} - 1.75 \frac{(1 - \varepsilon) \rho_g u^2}{\varepsilon^3 d_p} \quad (20)$$

where P is the pressure, μ_g is the viscosity of the gas mixture, and d_p is the diameter of the catalyst pellet. The boundary condition for the momentum balance equation is:

$$P|_{z=0} = P_{\text{in}} \quad (21)$$

where P_{in} is the total pressure at the reactor inlet.

2.3. Implementation

The mass, energy and momentum conservation equations for the redox process are solved using the commercial software COMSOL Multiphysics. The mesh number is set to 1600, as the simulation results are almost the same but computational cost increases significantly when further increasing the mesh number (see Fig. S1 in the Supplementary Material). The simulation parameters are given in Table 1. It is worth noting that the model for the conventional dehydrogenation process is also built, in order to compare

Table 1
Simulation parameters used in this work

Parameter	Value
Reactor length (L)/m	10
Reactor radius (R_0)/m	1
Superficial gas velocity in reactor (u)/m·s ⁻¹	0.75
Feed pressure (P_{in})/MPa	0.05–0.30
Feed temperature (T_{in})/K	773–973
Mole ratio of H ₂ to C ₃ H ₈ in feed ($x_{H_2}/x_{C_3H_8}$)	0–0.3
Mass fraction of PDH catalyst (y_{PDH})	0.1–0.9
Density of PDH catalyst (ρ_{PDH})/kg·m ⁻³	2000 ^①
Density of SHC catalyst (ρ_{SHC})/kg·m ⁻³	2000 ^①
Porosity of reactor bed (ε)	0.5
Initial fraction of MeO _x (C_{MeO_x})	0.15 ^①

^① Data from Abbas *et al.* [39].

the redox process with the conventional process. For the conventional process, only PDH catalysts are packed in the reactor, and the packing density of PDH catalysts keeps the same with the one in the redox process. The model for the conventional process is described and validated in the Supplementary Material, and the simulation parameters are the same to the ones in Table 1.

3. Results and Discussion

3.1. A typical case

A typical simulation is conducted to obtain the fundamental characteristics of propane dehydrogenation combined with chemical looping combustion of hydrogen, and these simulation results are compared with the ones of the conventional process (CPDH). Fig. 2(a) and (b) display the propane conversions and propylene yields of the redox process and the conventional process. The times are deliberately selected to cover the period of consuming MeO_x. For the conventional process, the propane conversion and propylene yield show a rapid increase along the axial position of the reactor before reaching a plateau, since the dehydrogenation reaction is very fast and can reach reaction equilibrium quickly. For the redox process, the propane conversion and propylene yield increase with the axial position of the reactor when the reaction time is less than 20 min, suggesting that chemical looping combustion of hydrogen can shift the reaction equilibrium towards propylene. Besides, the propane conversion and propylene yield for the redox process decrease with time, but they would not be lower than these for the conventional process. Generally, the propane conversion and propylene yield for the redox process are much higher than these for the conventional process. When the reaction time is in the range of 5–20 min, the outlet propane conversion and propylene yield for the redox process are 17.5%–140.5% and 23.8%–168.7% higher than these for the conventional process.

Fig. 2(c) shows the distributions of hydrogen mole fraction in the fixed bed reactor. For the conventional process, the hydrogen mole fraction increases to a plateau quickly, as the reaction equilibrium is reached; then, a very slight decrease of hydrogen mole fraction can be observed, and this can be attributed to the influence of ethylene hydrogenation reaction (see Eq. (2)). For the redox process, the hydrogen mole fraction firstly increases with the axial position of the reactor and then decreases, the hydrogen mole fraction increases with the reaction time, and the hydrogen mole fraction is much lower than that of the conventional process. For the redox process, hydrogen combustion reaction removes the hydrogen generated by the dehydrogenation reaction, which explains the lower hydrogen mole fraction. Besides, the amount of oxygen carrier decreases with time (see Fig. 2(e)), resulting in the decreased hydrogen mole fraction with time.

Fig. 2(d) gives the temperature distributions for the conventional process and the redox process. For the conventional process, the temperature decreases quickly before reaching a constant value (*i.e.*, 767 K), as the propane dehydrogenation consumes much heat. For the redox process, the temperature firstly decreases with the axial position of the reactor then increases, and it decreases again when the reaction time is short ($t \leq 10$ min). Besides, a significant temperature drop between inlet and outlet of the reactor is observed. These results can be explained by comparing the heat consumed by the propane dehydrogenation reaction with the heat generated by the hydrogen combustion reaction. The heat generated by the hydrogen combustion reaction should be lower than the heat consumed by the propane dehydrogenation reaction, resulting in the significant temperature drop between inlet and outlet of the reactor.

Fig. 2(e) shows the distributions of MeO_x mass fraction in the redox process. The MeO_x mass fraction decreases quickly with the axial position of the reactor and then increases, as the MeO_x at the reactor inlet is firstly depleted. Besides, the MeO_x mass fraction decreases with time, and most of MeO_x is consumed at $t = 20$ min.

Fig. 2(f) displays the outlet propylene yield as a function of reaction time for the redox process. The outlet propylene yield slightly increases and then decreases with time. The maximum yield is 73.4%, which is 177.0% higher than that for the conventional process (*i.e.*, 26.5%). In the beginning, propane dehydrogenation reaction quickly consumes a lot of heat, while much reaction heat has not been released into the system due to the low hydrogen combustion rate. After a few minutes, the heat generated by hydrogen combustion reaction accumulates and starts to drive propane dehydrogenation reaction. Therefore, a maximum yield is observed in Fig. 2(f). An operating time for dehydrogenation (t_o) is defined as the time when the outlet propylene yield is 80% of the maximum yield (see Fig. 2(f)). The operating time should be dependent on the reaction conditions and the fraction of MeO_x in the reactor. Besides, as seen from Fig. 2(f), the time-averaged yield of propylene within the operating time (Y_{ave}) can be calculated by:

$$Y_{ave} = \frac{\int_{t=0}^{t=t_o} Y(t)dt}{t_o} \quad (22)$$

For the redox process in Fig. 2, the operating time is 13.5 min, and the time-averaged yield is 67.3% that is 154.0% higher than the one for the conventional process. In addition, the three-dimensional distributions of propane conversion, propylene yield, mole fraction of hydrogen, temperature, and mass fraction of MeO_x are also given in Fig. S3 in the Supplementary Material.

3.2. Effects of operating conditions

Fig. 3(a) shows the effect of feed temperature on the time-averaged yield of propylene and the operating time. The time-averaged yield of propylene increases from 35.9% to 67.3% with the feed temperature changing from 773 K to 973 K, while the operating time decreases from 19 to 13.5 min. Fig. 3(b–d) display the time-dependent distributions of propylene yield at $T = 773$ K, 873 K, and 973 K. The outlet yield of propylene increases with the temperature at a specific reaction time. For example, at $t = 10$ min, the outlet yields of propylene are 35.4%, 52.6%, and 66.6% for the reaction temperatures of 773 K, 873 K, and 973 K, respectively. Besides, the outlet yields of propylene decrease more quickly with time when the reaction temperature is higher. Apparently, a high feed temperature is favorable for the redox process in terms of the time-averaged yield of propylene shown in Fig. 3(a). However, when choosing the feed temperature, other factors should also be accounted for. For example, the PDH catalyst would

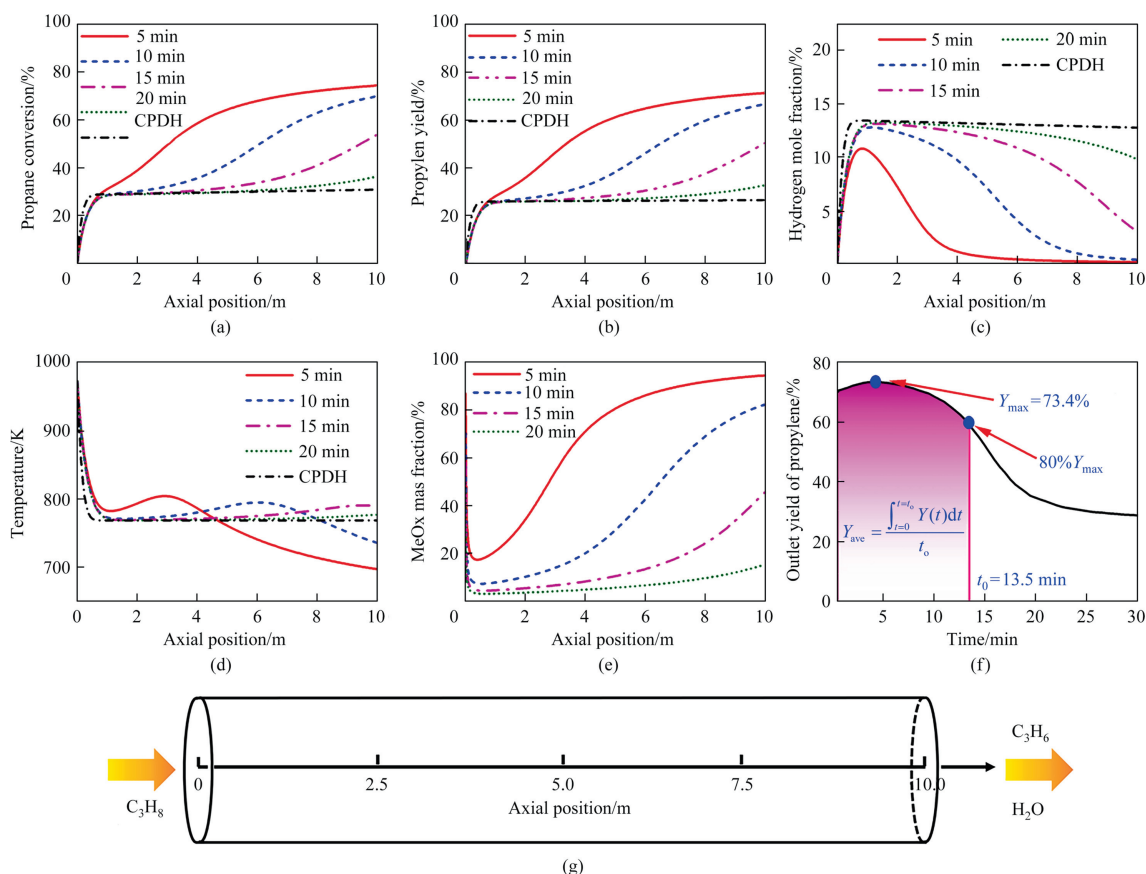


Fig. 2. Comparison of simulation results between the redox process and the conventional process (CPDH). (a) Propane conversion, (b) propylene yield, (c) mole fraction of hydrogen, (d) temperature, and (e) mass fraction of MeO_x along the axial position of the reactor; (f) the change of outlet propylene yield with time, (g) the schematic diagram of the redox reactor. Simulation parameters: $T_{in} = 973$ K, $P_{in} = 0.1$ MPa, $x_{H_2}/x_{C_3H_8} = 0$, and $y_{PDH} = 0.5$. The other parameters are given in Table 1.

deactivate quickly if the reaction temperature is above 973 K [3]. Thus, a feed temperature of 973 K is preferable for the redox process.

A higher feed temperature means more heat input from the feed, which would lead to a higher temperature in the reactor (see Fig. S4(a) in the Supplementary Material). The higher reaction temperature results in higher reaction rates for propane dehydrogenation and hydrogenation combustion, and subsequently leads to a higher hydrogen fraction and a lower MeO_x fraction (see Figs. S4(b) and (c)). Besides, the higher reaction temperature is more favorable to shift the reaction equilibrium towards propylene. These explain the increased time-averaged propylene yield and decreased operating time with the increase of reaction temperature.

Fig. 4(a) displays the effect of feed pressure on the time-averaged yield of propylene and the operating time. With the pressure increasing from 0.05 to 0.30 MPa, the time-averaged yield of propylene decreases from 70.3% to 59.2%, and the operating time decreases from 26 to 4.5 min. Fig. 4(b)–(d) gives the time-dependent distributions of propylene yield at $P_{in} = 0.05, 0.10$, and 0.30 MPa. The propylene yield decreases with the pressure at a specific reaction time. For example, at the reaction time of 5 min, the outlet propylene yields are 72.4%, 71.2%, and 53.2% for the pressures of 0.05, 0.10, and 0.30 MPa, respectively. Besides, the outlet propylene yield decreases very quickly when the pressure is high. A lower feed pressure is more favorable when only considering the time-averaged yield of propylene. However, when the reactor is operated at a pressure less than 0.1 MPa, a vacuum system is required, which significantly increases the capital and oper-

ating costs. Therefore, a feed pressure of 0.1 MPa is favorable for the redox process.

When the feed pressure is higher, the reaction rate of propane dehydrogenation is higher (see Eq. (4)) and thus more hydrogen is generated. Since the rate for the consumption of MeO_x increases with the concentration of hydrogen (see Eq. (8)), a higher feed pressure would lead to a faster depletion of MeO_x in the reactor (see Fig. S5(c) in the Supplementary Material). This explains the decreased operating time with the increase of feed pressure. Although the rate for propane dehydrogenation increases with the feed pressure, the mole flow rate of propane also linearly increases with the pressure. Besides, a higher feed pressure is not favorable in shifting the reaction equilibrium towards propylene. These explain the decreased time-averaged yield of propylene with the increase of feed pressure.

Fig. 5(a) shows the effect of hydrogen to propane mole ratio on the time-averaged yield of propylene and the operating time. The time-averaged yield of propylene reaches a maximum value of 77.0% at $x_{H_2}/x_{C_3H_8} = 0.15$. The operating time is not sensitive to the change of $x_{H_2}/x_{C_3H_8}$, only slightly decreases with $x_{H_2}/x_{C_3H_8}$. Fig. 5(b)–(d) exhibit the time-dependent distributions of propylene yield at $x_{H_2}/x_{C_3H_8} = 0.05, 0.15$, and 0.25. The outlet propylene yields at the reaction time of 5 min are 77.7%, 82.2%, and 77.4% for $x_{H_2}/x_{C_3H_8} = 0.05, 0.15$, and 0.25, respectively. According to the aforementioned results, there exists an optimal $x_{H_2}/x_{C_3H_8}$ to achieve a maximum time-averaged yield of propylene.

A higher $x_{H_2}/x_{C_3H_8}$ means a higher hydrogen combustion rate, which results in more reaction heat to drive the propane dehydrogenation reaction. This explains the increase of time-averaged

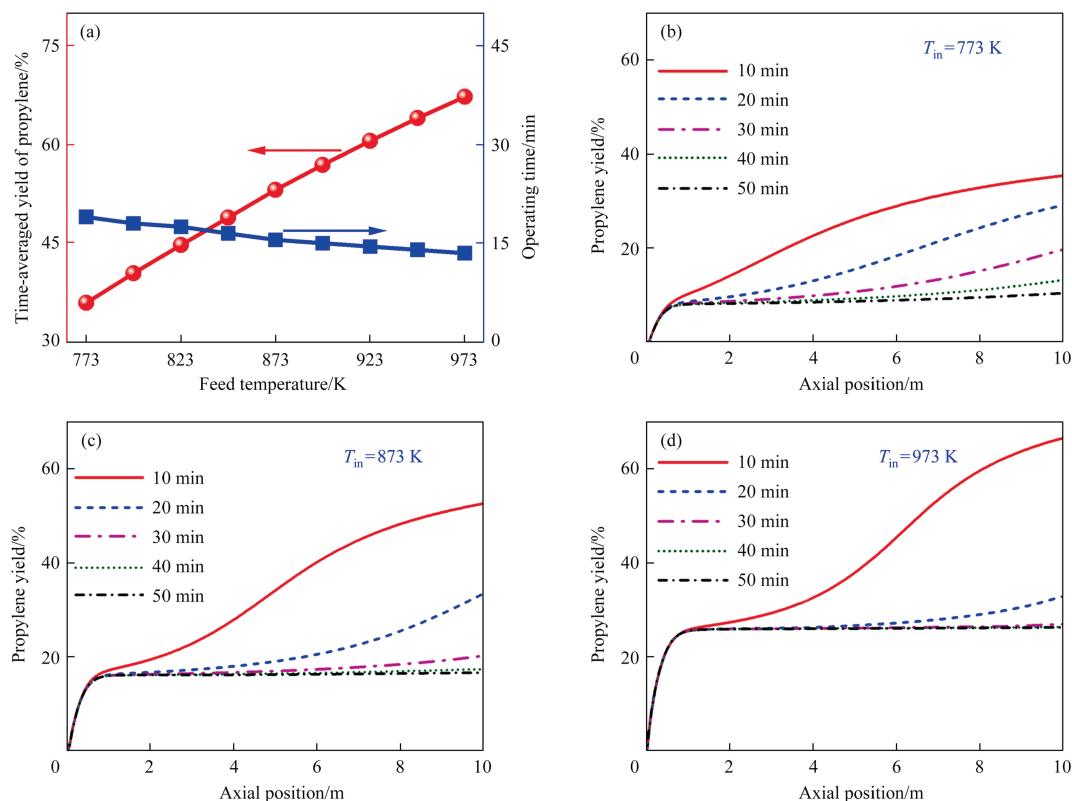


Fig. 3. (a) Time-averaged yield of propylene and operating time under the feed temperature of 773–973 K. Distributions of propylene yield at the feed temperatures of (b) 773 K, (c) 873 K, and (d) 973 K. Simulation parameters: $P_{in} = 0.1$ MPa, $x_{H_2}/x_{C_3H_8} = 0$, and $y_{PDH} = 0.5$. The other parameters are given in Table 1.

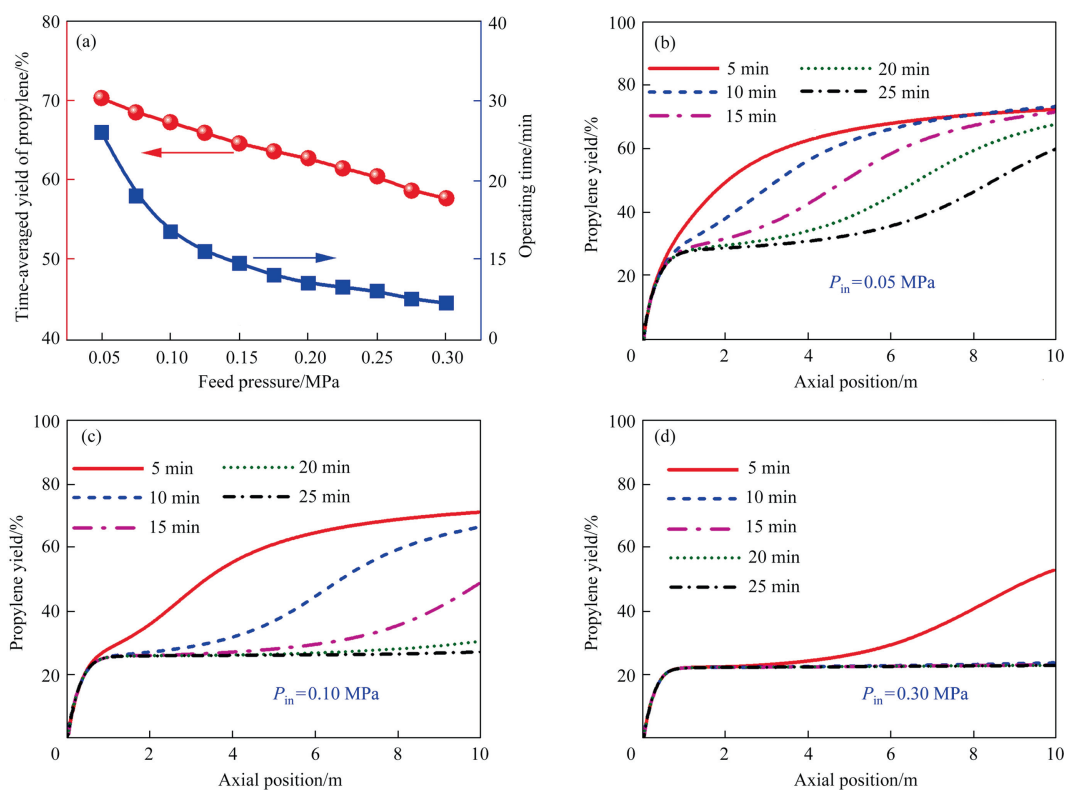


Fig. 4. (a) Time-averaged yield of propylene and operating time under the feed pressure of 0.05–0.30 MPa. Distributions of propylene yield at the feed pressures of (b) 0.05 MPa, (c) 0.1 MPa, and (d) 0.3 MPa. Simulation parameters: $T_{in} = 973$ K, $x_{H_2}/x_{C_3H_8} = 0$, and $y_{PDH} = 0.5$. The other parameters are given in Table 1.

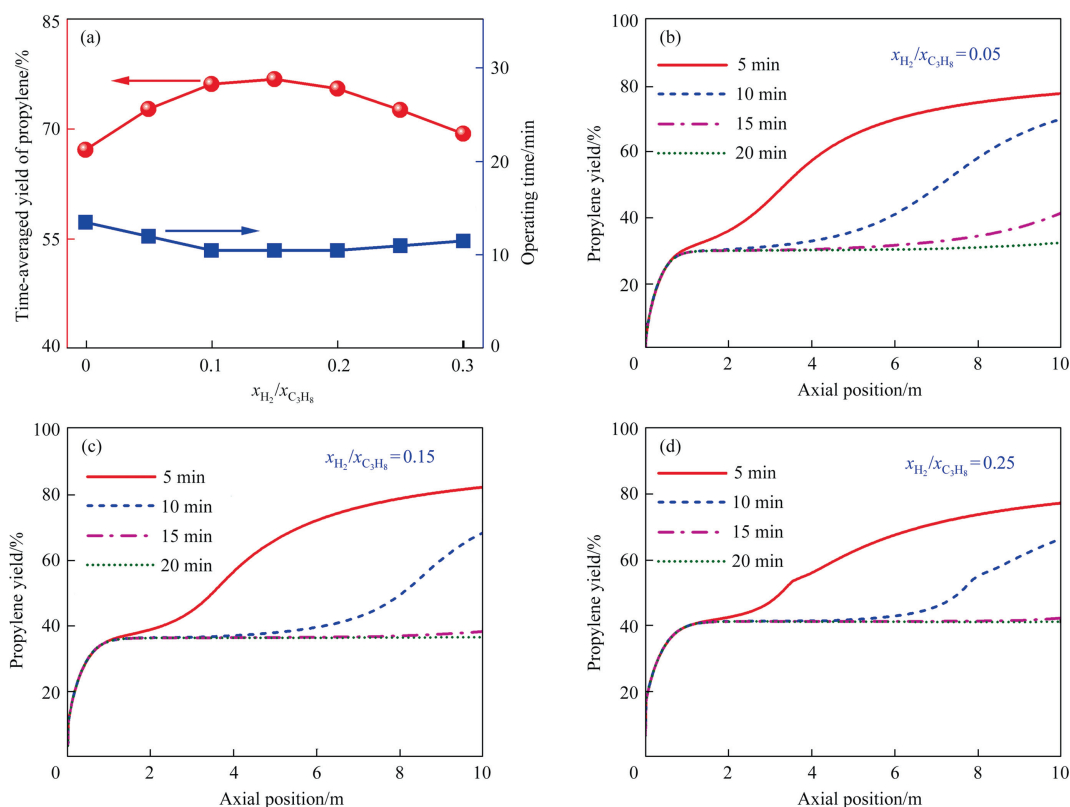


Fig. 5. (a) Time-averaged yield of propylene and operating time under the hydrogen to propane mole ratio of 0–0.3. Distributions of propylene yield at the hydrogen to propane mole ratio of (b) 0.05, (c) 0.15, and (d) 0.25. Simulation parameters: $T_{in} = 973$ K, $P_{in} = 0.1$ MPa, and $y_{PDH} = 0.5$. The other parameters are given in Table 1.

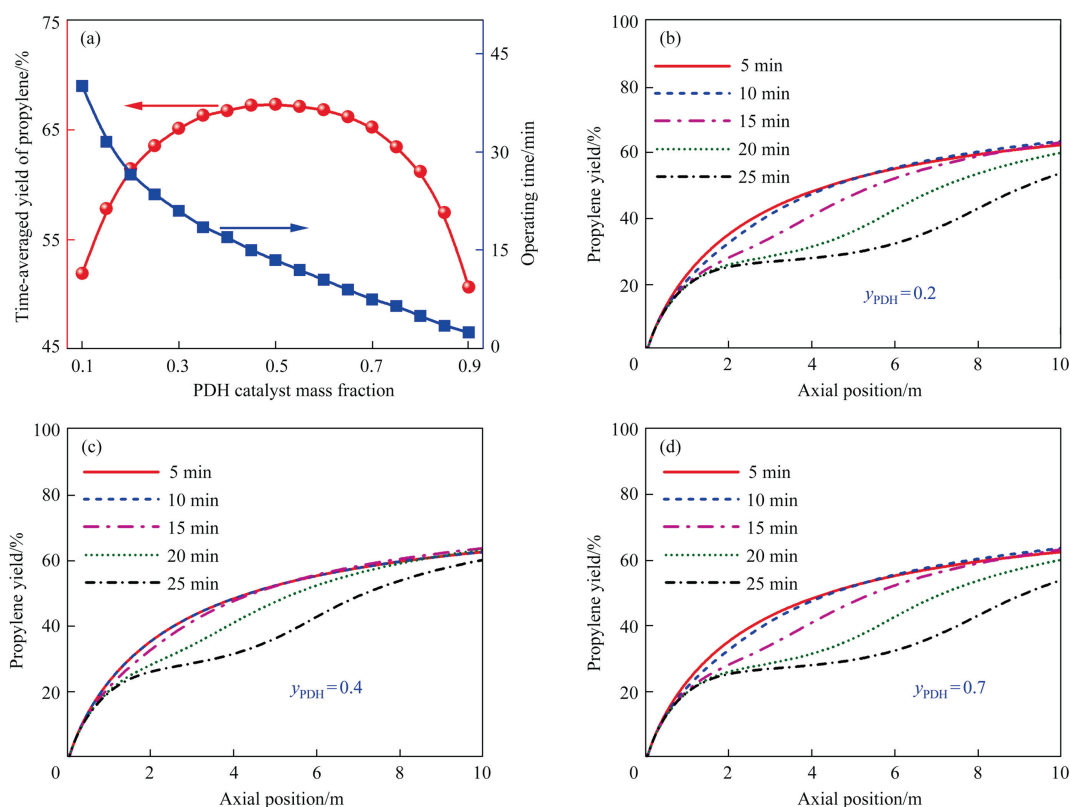


Fig. 6. (a) Time-averaged yield of propylene and operating time under the PDH catalyst mass fraction of 0.1–0.9. Distributions of propylene yield at the PDH catalyst mass fraction of (b) 0.2, (c) 0.4, and (d) 0.7. Simulation parameters: $T_{in} = 973$ K, $P_{in} = 0.1$ MPa, and $x_{H_2}/x_{C_3H_8} = 0$. The other parameters are given in Table 1.

yield of propylene with $x_{H_2}/x_{C_3H_8}$ when $x_{H_2}/x_{C_3H_8} \leq 0.15$. However, when the $x_{H_2}/x_{C_3H_8}$ is too high, the temperature in the reactor can be very high and this would significantly reduce the selectivity towards propylene. For example, when $x_{H_2}/x_{C_3H_8} = 0.25$, the reaction temperature can be as high as 1062 K at the reaction time of 10 min (see Fig. S6(a) in the Supplementary Material). Thus, the time-averaged yield of propylene decreases with $x_{H_2}/x_{C_3H_8}$ when $x_{H_2}/x_{C_3H_8} > 0.15$. Besides, adding some hydrogen in the feed is also helpful in preventing PDH catalyst from deactivation by coking [7]. The finding in this work indicates that adding an appropriate amount of hydrogen in the feed is favorable in the redox process.

3.3. Effect of PDH catalyst mass fraction

Fig. 6(a) exhibits the effect of PDH catalyst mass fraction on the time-averaged yield of propylene and the operating time. The time-averaged yield of propylene firstly increases and then decreases with PDH catalyst mass fraction changing from 0.1 to 0.9, resulting in a maximum time-averaged yield of propylene of 67.3% at $y_{PDH} = 0.5$. The operating time decreases significantly from 40 to 2.5 min. Fig. 6(b–d) display the time-dependent distributions of propylene yield at $y_{PDH} = 0.2, 0.4$, and 0.7 . The outlet propylene yield for $y_{PDH} = 0.2$ and 0.7 decreases more quickly with time than that for $y_{PDH} = 0.4$. Generally, the preferable PDH catalyst mass fraction for the redox process is 0.5.

More PDH catalyst means a faster rate for propane dehydrogenation, which is favorable to enhance the propylene yield. While more PDH catalyst also indicates less MeO_x in the reactor, which is unfavorable to increase the propylene yield. The reaction of MeO_x with hydrogen can shift reaction equilibrium towards propylene and provide much heat to drive the propane dehydrogenation reaction. Due to the two competing factors, there exists an optimal PDH catalyst mass fraction when only considering the time-averaged yield of propylene. When the mass fraction of MeO_x in the reactor is low, less time is required to consume MeO_x , as indicated by Fig. S7(c) in the Supporting Material. This explains the decreased operating time with the increase of PDH catalyst mass fraction.

4. Conclusions

In this work, a redox process combining propane dehydrogenation with selective hydrogen combustion is proposed. In this process, the propane dehydrogenation catalyst and the hydrogen selective combustion catalyst are mixed and loaded into a fixed-bed reactor. Since two reactions proceed simultaneously, hydrogen can be removed in situ to shift the reaction equilibrium towards propylene, and the reaction heat of hydrogen combustion can be used to drive the propane dehydrogenation reaction. A two-dimensional dynamic mathematical model is established to describe the coupled mass transfer, heat transfer and chemical reaction in the fixed-bed reactor during the dehydrogenation stage. The simulation results of this redox process are compared with these of a conventional process, and the effects of operating conditions (*i.e.*, feed temperature, pressure and composition) and PDH catalyst mass fraction on the performance of the redox process are investigated.

In a typical case, the redox process performs much better than the conventional process, showing a propylene yield up to 73.4% that is 177.0% higher than that for the conventional process (*i.e.*, 26.5%). The outlet propylene yield for the redox process is time-dependent since the oxygen carrier is continuously consumed, and thus an operating time when the outlet propylene yield is above 80% of the maximum one is defined. The operating time is 13.5 min and the time-average propylene yield is 67.3% in the typical case. Considering the time-average propylene yield, operating

time, and other factors, the preferable operating conditions and PDH catalyst mass fraction are obtained for the redox process. A feed temperature of 973 K, a feed pressure of 0.1 MPa, a mole ratio of H_2 to C_3H_8 of 0.15, and a PDH catalyst mass fraction of 0.5 are favorable for the redox process. It is worth noting that these preferable operating conditions are obtained by the parametric sweep method and they are not globally optimal. A more elegant method is performing global optimization. However, to do this, a global optimization model including many complex factors should be developed. This is out of the scope of this work, and is the subject of future work. This work should provide a mathematical model and some useful guidance for developing the redox processes combining propane dehydrogenation with selective hydrogen combustion.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (22078090 and 92034301), the Shanghai Rising-Star Program (21QA1402000), the Natural Science Foundation of Shanghai (21ZR1418100), and the Open Project of State Key Laboratory of Chemical Engineering (SKL-ChE-21C02).

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.07.032>.

References

- [1] Z. Nawaz, Light alkane dehydrogenation to light olefin technologies: A comprehensive review, *Rev. Chem. Eng.* 31 (5) (2015) 413–436.
- [2] J.C. Bricker, Advanced catalytic dehydrogenation technologies for production of olefins, *Top. Catal.* 55 (19–20) (2012) 1309–1314.
- [3] J.J.H.B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, B.M. Weckhuysen, Catalytic dehydrogenation of light alkanes on metals and metal oxides, *Chem. Rev.* 114 (20) (2014) 10613–10653.
- [4] F.T. Zangeneh, A. Taeb, K. Gholivand, S. Sahebdelfar, Thermodynamic equilibrium analysis of propane dehydrogenation with carbon dioxide and side reactions, *Chem. Eng. Commun.* 203 (4) (2016) 557–565.
- [5] M. Farsi, Dynamic modelling, simulation and control of isobutane dehydrogenation in a commercial Oleflex process considering catalyst deactivation, *J. Taiwan Inst. Chem. Eng.* 57 (2015) 18–25.
- [6] B.V. Vora, Development of dehydrogenation catalysts and processes, *Top. Catal.* 55 (19–20) (2012) 1297–1308.
- [7] M.M. Bhasin, J.H. McCain, B.V. Vora, T. Imai, P.R. Pujadó, Dehydrogenation and oxydehydrogenation of paraffins to olefins, *Appl. Catal. A: Gen.* 221 (1–2) (2001) 397–419.
- [8] O. Czuprat, S. Werth, J. Caro, T. Schiestel, Oxidative dehydrogenation of propane in a perovskite membrane reactor with multi-step oxygen insertion, *AIChE J.* 56 (2010) 2390–2396.
- [9] R.K. Grasselli, D.L. Stern, J.G. Tsikoyiannis, Catalytic dehydrogenation (DH) of light paraffins combined with selective hydrogen combustion (SHC): II. DH +SHC catalysts physically mixed (redox process mode), *Appl. Catal. A: Gen.* 189 (1) (1999) 9–14.
- [10] S. Kaneko, T. Arakawa, M.A. Ohshima, H. Kurokawa, H. Miura, Dehydrogenation of propane combined with selective hydrogen combustion over Pt–Sn bimetallic catalysts, *Appl. Catal. A: Gen.* 356 (1) (2009) 80–87.
- [11] Y. Shan, Z. Sui, Y. Zhu, J. Zhou, X. Zhou, D.e. Chen, Boosting size-selective hydrogen combustion in the presence of propene using controllable metal clusters encapsulated in zeolite, *Angew. Chem. Int. Ed. Engl.* 57 (31) (2018) 9770–9774.

- [12] R. Hu, X. Li, Z.J. Sui, G.H. Ye, X.G. Zhou, Process simulation and optimization of propane dehydrogenation combined with selective hydrogen combustion, *Chem. Eng. Process. – Process. Intensif.* 143 (2019) 107608.
- [13] J. Beckers, G. Rothenberg, Sustainable selective oxidations using ceria-based materials, *Green Chem.* 12 (6) (2010) 939–994.
- [14] X. Zhu, Q. Imtiaz, F. Donat, C.R. Müller, F. Li, Chemical looping beyond combustion – a perspective, *Energy Environ. Sci.* 13 (3) (2020) 772–804.
- [15] L. Zeng, Z. Cheng, J.A. Fan, L.-S. Fan, J. Gong, Metal oxide redox chemistry for chemical looping processes, *Nat. Rev. Chem.* 2 (11) (2018) 349–364.
- [16] J. Beckers, A. Lee, G. Rothenberg, Bismuth-doped ceria, $\text{Ce}_{0.90}\text{Bi}_{0.10}\text{O}_2$: A selective and stable catalyst for clean hydrogen combustion, *Adv. Synth. Catal.* 351 (10) (2009) 1557–1566.
- [17] J.H. Blank, J. Beckers, P.F. Collignon, F. Clerc, G. Rothenberg, A “green route” to propene through selective hydrogen oxidation, *Chemistry* 13 (18) (2007) 5121–5128.
- [18] R.K. Grasselli, D.L. Stern, J.G. Tsikoyiannis, in: *Strategies for combining light paraffin dehydrogenation (DH) with selective hydrogen combustion (SHC). Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 2000 (773–778).
- [19] J.H. Blank, J. Beckers, P.F. Collignon, G. Rothenberg, Redox kinetics of ceria-based mixed oxides in selective hydrogen combustion, *ChemPhysChem* 8 (17) (2007) 2490–2497.
- [20] G. Rothenberg, E.A. de Graaf, A. Blik, Solvent-free synthesis of rechargeable solid oxygen reservoirs for clean hydrogen oxidation, *Angew. Chem. Int. Ed. Engl.* 42 (29) (2003) 3366–3368.
- [21] J. Beckers, G. Rothenberg, $\text{Ce}_{0.95}\text{Cr}_{0.05}\text{O}_2$ and $\text{Ce}_{0.97}\text{Cu}_{0.03}\text{O}_2$: Active, selective and stable catalysts for selective hydrogen combustion, *Dalton Trans.* 29 (2009) 5673–5682.
- [22] M.S.C. Chan, H.G. Baldovi, J.S. Dennis, Enhancing the capacity of oxygen carriers for selective oxidations through phase cooperation: Bismuth oxide and ceria–zirconia, *Catal. Sci. Technol.* 8 (3) (2018) 887–897.
- [23] L. Lâte, W. Thelin, E.A. Blekkan, Selective combustion of hydrogen in the presence of hydrocarbons: Part 2. Metal oxide based catalysts, *Appl. Catal. A: Gen.* 262 (1) (2004) 63–68.
- [24] J. Beckers, G. Rothenberg, Lead-containing solid “oxygen reservoirs” for selective hydrogen combustion, *Green Chem.* 11 (10) (2009) 1550.
- [25] E.A. de Graaf, A. Andreini, E.J.M. Hensen, A. Blik, Selective hydrogen oxidation in a mixture with ethane/ethene using cerium zirconium oxide, *Appl. Catal. A: Gen.* 262 (2) (2004) 201–206.
- [26] L. Van der Zande, E. De Graaf, G. Rothenberg, Design and parallel synthesis of novel selective hydrogen oxidation catalysts and their application in alkane dehydrogenation, *Adv. Synth. Catal.* 344 (8) (2002) 884–889.
- [27] A. Abad, J. Adánez, F. García-Labiano, L.F. de Diego, P. Gayán, Modeling of the chemical-looping combustion of methane using a Cu-based oxygen-carrier, *Combust. Flame* 157 (3) (2010) 602–615.
- [28] S.Z. Abbas, V. Dupont, T. Mahmud, Modelling of high purity H_2 production via sorption enhanced chemical looping steam reforming of methane in a packed bed reactor, *Fuel* 202 (2017) 271–286.
- [29] J. Francisco Morgado, S. Cloete, J. Morud, T. Gurker, S. Amini, Modelling study of two chemical looping reforming reactor configurations: Looping vs. switching, *Powder Technol.* 316 (2017) 599–613.
- [30] L. Han, Z. Zhou, G.M. Bollas, Heterogeneous modeling of chemical-looping combustion. Part 1: Reactor model, *Chem. Eng. Sci.* 104 (2013) 233–249.
- [31] D.-A. Chisalita, A.-M. Cormos, Dynamic simulation of fluidized bed chemical looping combustion process with iron based oxygen carrier, *Fuel* 214 (2018) 436–445.
- [32] S. Noorman, F. Gallucci, M. van Sint Annaland, J.A.M. Kuipers, A theoretical investigation of CLC in packed beds. Part 2: Reactor model, *Chem. Eng. J.* 167 (1) (2011) 369–376.
- [33] M.P. Lobera, C. Téllez, J. Herguido, M. Menéndez, Transient kinetic modelling of propane dehydrogenation over a Pt-Sn-K/Al₂O₃ catalyst, *Appl. Catal. A: Gen.* 349 (1–2) (2008) 156–164.
- [34] A. Abad, J. Adánez, F. García-Labiano, L.F. de Diego, P. Gayán, J. Celaya, Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion, *Chem. Eng. Sci.* 62 (1–2) (2007) 533–549.
- [35] D.F. Fairbanks, C.R. Wilke, Diffusion coefficients in multicomponent gas mixtures, *Ind. Eng. Chem.* 42 (3) (1950) 471–475.
- [36] R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases & Liquids*, McGraw Hill Book Company, New York, 1988.
- [37] J.T. Richardson, S.A. Paripatyadar, Carbon dioxide reforming of methane with supported rhodium, *Appl. Catal.* 61 (1) (1990) 293–309.
- [38] H.S. Fogler, *Elements of Chemical Reaction Engineering*, 4th ed., Prentice Hall PTR, Upper Saddle River, 2006.
- [39] S.Z. Abbas, V. Dupont, T. Mahmud, Modelling of H_2 production in a packed bed reactor via sorption enhanced steam methane reforming process, *Int. J. Hydrog. Energy* 42 (30) (2017) 18910–18921.