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Simulation of selective reactions' performance in transient regimes with periodical separate feeding of reagents Case study: Propane oxidative dehydrogenation in adiabatic V–Ti catalyst bed

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Abstract

The model simulation study has shown that the anaerobic process of oxidative dehydrogenation of propane under periodic alteration of feeding between propane and air may be realized in adiabatic catalyst beds in stable continuous cyclic mode in two-reactor scheme. In case of appropriate choice of process parameters (cycle duration and residence times), the process appears to be autothermal, i.e. it does not require any inlet gas preheating for stable operation. Compared to similar steady-state adiabatic process, the proposed process is characterized with much lower maximum catalyst temperatures, giving the way to process pure propane without diluting it with inert gases, thus simplifying downstream procedure of product separation. Predicted propylene yield is competitive with one for the steady-state adiabatic process, while sufficient technological benefits of the new technology are expected (decrease of energy consumption and minimization of heat-exchange environment, simplification of product separation procedure, process safety improvement, suppression of coke formation and efficient coke incineration). Notably, the proposed process is characterized with much more degrees of freedom available for further development and optimization than conventional steady-state technologies.

Keywords: Propane; Propylene; Dehydrogenation; Anaerobic oxidation; Selectivity; Cyclic operation; Simulation

1. Introduction

Improvement of selectivity and desired product yield in complex reaction systems is one of the major problems in catalytic reaction engineering and also one of the main challenges in the catalytic reaction engineering area. Usually such problems are solved by development of new highly selective catalysts and by optimization of process operation parameters, though it cannot guarantee the achievement of desired results in all cases.

One of the most prospective approaches for solution of the problem is the application of "forced feed composition cycling" (FFCC) operation [1,2] and, in particular, periodical separate feeding of reagents, using catalyst surface storage capacities. In case of selective oxidation and oxidative dehydrogenation of hydrocarbons, such operation consists in separate feeding of reductant and oxidant (e.g. oxygen), where oxidation is provided by lattice oxygen during reduction (hydrocarbon feeding) phase of the process cycle with periodic replenishment of catalyst oxygen chemisorption capacity during reoxidation (air feeding) phase.

Theoretically, lattice oxygen may behave like more "mild" oxidant than molecular oxygen and, therefore, increase of selectivity and aim product yield may be expected. This hypothesis was experimentally confirmed for numerous selective oxidation reactions, performed in "anaerobic" conditions, such as oxidation of methane to syngas [3–6] at transient metal oxides, ethylene to ethylene oxide [7,8] and propylene to propylene oxide [9] at supported silver catalysts, butane to butadiene at Sb/Sn oxide catalyst [10], *n*-butane to butane and butadiene at vanadia–magnesia catalyst [11], propane to propylene [12–16] and many others.

Practically, all this optimistic and promising results were obtained under isothermal conditions. From scale-up point of view, it is possible to realize isothermal process practically (say, in tubular or fluidized bed reactors), but such processes will be characterized with relatively high capital cost and operation complexity. Evidently, more attractive is the application of reactors with adiabatic fixed beds of catalyst, but in this case scale-up

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Nomenclature

a_{max}	maximum chemisorption capacity of catalyst surface in respect to lattice oxygen (st.m^3 of oxygen per m^3 of catalyst bed)
c_i	molar concentrations of gas species (volume fraction or st.m^3/m^3 of gas mixture)
h_i	enthalpies of individual components of reaction mixture (kJ/st.m^3)
H_{cat}	enthalpy of the catalyst (kJ/m^3 of the bed)
H_g	enthalpy of gas (kJ/st.m^3)
$\Delta H_{V_2O_5}$, $\Delta H_{V_2O_4}$	enthalpies of formation of V_2O_5 and V_2O_4, respectively (kJ/m^3 of the bed)
k_j	rate constants (s^{-1})
l	axial coordinate in catalyst bed (m)
L	catalyst bed length (m)
t	time (s)
T	temperature (K)
u	superficial gas velocity (st.m/s)
w_j	reaction rates (s^{-1} or st.m^3 of substance per m^3 of catalyst bed/s)

Greek letters

γ	heat capacity of catalyst support material (kJ/(K m^3) of the bed)
ε	catalyst bed porosity
θ	surface fraction of oxidized active sites [V_2O_5] at the catalyst surface (undimensional)
ν_{ij}	stoichiometric coefficients of ith species in jth reactions (undimensional)

Indexes

i	substance index (i = C_3H_8, C_3H_6, CO_2, H_2O, O_2, N_2)
in	values at the bed inlet
init	initial values (at the beginning of the cycle)
j	reaction index (j = 1–4 correspond to reactions (1)–(4))

requires the accurate account of reaction heat effects and consequent dynamic changing of catalyst temperature along the catalyst bed with time. At least, it is necessary to understand how the temperature effects will influence the reaction performance. As a maximum challenge, efficient conjugation of temperature and catalyst surface composition nonstationarity may open the way for the development of novel technologies and process control strategies, which is more advantageous than for isothermal ones.

At the same time, there is a lack of research and lack of understanding in this area. Earlier author has made some attempts to simulate transient temperature and composition phenomena in an adiabatic packed catalyst bed arising under periodical separate feeding of reagents for a complex consecutive system of model reactions with arbitrary kinetics [17]. It was shown that such operation mode may provide higher yield of target product with significantly lower maximum process temperature than that of an equivalent steady-state process. From the other side, this study demonstrated that there is a vast amount of various process performance modes, significantly depending upon many process parameters, and generally it is not worthy trying to formulate all process regularities on the basis of common model task formulation. Much more reasonable is to focus the research on case study of definite reaction.

2. Task formulation

The current research is devoted to the case study of selective oxidative dehydrogenation of propane to propylene. This reaction system was chosen because of both high commercial potential of its industrial application and evident problems with achievement of high propylene yield in steady-state technologies, resulting, first of all, from complications with process heat management [18]. Reaction of oxidation of propane to propylene is exothermal and, moreover, selectivity of oxidation decreases with temperature, so selective oxidation in an adiabatic catalyst bed is possible in relatively narrow temperature window. This circumstance requires dilution of feed by inert gases, therefore limiting maximum inlet propane and oxygen concentrations, resulting in decrease of unit catalyst productivity (per unit volume of the bed). Range of admissible feed inlet temperature and composition may be expanded by the application of reactors with heat removal from reaction zone, but these approaches lead to significant technological complications and significantly increase capital cost of processing unit; so their feasibility does not look evident.

This study was directed towards simulation of the adiabatic fixed bed of the catalyst undergoing periodic cyclic feeding of propane/air. At this stage of the research, the task was to discover the most common regularities of process performance; so simplified mathematical model was used.

The choice of vanadia–titania catalyst for the case investigation was mostly defined by the availability of the literature data on nonstationary kinetics [14] for this reaction and author actually does not pretend to recommend this catalyst as an optimal one for the process.

3. Model formulation

As it was demonstrated in [14], the propane conversion at vanadia–titania catalyst may be described by Eley–Rideal mechanism, proposing that oxygen is involved into reaction via stage of chemisorption, while hydrocarbon species react with chemisorbed lattice oxygen only (and not the gas phase one). In this case the reaction scheme may be formulated as follows [14]:

$$C_3H_8 + [V_2O_5] \Rightarrow C_3H_6 + H_2O + [V_2O_4] \tag{1}$$

$$C_3H_6 + 9[V_2O_5] \Rightarrow 3CO_2 + 3H_2O + 9[V_2O_4] \tag{2}$$

$$C_3H_8 + 10[V_2O_5] \Rightarrow 3CO_2 + 4H_2O + 10[V_2O_4] \tag{3}$$

$$[V_2O_4] + 1/2O_2 \Rightarrow [V_2O_5] \tag{4}$$

During the formulation of the process mathematical model two important factors were taken into account: possibility of significant changing of both the reaction mixture volume and heat capacity in course of reaction performance. To simplify the model at this stage of research, the dispersion factors (heat conductivity of the catalyst bed and mass transfer by gas diffusion), as well as inter-phase heat/mass exchange were excluded from the description (quasi-homogeneous approach). The bed was accounted as adiabatic and one-dimensional.

With account of these factors, the mass balance for species in the gas phase was expressed in quasi-stationary form:

$$\frac{\partial(uc_i)}{\partial l} = \sum \nu_{ij} w_j \tag{5}$$

with boundary conditions:

$$l = 0 \Rightarrow u = u_{\text{in}}; \qquad c_i = c_i^{\text{in}} \tag{6}$$

Mass balance for lattice oxygen at the catalyst surface was given by equation:

$$a_{\max}\frac{\partial\theta}{\partial t} = \sum_j \nu_{ij} w_j \tag{7}$$

Kinetic equations (as well as values of their parameters) for w_j were taken in accordance with [14]:

$$\begin{aligned} &w_1 = k_1 c_{\mathrm{C_3H_8}}\theta, \qquad w_2 = k_2 c_{\mathrm{C_3H_6}}\theta^2, \\ &w_3 = k_3 c_{\mathrm{C_3H_8}}\theta^2, \qquad w_4 = k_4 c_{\mathrm{O_2}}(1-\theta) \end{aligned} \tag{8}$$

Due to significant changing of gas heat capacity in course of reaction it was impossible to use conventional technique of adiabatic heat rises; therefore, energy balance was formulated in enthalpy terms:

$$(1-\varepsilon)\frac{\partial H_{\text{cat}}(T,\theta)}{\partial t} = -\frac{\partial(uH_{\text{g}}(T,\bar{c}))}{\partial \ell} \tag{9}$$

Taking into account that catalyst enthalpy consists of enthalpy of support (changing with temperature) and enthalpy of surface compounds (changing with both temperature and surface composition) and assuming that gas enthalpy is equal to sum of components' individual enthalpies, Eq. (9) may be converted into

$$(1-\varepsilon)\gamma\frac{\partial T}{\partial t} + a_{\max}\,\Delta H_\theta\frac{\partial\theta}{\partial t} = -\frac{\partial\left(u\sum_i c_i h_i(T)\right)}{\partial \ell} \tag{10}$$

where $\Delta H_\theta = \Delta H_{\mathrm{V_2O_5}} - \Delta H_{\mathrm{V_2O_4}}$, with boundary conditions:

$$\begin{aligned} &\ell = 0 \Rightarrow u = u_{\text{in}}; \quad T = T_{\text{in}}, \qquad t = 0 \Rightarrow T(\ell) = T_{\text{init}}(\ell); \\ &\theta(\ell) = \theta_{\text{init}}(\ell) \end{aligned} \tag{11}$$

The analysis of thermodynamic data showed that it is possible to neglect temperature dependence for γ and ΔH_θ, and to simplify polynomial functions $h_i(T)$ by linear dependencies. Thermodynamic properties of surface species (V_2O_4 and V_2O_5) were assumed to be equal to the ones for the bulk state of these compounds.

4. Estimation of heat effects

Although the heat effects of stages (1–4) were not used in the model directly, it is interesting to consider them for better understanding of the following results.

Preliminary estimation of heat effects for reactions (1)–(4) showed that stage of surface selective oxidation (1) has slightly negative heat effect (approximately −4.6 kJ/mol of propane), while total exothermal character of bulk selective oxidation reaction (116.8 kJ/mol) is caused by high enough heat effect of catalyst reoxidation stage (4) equal to 121.4 kJ/mol of [V_2O_4]. At the same time both deep oxidation stages (2 and 3) have fairly expressed positive heat effect (equal to ~840 kJ/mol for both stages).

Two important consequences follow from this observation. First of all, it shows that propylene production stage of the process in case of high selectivity of propylene formation is characterized with practically zero heat generation; therefore, this stage may be performed in practically isothermal mode in adiabatic bed, without visible overheating even in case of high inlet propane concentration.

The second consequence is that heat generation distribution between stages (1–4) will significantly depend upon the bonding energy of lattice oxygen. For example, application of catalysts with higher lattice Me–O bonding energy than for V–O one (such as iron, cobalt, and molybdenum) will shift heat distribution to more endothermic propylene formation stage (1) and more exothermic reoxidation stage (4). Vice versa, catalyst with lower bonding energy (e.g. ceria-based) will provide expressed exothermal effect of stage (1) with simultaneously lower heat effect of stage (4). In other words, the maximum temperature in the cyclic process may be manipulated by the selection of catalysts with different oxygen bonding energy, which is even theoretically impossible in case of steady-state process. This circumstance should be accounted as additional unique feature for nonstationary process development and optimization.

5. Simulation results

The simulation of the process considered the two phases of the cycle: (a) propane feeding to the bed of oxidized catalyst and (b) air feeding to the bed of reduced catalyst.

Properties of the propane feeding cycle were shown to be strongly dependent upon the initial catalyst temperature in the beginning of the cycle and inlet temperature of the feed. When cold gas (e.g. at ambient temperature) is fed into the cold bed, the reaction does not occur at all. When preheated gas is fed into preheated bed propylene, formed in the reaction, is intensively oxidized in the outlet part of the bed, and process selectivity is close to zero. The similar picture is observed during feeding of cold gas into preheated bed.

The most interesting operation mode is provided under feeding of preheated gas into cold bed (Fig. 1). It is seen that (due to practically zero heat effect of target reaction (1)) the maximum

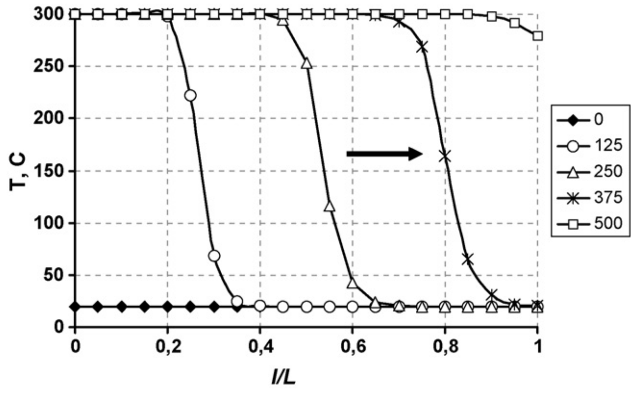

Fig. 1. Temperature profiles vs. catalyst bed length at different time points (time from cycle beginning is given at the right in seconds) under feeding of pure propane into oxidized catalyst bed. Conditions: $c_{C_3H_8}^{in}=1$, $c_{O_2}^{in}=0$, $T_{in}=300\,°C$, $T_{init}=20\,°C$, $\theta_{init}=1$, $L=1$ m, $u=1$ m/s, $a_{max}=20.8$. Gas flow direction is shown by arrow.

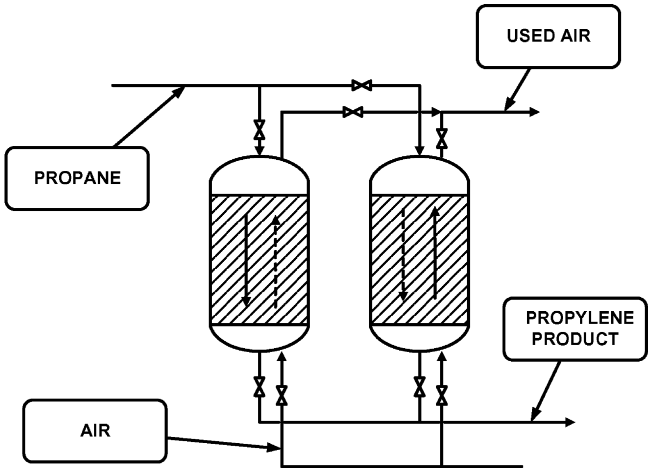

Fig. 2. Process flow-sheet. Propane flow direction in reactors is always downward, air flow—upward. Solid and dashed arrows show flow directions in different phases of the operation cycle.

temperature of the catalyst does not significantly exceed the inlet gas temperature. In such conditions, the observed average-per-cycle selectivity of propane conversion into propylene is higher than that in steady-state processes.

In turn, reoxidation of the cold reduced catalyst by preheated air also occurs at moderate maximum temperatures (not exceeding 400 °C); therefore, the process may be realized without catalyst overheating even in case of using undiluted propane as feed. Such moderate temperatures in both phases are explained by the fact that part of the reaction heat is consumed for heating of preliminary cold catalyst.

At the same time, permanent preheating of the inlet flows does not look too attractive from technological point of view. First, it requires application of heat exchangers and energy supply for preheating. Second, the efficient operation mode in both phases requires the low initial temperature of the bed, therefore, additional stages of bed cooling must be introduced into the phases sequence of the cycle.

This complication may be avoided by application of autothermal cyclic operation approach. Such procedure means that the catalyst bed is preheated once, before the process startup. Afterwards, both (propane and air) flows are fed into the bed without preheating. To provide autothermal character of the process the feeding of propane and air should be performed in counter-current directions.

Such process may be realized in a continuous mode in a flow sheet with two catalyst beds presented in Fig. 2. While one of the beds is fed by propane, the other one is fed by counter-current flow of air, with periodical repeated switching of flows between beds.

As soon as the process, in total, of two cycle phases is exothermic, after some number of flow switching the established cyclic operation mode should be achieved. The term “established” here means accurate self-sufficient repeating of all process parameters from cycle to cycle, giving the possibility of unlimited in time operation without additional energy inputs and other external interference into operation.

Fig. 3 demonstrates the simulated evolution of catalyst temperature profiles in time in both phases of propane feeding (Fig. 3a) and reoxidation (Fig. 3b) with corresponding evolution of catalyst oxidation fraction profiles, shown in Fig. 4, in established cyclic operation mode.

It is seen that the initial temperature profile in the beginning of propane feeding phase coincides with the final profile in the

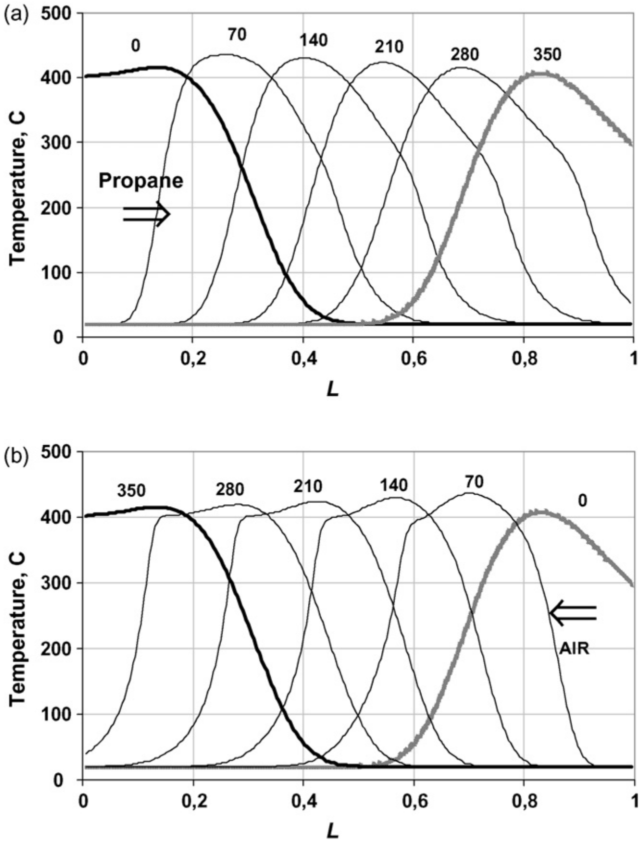

Fig. 3. Temperature profiles vs. catalyst bed length at different time points (time from cycle beginning is given at curves in seconds) in propane (a) and air (b) feeding phases of the cycles. Conditions: propane feeding phase: $c_{C_3H_8}^{in}=1$, $c_{O_2}^{in}=0$, $u=1$ m/s, $T_{in}=20\,°C$; air feeding phase : $c_{C_3H_8}^{in}=0$, $c_{O_2}^{in}=0.21$, $u=4.3$ m/s, $T_{in}=20\,°C$; semi-cycle duration: 350 s, $T_{init}=250\,°C$, $\theta_{init}=1$, $L=1$ m, $a_{max}=20.8$. Gas flow direction is shown by arrow.

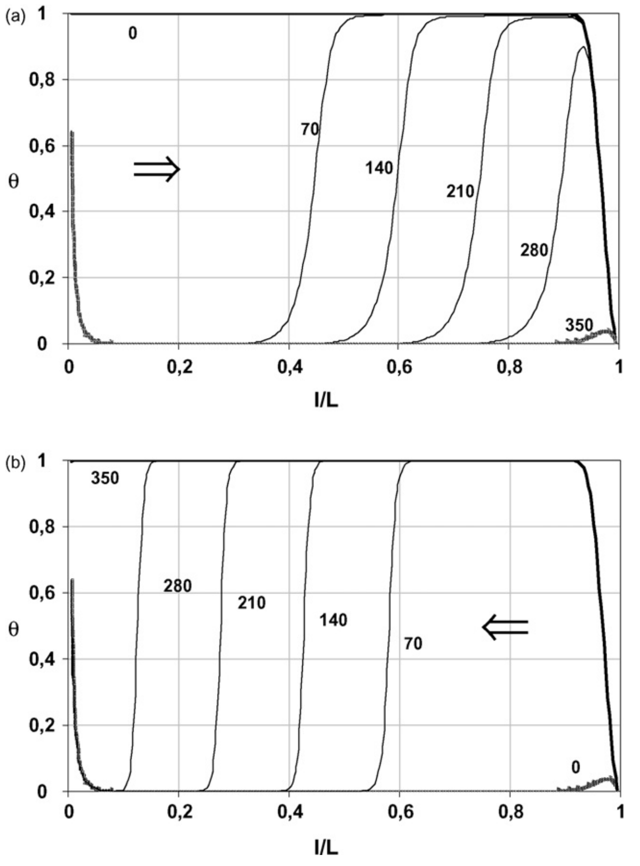

Fig. 4. Catalyst oxidation degree profiles vs. catalyst bed length at different time points (time from cycle beginning is given at curves in seconds) in propane (a) and air (b) feeding phases of the cycles. Conditions: see Fig. 3.

end of reoxidation phase and vice versa. The same picture is observed for the profiles of another inertial parameter of the system—catalyst oxidation degree. This circumstance confirms established character of the cyclic regime.

It should be noted that to achieve the established nonstationary operation mode it is necessary to provide efficient conjugation of duration of catalyst reduction/reoxidation phases, which is not a simple problem due to significant difference in the kinetics of reduction and reoxidation reactions. Particularly, simulation has shown that, from one side, reoxidation phase should be long enough to provide complete oxidation of catalysts surface and, from the order hand, short enough to keep necessary amount of heat accumulated in the bed to provide stable autothermal process performance.

Another important issue is that due to different reaction rates the required duration of cycle phases in a general case may be different. Such situation is undesirable, because it will require more than two reactors in the process scheme for efficient continuous operation. This complication may be avoided by proper selection of feed flow rates at both cycle phases. For example, in given conditions (see. Fig. 3) equal semi-cycle duration at reduction/reoxidation stages may be achieved when air feeding flow rate is by a factor of ∼4.3 higher than propane feeding flow rate.

In any case, even for the cycle with balanced phases duration, there exists maximum cycle duration. For longer cycles the heat loss overcome heat generation in reactions and the process loses its autothermal character and finally fades. From the other hand, too short cycles may lead to bed overheating, resulting in decrease of selectivity; therefore, there exists optimal range of cycle duration. Definition of optimal cycle duration is an extremely important issue for process efficiency. Of course, in simulation study the problem may be quite easily solved by tuning of various values, but, evidently, in real operation practice such procedure is impossible and decision on flow switching must be based on technologically available process information (such as indication of thermocouples in the catalyst beds). Undoubtedly, the development of the efficient process control strategy is one of the most challenging scientific issues to be resolved in further studies.

As it is seen from Fig. 3, during the whole propane feeding phase temperature in the moving reaction zone is decreasing towards the outlet of the bed, thus preventing downstream oxidation of formed propylene and providing high reaction selectivity, in which average per cycle value being as high as 85%.

At the same time, the observed propane conversion is rather low (ca. 2%), so average yield of propylene for given conditions does not exceed 1.6%. It is interesting, that unlike steady-state process, conversion in nonstationary process cannot be increased by an increase of catalyst loading residence time, because it is defined mostly by self-sufficient parameters of the heat front, first of all – by the width of reaction zone, depending upon many system characteristics – reaction kinetics, chemisorption capacity of the catalyst, relation between heat capacities of gas phase and catalyst, etc.

Fig. 5 demonstrates influence of catalyst unit surface area on propylene yield. Here the surface area increase from the basic value of 44 m^2/g [14] leads to the proportional rise of both rate constants (k_i in (8)) and chemisorption capacity of the catalyst (a_{max}). It is seen that at technically achievable value of surface area of 200–250 m^2/g, it is possible to reach the level of propylene yield as high as ∼4%.

It should be noted that this value refers to pure propane feeding, and to compare this level with steady-state process (where propane must be diluted with inert gas) it is more useful to use outlet concentrations of propylene. Simulations of

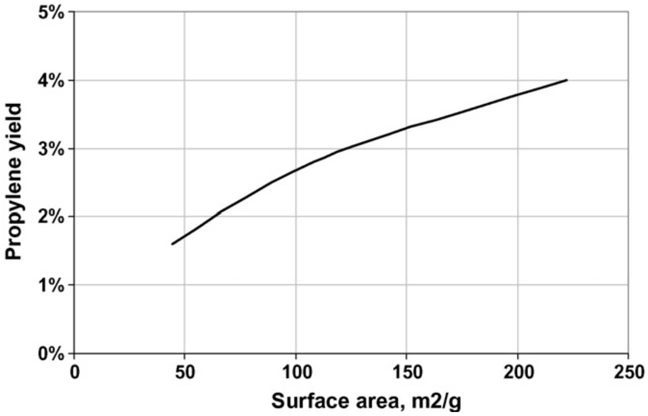

Fig. 5. Average per cycle propylene yield in established cyclic nonstationary process vs. unit surface area of the catalyst.

the steady-state process using the same model showed that under reasonable limitations (maximum catalyst temperature not exceeding 750 °C, selectivity not lower than 50%) the maximum achievable level of propylene concentration does not exceed 5%, so data on nonstationary process looks competitive, especially, taking into account much more expressed potential of nonstationary process for further optimization.

6. Technological analysis of the process

Though the results of this model study are very preliminary, some technological analysis may be already done.

Evidently, application of undiluted propane feed together with high selectivity provide competitive unit propylene (per catalyst unit volume) output, compared to adiabatic steady-state propane oxidative dehydrogenation processes, despite lower observed average propane conversion.

At the same time, the cyclic nonstationary process does not need propane/air preheating in both process phases; therefore, significant decrease of energy consumption may be achieved and it will become possible to minimize heat-exchange environment of the process, thus decreasing both operating and capital costs.

Among other process advantages (compared to steady-state processes) the following may be stated:

- absence of inert diluents in outlet gases will simplify separation of product propylene;
- absence of direct contact between hydrocarbon flammable species and oxygen, impossibility of catalyst overheating will improve process safety;
- air may be used as oxidative agent instead of pure oxygen without complication of downstream product separation procedure;
- low coke formation (due to moderate process temperatures) as well as efficient incineration of deposited coke during each reoxidation cycle may lead to higher lifetime of the catalyst.

7. Conclusion

The model simulation study has shown that the anaerobic process of oxidative dehydrogenation of propane under periodic alteration of feeding between propane and air may be realized in adiabatic catalyst beds in stable continuous cyclic mode in two-reactor scheme. In case of appropriate choice of process parameters (cycle duration, feeding flow rates) the process appears to be autothermal, i.e. it does not require any inlet gas preheating for stable operation. Compared to similar steady-state adiabatic process, the proposed process is characterized with much lower maximum catalyst temperatures, giving the way to process pure propane without diluting it with inert gases, thus simplifying downstream procedure of product separation. Predicted propylene yield is competitive with one for the steady-state adiabatic process, while sufficient technological benefits of the new technology are expected (decrease of energy consumption and minimization of heat-exchange environment, process safety improvement, suppression of coke formation and efficient coke incineration).

The study showed that temperature regime of the process is to a great extent defined by the distribution of heat effects between catalyst reduction and reoxidation stages, which, in turn, depend upon thermodynamic properties of the catalyst (lattice oxygen bonding energy). This circumstance opens the additional way for process optimization by the choice of the catalyst with appropriate thermodynamic parameters, which is inapplicable for steady-state processes in general.

Of course, for more reliable technological decisions and estimations much more detailed simulation is required, including application of more detailed model, accounting for external and internal heat and mass transfer limitations and using more detailed kinetic model (accounting, for instance, for existence of different forms of lattice oxygen at catalyst surface with different reaction activity and different bonding energy, for formation of other possible by-products, such as CO and oxygenates, etc.). Evidently, there is also a lot of future work related to choice of the optimal catalyst in situation when choice criteria will be more numerous and quite different from those for steady-state processes. Among other challenges in the area, the development of efficient process control procedure (including elaboration of rules for definition of optimal cycle duration from technically available process information) should be mentioned.

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