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Stationary spatially periodic and aperiodic solutions in membrane reactors

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Abstract

The formation of stationary spatially patterns is analysed for a detailed reaction mechanism of the oxidative dehydrogenation of ethane. In the first step, a simple steady-state model of an ideal plug flow membrane reactor is investigated by numerical bifurcation analysis. The model shows a complex nonlinear behaviour including period doubling bifurcations and aperiodic spatial patterns. In the next step, the influence of axial heat dispersion is studied. Finally, a more detailed model of a fixed bed membrane reactor is considered. It is found that pattern formation is possible under operation conditions realisable in a laboratory reactor.

Keywords: Membranes; Chemical reactors; Nonlinear dynamics; Stationary pattern; Bifurcation; Selective oxidation

1. Introduction

Membrane reactors are multi-functional process units, which combine reaction and separation in one apparatus. Compared to conventional reactors, they may offer advantages with respect to yield, selectivity, and energy integration (Saracco et al., 2000). Two main operation schemes of membrane reactors can be distinguished: selective product removal and distributed injection of reactants. In the first case, the membrane is used to increase the conversion of equilibrium limited reactions. In the second case, supplying reactants along the reactor rather than only with the feed may help to improve the selectivity of consecutive reactions, e.g. in partial oxidation reactions. By changing the permeability of the membrane or the concentration of the reactants supplied through the membrane, one may be able to create an optimal concentration profile of reactants along the reactor coordinate and thus to maximize the yield of the reaction.

A number of publications (Nekhamkina et al. 2000a,b; Sheintuch and Nekhamkina, 2003; Travnickova et al., 2004) show that the side injection of reactants may cause complicated nonlinear behaviour like the formation of spatiotemporal patterns. Sheintuch and co-workers pointed out an analogy between the dynamic behaviour of a CSTR and the steady-state behaviour of an ideal plug flow membrane reactor. They showed that for small axial dispersion of heat spatially periodic patterns can emerge for an exothermic first order reaction (Nekhamkina et al., 2000a), and that complex aperiodic patterns may exist in the case of a simple consecutive reaction with two reaction steps (Sheintuch and Nekhamkina, 2003). Travnickova et al. (2004) found complex aperiodic spatiotemporal patterns in a cross-flow reactor with a first-order reaction and high axial dispersion of heat (Travnickova et al., 2004).

The purpose of this work is to explore the possibility of obtaining and measuring stationary spatially periodic patterns in a laboratory membrane reactor. Different models of a membrane reactor with a porous membrane and a catalytic fixed bed are considered. All models use an experimentally validated reaction scheme for the partial oxidation of ethane. The simplest model variant assumes ideal plug flow behaviour in the fixed bed. It is studied in the first step by a bifurcation analysis and by dynamic simulations. In the second step, dispersive effects are included in the analysis. In the last step, the results are compared with a more detailed spatially distributed model of the membrane reactor.

2. Analysis of a simple membrane reactor model

Klose et al. (2004) investigated the oxidative dehydrogenation of ethane over a VO_x/γ–Al_2O_3 catalyst in a laboratory

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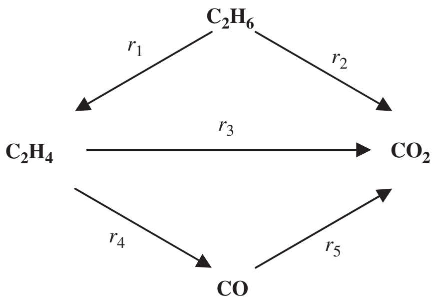

Fig. 1. Reaction network for the oxidative dehydrogenation of ethane (Klose et al., 2004).

Table 1
Reaction kinetics for the reaction network in Fig. 1

Reaction	Equation
1	$r_1 = \left[\dfrac{k_{\text{red}} c_{C_2H_6} k_{\text{ox}} c_{O_2}^{0.5}}{k_{\text{red}} c_{C_2H_6} + k_{\text{ox}} c_{O_2}} \right]$
2	$r_2 = k_2 \left[\dfrac{K_{C_2H_6} c_{C_2H_6}}{1 + K_{C_2H_6} c_{C_2H_6} + K_{CO_2} c_{CO_2}} \times \dfrac{K_{O_2}^{0.5} c_{O_2}^{0.5}}{1 + K_{O_2}^{0.5} c_{O_2}^{0.5}} \right]$
3	$r_3 = k_3 \left[\dfrac{K_{C_2H_4} c_{C_2H_4}}{1 + K_{C_2H_4} c_{C_2H_4} + K_{CO} c_{CO}} \times \dfrac{K_{O_2}^{0.5} c_{O_2}^{0.5}}{1 + K_{O_2}^{0.5} c_{O_2}^{0.5}} \right]$
4	$r_4 = k_4 \left[\dfrac{K_{C_2H_4} c_{C_2H_4}}{1 + K_{C_2H_4} c_{C_2H_4} + K_{CO_2} c_{CO_2}} \times \dfrac{K_{O_2}^{0.5} c_{O_2}^{0.5}}{1 + K_{O_2}^{0.5} c_{O_2}^{0.5}} \right]$
5	$r_5 = k_5 \frac{K_{CO} c_{CO} K_{O_2}^{0.5} c_{O_2}^{0.5}}{[1 + K_{CO} c_{CO} + K_{O_2}^{0.5} c_{O_2}^{0.5} + K_{CO_2} c_{CO_2}]^2}$

An Arrhenius approach is used for the rate factors, i.e. $k_i = k_{0i} \exp(E_i/R/T)$, $i = \text{red}, \text{ox}, 1, 2, \ldots, 5$ (Klose et al., 2004). c_i represents the molar concentration of component i in mol/l at 298 K and 1 atm.

Table 2
Kinetic parameters for the reaction network in Fig. 1

$k_{0,\text{red}} = 4.3 \times 10^9$ l/kg/h	$E_1 = 94$ kJ/mol
$k_{0,\text{ox}} = 1.1 \times 10^8$ mol$^{0.5}$ l$^{0.5}$/kg/h	$E_2 = 114$ kJ/mol
$k_{02} = 1.6 \times 10^7$ mol/kg/h	$E_3 = 51$ kJ/mol
$k_{03} = 2.0 \times 10^4$ mol/kg/h	$E_4 = 51$ kJ/mol
$k_{04} = 1.0 \times 10^3$ mol/kg/h	$E_5 = 118$ kJ/mol
$k_{05} = 1.1 \times 10^7$ mol/kg/h	
$K_{C_2H_6} = 4769.76$ l/mol	
$K_{O_2} = 1002.58$ l/mol	
$K_{C_2H_4} = 3025.57$ l/mol	
$K_{CO_2} = 3455.82$ l/mol	
$K_{CO} = 3233.91$ l/mol	

fixed bed reactor. The reaction network proposed in (Klose et al., 2004) consists of five reaction steps (see Fig. 1). Reaction 1 is described by a Mars van Krevelen mechanism. For reactions 2–5, a Langmuir Hinshelwood approach is used. All kinetic equations and parameters are given in Tables 1 and 2.

In this work, the oxidative dehydrogenation of ethane is investigated in a fixed bed membrane reactor as shown in Fig. 2. The reactor consists of a porous tubular membrane and a catalytic fixed bed inside the tube. The shell side of the membrane is empty. Reactants can be fed directly to the inlet of the fixed bed with concentrations $c_{i,\text{in}}$ and a temperature T_{in}; alternatively, they can enter the fixed bed in a spatially distributed manner via the shell side across the membrane with inlet concentrations c_{0i} and an inlet temperature T_0.

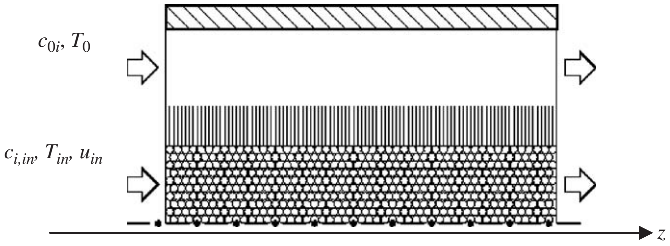

Fig. 2. Scheme of the fixed bed membrane reactor studied in this work.

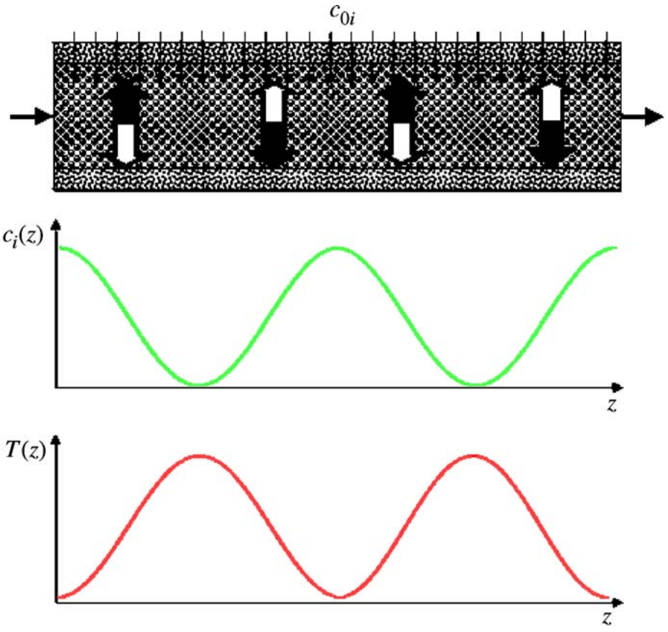

Fig. 3. Physical interpretation of the stationary pattern formation in a fixed bed membrane reactor; meaning of filled arrows: ∩ = charging of energy storage by chemical reaction; ∪ = discharging of energy storage by heat losses; meaning of open arrows: ∩ = charging of mass storage by mass supply through membrane; ∪ = discharging of mass storage by chemical reaction.

Fig. 3 gives a simple physical explanation for the possible formation of spatial patterns in such a reactor. The fluid flowing through the fixed bed possesses a storage capacity for material of reactants and for heat. A spatial pattern is caused by the alternate charging and discharging of the material storage and the heat storage resulting from the chemical reaction. In sections of high conversion, the material storage is discharged, and the reaction heat released charges the energy storage. In sections of low conversion, the material storage is reloaded by mass transfer from the sweep gas side through the membrane, while heat losses reduce the temperature of the fixed bed and hence discharge the energy storage.

In order to verify the pattern formation in the case of ethane oxidation, a one-dimensional pseudo-homogeneous model of