Modeling Ethane Oxy-Dehydrogenation Over Monolithic Combustion Catalysts

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A numerical approach is used to investigate the role of a combustion catalyst in the oxidative dehydrogenation of ethane at short contact times for ethylene production. A two-dimensional (2-D) model, with mass and energy equations coupled with the Navier-Stokes equations, is applied to show that an oxidation catalyst can beneficially affect the formation of ethylene, by optimizing the sacrifice of ethane for producing heat with a larger selectivity to CO_2 than a purely homogeneous process. Simulations also showed that for exceedingly high catalyst activity hot spots are formed on the catalyst walls, as the characteristic times of heat production become comparable with those of heat transfer. This may result into the formation of byproducts that reduce ethylene selectivity. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 2233–2245, 2004

Keywords: Mathematical modeling, ethylene production, short contact time, monolith reactor, ethane ODH

Introduction

Background

In the past few years, the oxidative dehydrogenation of ethane (ODH) for ethylene production has received a renewed interest, due to the evidence that olefins can be efficiently produced with high yields in short contact time reactors (SCTR) (Huff and Schmidt, 1993; Bodke et al., 1998; Flick and Huff, 1999; Bodke et al., 2000). Until recently, SCTRs for ethane ODH were mainly Pt-based, in the convincement that this active phase played a decisive role in addressing ethylene formation (Huff and Schimdt, 1993; Schmidt and Huff 1994; Schmidt et al., 1994; Yokoyama et al., 1996; Bodke et al., 1998), and in the evidence that it was the only reliable and stable active phase for the process, as the application of non-noble-metal catalysts was limited by a short lifetime or coke formation (Flick and Huff, 1999; Beretta and Forzatti, 2001).

In a recent experimental work we investigated $LaMnO_3$ perovskite-based honeycomb monoliths (Donsì et al., 2002) as alternative to Pt. On such a catalytic system, we carried out the reaction of ODH with high ethylene yields, larger than on Pt, and without any deactivation for many hours (up to 90) of reaction. The intrinsic activity of Pt and perovskites is greatly different. It has been satisfactorily demonstrated that Pt catalyst is able to promote catalytically only the conversion of ethane into CO and CO_2 (Beretta et al., 2001b; Henning and Schmidt, 2002), whereas we showed that the perovskite-based catalysts are much more selective toward CO_2 among CO_x , and also able to convert a fraction of C_2H_6 directly and catalytically to C_2H_4, even though in very limited amounts.

The evidence that an oxidation catalyst completely different from Pt can be similarly effective in this process, or even better, strengthened, hence, the recent hypotheses of homogeneous formation of ethylene in such reactors, and of denial of any direct role played by the catalyst in the ODH reaction (Lødeng et al., 1999; Mulla et al., 2001; Beretta et al., 2001b; Henning and Schmidt, 2002). However, the variation observed in ethylene selectivity at changing the active phase or the

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support morphology (Huff and Schimdt, 1993; Yokoyama et al., 1996; Bodke et al., 1998; Flick and Huff, 1999; Mulla et al., 2001 and 2002; Beretta and Forzatti, 2001; Donsì et al., 2002) leaves space to many doubts about the effective role of the catalyst in the process.

In recent literature, many studies both experimental and theoretical were focused on understanding the role of the catalyst in such processes. Experimental works of Lødeng et al. (1999) and Mulla et al. (2001 and 2002) suggested that the catalyst basically plays the role of ignitor of gas-phase reactions.

However, due to the extremely large difficulty in separating the effects of heterogeneous and homogeneous reaction paths, it seems not possible to refer only to experimental results to get insights about the role of the catalyst. Mathematical modeling is, thus, a useful tool in investigating such effects, as it makes possible to consider for the most part the detailed ODH mechanism in the gas phase, and the catalytic surface chemistry.

Huff and Schmidt (1996) first proposed a one-dimensional (1-D) model of ODH on Pt, whose basic assumption was that all the chemistry occurs on the catalyst surface, the gas phase reactions playing no role basically due to the very small residence times adopted. Nevertheless, a purely heterogeneous chemistry is reasonable only at moderate temperatures, whereas above 800°C, the proceeding of homogeneous reactions cannot be neglected, even for millisecond residence timescales, as clearly shown by both experimental (Beretta et al., 2001a,b; Henning and Schmidt, 2002) and theoretical investigations (Zerkle et al., 2000; Huff et al., 2000; Beretta et al., 2001b).

A relatively simple 1-D pseudohomogeneous model was also developed by Huff et al. (2000) to reproduce the behavior of their lab-scale reactor (Flick and Huff, 1999). The kinetic model was heterohomogeneous, and the role of the catalyst consisted only in oxidizing a fraction of the fuel to CO_x and H_2O. In this reactor model the catalyst initiates gas-phase chemistry through the acceleration at the front of the reactor of exothermic reactions, which increases the gas temperature up to the point where gas-phase reactions readily occur. Nevertheless, the excessively simple nature of this model, which neglects the radial profiles, and assumes infinitely fast mass and heat transfer, underestimates the complexity of the phenomena occurring in the reactor.

A qualitative description of the reactor behavior was given by Bodke at al. (2000), who depicted the contribution of the catalyst within the reactor with a two-zone schematization: in the first zone oxygen is consumed in the oxidation of C_2H_6 to CO_x and H_2O, with a consequent temperature increase, whereas in the second zone, where O_2 is absent, the endothermic dehydrogenation of ethane to ethylene and H_2 occurs. Nevertheless, this interpretation of the role of the catalyst is disguising, because oxygen presence seems to be involved in the production of ethylene in accelerating its formation in the gas phase at short contact times, as we previously stated (Donsì et al., 2002).

Zerkle et al. (2000) implemented the assumption of the formation of ethylene occurring both on the catalyst and in the gas phase in a 2-D model, in which coupling of energy and mass balances with momentum balance equation was taken into account. The 2-D model was used because as the authors claimed, mass and heat transfer are extremely significant factors in determining the behavior of monolithic reactors. Rate constants for elementary surface reactions are determined from literature sources (Wolf et al. (1999) for nonoxidative methane conversion on Pt), or by fitting model predictions to experimental data (mainly for oxidative steps). The surface-catalyzed reaction steps were then coupled to a simplified version of the detailed homogenous mechanism of Marinov et al. (1998). The model of Zerkle et al. (2000) predicted a percentage of formation of ethylene on the catalyst surface, dependent on the composition of the feed, the ethylene being formed mainly heterogeneously when H_2 was added to the reacting mixture. However, these findings are not in agreement with some recent experimental results (Henning and Schmidt, 2002; Beretta et al., 2001b), which tend to exclude the ability of Pt catalysts to show intrinsic properties of directly catalyzing ethylene formation. In addition, as the authors recognized, "the chemical mechanisms based on a limited set of experimental data can be neither unique nor complete in their description of the detailed kinetics".

In summary, the available models do not lead to a final and general conclusion on the role of the catalyst.

Aim of this work

Even though the scientific community seems oriented to consider the catalyst playing no effective role in addressing the process toward the actual products distribution, but important only as ignitor of gas-phase reactions (thus, making the process feasible and stabilizing the homogeneous reactions within a limited length), it seems that the catalyst composition, and the presence of any catalyst itself, strongly influence ethylene selectivity and yield. However, the intrinsic capability of Pt of directly catalyzing the ODH reaction appears very unlikely, whereas the same property does not seem exhaustively decisive in controlling the performances of the catalytic monoliths, based on $LaMnO_3$ that we studied in a previous work.

For these reasons, we are interested in investigating the formation of ethylene in the ODH of ethane in short contact time reactors from a more general standpoint, possibly independently on the active phase, based on the assumption that the catalyst is not able to directly catalyze the selective conversion of ethane into the desired product. In other words, since most of the recent literature seems to agree on the exclusively homogeneous formation of ethylene, we are going to answer to the following question: under the hypothesis that the catalyst is only able to completely oxidize ethane into CO_2, igniting the reactions in the gas phase for the consequent thermal effects, is it possible that it affects the overall selectivity to ethylene of the process? And, under such hypotheses, what happens in the reactor, which are the controlling phenomena?

Actually, it is very likely that the effect of the catalyst in such reactors is much more complex than the only capability of converting a fraction of ethane into carbon dioxide and water releasing heat, especially for what concerns the eventual influence on radical reactions (catalyst may act as a radical promoter or quencher, third body, and so on). However, since the role of the catalyst in promoting the total oxidation to CO_x and H_2O appears the main effect and an unavoidable consequence of its presence, this approach can be retained as a fruitful first step in the comprehension of the complex mechanisms, ruling the behavior of the short contact time reactor for ethane ODH.

To achieve this, the reactor behavior was modeled via the following approach:

(1) Ethylene is formed in the homogeneous phase, and consequently the model implements a detailed homogeneous chemistry (Marinov et al., 1998).

(2) The catalyst is exclusively active in the complete oxidation of ethane to CO_2 and water.

(3) A correct description of mass and heat transfer, and the radial gradients along the channel is included in the model, as they are extremely important in this process, and can influence ethylene formation; hence, a full 2-D model is adopted, with the unique simplification of the boundary-layer assumption.

The extent of the effect of the catalyst is parametrically modulated changing the kinetic constant of the heterogeneous oxidation of ethane.

Reactor model

The monolithic reactor is described by means of a 2-D model. The coupling of heat and mass transfer with fast surface reactions and gas-phase reactions, requires a detailed description of radial temperature, velocity, and concentrations profiles, as a 1-D model is unable to correctly describe bulk-surface mass and heat transport for the lack of reliable transfer coefficients in channels with surface reactions (Gupta and Balakotaiah, 2001; Di Benedetto et al., 2003b).

Mass and energy balance equations are coupled with the Navier-Stokes equations under the boundary-layer assumption. The reactor is modeled as adiabatic, since, in most of the experimental conditions, the very high value of flow rate adopted brought about a very fast energy production in comparison with the heat losses toward the external environment. The heat conduction along the reactor walls is neglected as it is simulated the steady-state behavior of an adiabatic monolithic reactor with a ceramic support. The very low values of thermal conductivity typical for ceramic supports, do not significantly affect the steady behavior of adiabatic monolithic reactors (Groppi et al., 1999, Di Benedetto et al., 2003a).

The channel of the monolith is modeled as a cylindrical tubular reactor of 0.42 mm dia., which is with good approximation extensible also to other channel morphologies, such as square channels, where the application of the washcoat tends to round the corners (Hayes and Kolaczkowski, 1994), or the tortuous channels of foam monoliths under the flow conditions investigated (Zerkle et al., 2000). In the channel a flow velocity, corresponding to a velocity of ~1 m/s at 500°C, is assumed, and a C_2H_6/O_2 ratio in the feed of 2.

The system of partial-differential equations, solved using the module CRESLAF of the commercial code CHEMKIN 3.7 package (Kee et al., 1990), is reported here:

Mass continuity

$$\frac{\partial \rho v_z}{\partial z} + \frac{1}{r}\frac{\partial r \rho v_r}{\partial r} = 0 \tag{1}$$

Axial momentum

$$\rho v_z \frac{\partial v_z}{\partial z} + \rho v_r \frac{\partial v_z}{\partial r} = -\frac{\partial P}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}\left(\mu r \frac{\partial v_z}{\partial r}\right) \tag{2}$$

Species mass balance

$$\rho v_z \frac{\partial w_i}{\partial z} + \rho v_r \frac{\partial w_i}{\partial r} = r_i W_i + \frac{1}{r}\frac{\partial r J_{r,i}}{\partial r} \tag{3}$$

Energy balance

$$\rho c_P\left(v_z \frac{\partial T}{\partial z} + v_r \frac{\partial T}{\partial r}\right) = \frac{1}{r}\frac{\partial}{\partial r}\left(\lambda r \frac{\partial T}{\partial r}\right) - \sum_i c_{P,i} J_{r,i} \frac{\partial T}{\partial r} - \sum_i h_i r_i W_i \tag{4}$$

where r_i is reaction rate of species i in the gas phase, and the spatial components of mass flux J are given as in Eq. 5

$$J_{r,i} = -\rho \frac{W_i}{\bar{W}} D_{i,m} \frac{\partial Y_i}{\partial r} - D_i^T \frac{1}{T}\frac{\partial T_i}{\partial r} \tag{5}$$

Boundary conditions

$$z = 0, \quad \forall r: \qquad v_z = V_0, \quad v_r = 0, \quad T = T_{in}, \quad w_i = w_{i,in} \tag{6}$$

$$\forall z, \quad r = 0: \qquad \frac{\partial v_z}{\partial r} = v_r = \frac{\partial T}{\partial r} = \frac{\partial w_i}{\partial r} = 0 \tag{7}$$

$$\forall z, \quad r = \frac{d_c}{2}: \qquad v_z = v_r = 0, \quad J_{r,i} = r_i^s W_i, \quad \frac{1}{r}\frac{\partial}{\partial r}\left(\lambda r \frac{\partial T}{\partial r}\right) = -\sum_i h_i r_i^s W_i \tag{8}$$

where r_i^s is the reaction rate of i at the catalyst surface.

Results along the radius are integrated according to Eq. 9, to get the average values of temperature and concentration in the gas phase

$$\varphi_{av} = \frac{\displaystyle\int_0^{d_c/2} \rho v_z \varphi r dr}{\displaystyle\int_0^{d_c/2} \rho v_z r dr} \tag{9}$$

In the following, the calculation of reaction rates in the gas phase (r_i), and at the catalytic wall (r_i^s), is described in detail.

Homogeneous mechanism

The homogeneous reaction mechanism is crucial in the correct implementation of the model. For this reason, several mechanisms of gas-phase hydrocarbon oxidation were examined under conditions of ethane ODH. The widely used GRI mechanism (GRI-Mech, 1999) did not result to be satisfactorily adequate to the conditions investigated, being derived for oxygen-rich mixtures. The Mims-Dean mechanism (Mims et al., 1994), obtained for hydrocarbon steam cracking, and the Marinov mechanism (Marinov et al., 1998), for hydrocarbons up to C_4 in oxygen-poor conditions, appeared both suitable for ethane ODH conditions. Both the Marinov and Mims-Dean mechanisms were tested, which did not result in any significant differences. Hence, in this work the results obtained using the Marinov mechanism (Marinov et al., 1998) are always presented.

Heterogeneous mechanism

At the operation temperature of a SCTR for ethane ODH (~900°C) the gas-phase reactants can be either involved in reactions in the homogeneous phase, or transferred to the surface where the complete combustion is promoted by the catalyst. Homogeneous reactions and mass-transfer phenomena are in parallel, whereas mass transfer and surface reactions are in series.

Below the temperature of ignition of gas-phase reactions, product distribution depends only on the type of catalyst used. Beretta et al., (2001a, b) reported that on Pt, CO is largely produced in the medium-temperature range, and is the main oxidation product above 550°C. Instead we found that on $LaMnO_3$-based catalysts ethane is oxidized more selectively toward CO_2, which is always the main reaction product, although in the temperature range investigated (400–550°C), also a small fraction of ethylene is catalytically produced (Donsì et al., 2002).

In this model the catalyst is assumed to act only in the total oxidation of C_2H_6 to CO_2 and H_2O. In comparison with Pt this may appear as an over-simplification, due to the other compounds formed on the surface of such catalyst (at least also CO and H_2), whereas in comparison with $LaMnO_3$, it is a conservative assumption, since the formation of some ethylene on the catalytic surface is neglected.

The rate of heterogeneous reaction of ethane, when it is not used as variable parameter, is that obtained from low-temperature experimental data on perovskites (Donsì et al., 2002), and is reported in Eqs. 10 and 11

$$r^s_{iC_2H_6} = -k_s \cdot c_{C_2H_6} \cdot c_{O_2}^{0.5} \quad [\text{mole/s} \cdot \text{m}^2] \qquad (10)$$

$$k_s = k_{s,0} \cdot e^{-(E_a/R_gT)} = 62.8 \cdot e^{-(55000/R_gT)} \quad [\text{m}^{2.5}/\text{s} \cdot \text{mole}^{0.5}] \qquad (11)$$

Results

Comparison between a homogeneous and a catalytic adiabatic reactor

The comparison between the behavior of a catalytic and homogeneous reactor has been carried out by simulating the gas composition and temperature along an adiabatic reactor at an inlet gas temperature equal to 1,000°C, in the absence, and in the presence of catalyst.

It is quite evident that the two cases remarkably differ in products selectivity, gas temperature and reaction characteristic timescales. Figure 1a shows that the average on the section of ethane conversion goes to completion at around 1.4 ms residence time in the absence of catalyst, whereas when the catalyst is present, a much shorter time of 0.2 ms is needed. The yield of ethylene passes through a maximum, since C_2H_4 is an intermediate product. The maximum C_2H_4 production occurs significantly before ethane is completely converted (at about 1 ms in the absence of catalyst, and at about 0.08 ms when catalyst is present), and reaches a higher value (~60%) in the catalytic reactor than in the homogeneous one (~58%).

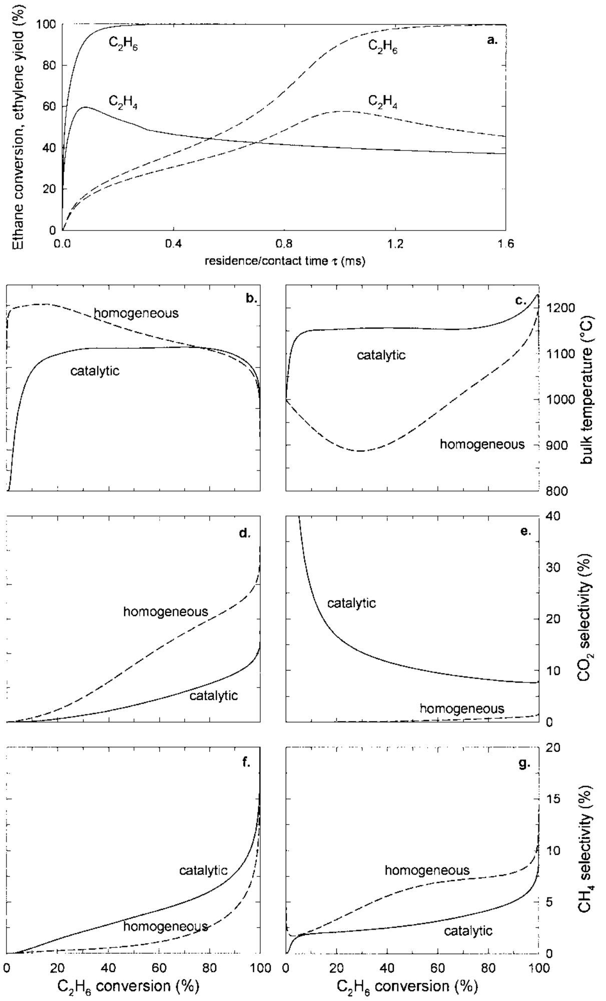

Figure 1. Catalytic (solid line) and homogeneous reactor (dashed lines): (a) conversion of C_2H_6 and C_2H_4 yield as a function of residence time; (b) C_2H_4 selectivity, (c) gas temperature, (d) CO, (e) CO_2 (f) C_2H_2, (g) and CH_4 selectivity (g) as functions of C_2H_6 conversion.

Tm=1,000°C, $C_2H_6/O_2/N_2$=46.7/23.3/30.

At low ethane conversion the mathematical model predicts higher selectivity to ethylene in the homogeneous case (S_{C2H4} = ~90%, Figure 1b), and a concurrent decrease in temperature (Figure1c), because the initiation stages of ethane consumption consist of purely dehydrogenation reactions. The endothermic reaction steps also control the maximum temperature in both the homogeneous and the catalytic reactor, which stays below 1,200°C.

In the homogeneous reactor the exothermic reactions of consumption of oxygen are delayed, thus, generating the trend of C_2H_4, CO, CO_2, C_2H_2, and CH_4 selectivities shown in Figure 1. Basically, carbon monoxide is by far the most relevant of byproducts containing oxygen, as the presence of CO_2 can be observed only in small amounts, and at very high ethane conversion. Due to the high-temperature values, significant amounts of CH_4 and C_2H_2 (Figure1f and g), are also produced via endothermic reactions, which appear dramatically favored at very high ethane conversion.

In the presence of the catalyst, ethylene selectivity is nearly zero at the inlet of the reactor, because ethane is catalytically oxidized to CO_2 (Figure 1e) and H_2O. Quite surprisingly at high ethane conversion the model predicts almost the same ethylene selectivity in the catalytic reactor, which becomes even slightly higher for $X_{C2H6} > 75\%$. Indeed, Figure 1d shows that CO selectivity in the presence of the catalyst is much lower than in the homogeneous reactor, with a consequent lower carbon consumption to form undesired oxygenated compounds. Nevertheless, the beneficial effect of the reduction of C_2H_6 consumption due to the larger CO_2 formation in the catalytic reactor is partly reduced by the higher C_2H_2 formation, as a consequence of ethylene degradation, caused by the higher-temperature attained in the presence of the catalyst.

The results reported in Figure 1, show the double role of the catalyst in an ODH reactor: the "thermal" and the "chemical" role. The thermal role consists in increasing the surface temperature via the promotion of the catalytic deep oxidation of ethane. Consequently, not only the gas-phase reactions are ignited and sustained, but also high-temperature values are achieved and reactions speed up. The chemical role consists in promoting the conversion of oxygen and ethane to CO_2, changing the C/O ratio available for gas-phase reactions: ethylene production is favorably influenced, even without the direct catalysis of the reaction of C_2H_4 formation. This is true, not only for our model, where all of oxidized ethane goes to CO_2, but for any oxidation catalyst, whose CO_2 selectivity is higher than in the gas phase (where it is nearly zero).

Hence, the catalyst is not only functional in igniting, but it can effectively change the ethylene selectivity even if it is a combustion catalyst.

In the following, the weight of the thermal and the chemical role on ethylene selectivity will be investigated by changing the operating variables (inlet temperature), and the catalyst activity (kinetic constant and activation energy).

Effect of changing the inlet temperature

In Figure 2, the results of the simulations carried out at varying the inlet temperature are shown. Simulations reported in Figure 2a show that, when the reactants are fed at an inlet temperature of 300°C, a relatively high fraction of ethane must be consumed (~10%) before the threshold temperature of gas-phase reactions (T_{th}, which under the range of residence times investigated, can be fixed at about 850°C) is reached, whereas for higher inlet temperatures, the fraction of ethane burned to carbon dioxide is lower. Nevertheless, from Figure 2d, which reports the maximum ethylene selectivity and yield reached along the reactor for any inlet temperature investigated, it appears that the highest values are attained for the lowest inlet-temperature. This means that, even though the fraction of ethane catalytically oxidized to CO_2 at the reactor entrance increases, an overall increase of C_2H_4 selectivity at high C_2H_6 conversions is attained.

To understand this behavior, ethylene selectivity and bulk gas temperature are plotted at varying ethane conversion for any inlet temperature (Figures 2a,b). Results show that in the range of low ethane conversion, smaller ethylene selectivity is observed at decreasing the inlet temperature, since larger amounts of ethane are heterogeneously burned. However, for $X_{C2H6} > 60\%$ an inversion in the curves of ethylene selectivity can be observed, due to the production of larger amounts of ethylene at lower inlet- temperature. This effect could become evident at very high ethane conversion, producing a significant increase of the overall yield to ethylene, also with respect to a pure homogeneous ODH process (Figure 1b).

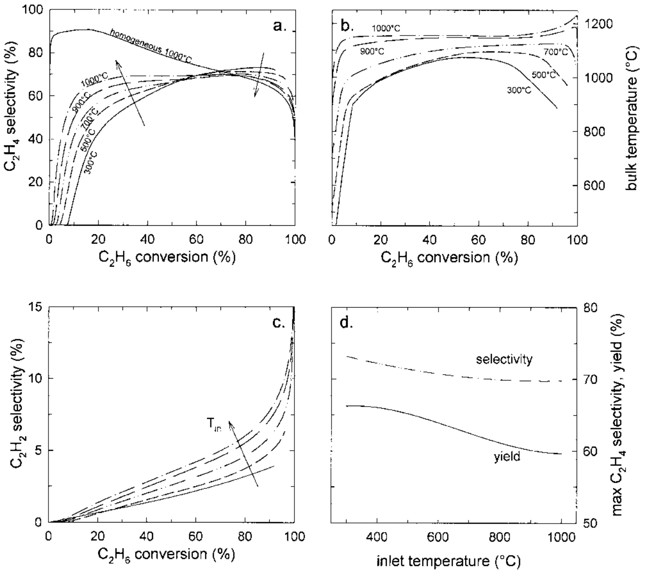

Figure 2. Calculated average (a) C_2H_4 selectivity, (b) gas temperature, and (c) and C_2H_2 selectivity along the reactor as a function of C_2H_6 conversion at varying inlet temperature, (d) maximum values of C_2h_4 yield and selectivity attained at different inlet temperatures (d) for $C_2H_6/O_2/N_2$=46.7/23.3/30.

The chemical role acts by increasing the C/O ratio, thus favoring the C_2H_4 yield. Moreover, by decreasing the inlet temperature, the temperature profile attained along the reactor is lower, determining a subsequent decrease of acetylene and methane formation.

Via the inlet gas temperature, a control can be introduced of the maximum temperature value, thus leading to the optimization of the thermal role of the catalyst, and the reduction of the amounts of byproducts C_2H_2 and CH_4. The reactor with the lowest inlet temperature, hence, represents the most convenient case, able to give a significantly higher ethylene yield in comparison with a purely homogeneous reactor (which anyway requires higher inlet temperatures) in the same range of short contact times investigated.

Profiles along the catalytic reactor

In Figure 3 are reported, the 2-D profiles of temperature and species concentration, highlighting the importance of radial gradients of temperature and concentration. In particular, for an inlet T of 500°C, it is shown only the first half mm catalytic

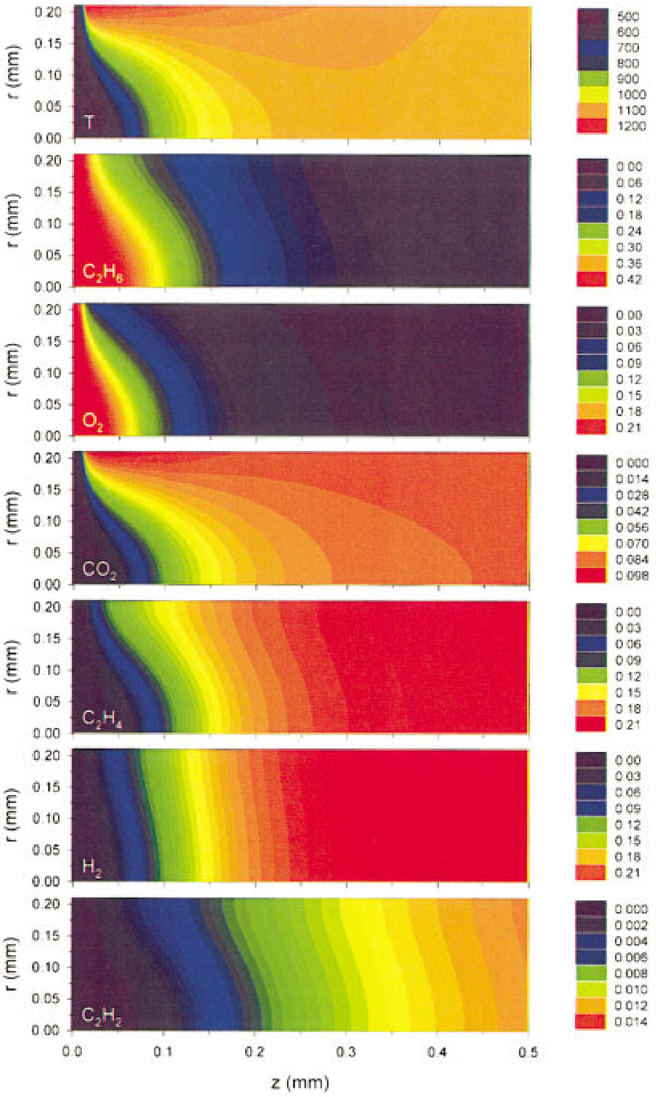

Figure 3. Contour plots of temperature and molar fraction of selected species in the first 0.5 mm of the catalytic reactor, between the center (r=0) and the wall (r=0.21) of the channel.

Conditions: T_{in}=500°C, $C_2H_6/O_2/N_2$=46.7/23.3/30.

reactor (that is, 10 mm long), where the transition can be appreciated from a purely heterogeneous reaction zone to a zone where heterogeneous and homogeneous reactions are concurrent. For $x \leq 0.05$ mm temperature quickly rises at the reactor wall up to 1,200°C, producing a hot spot, whereas in the bulk gas it is still 500°C. After 0.4 mm the radial temperature difference is reduced from 700°C to quite uniform along the radius.

The transition from a purely heterogeneous to a heterogeneous-homogeneous reaction zone is also revealed by species concentration profiles. At the inlet ($x \leq 0.02$ mm), a limited fraction of ethane (~3%), and a significant amount of oxygen, (~20%) are consumed at the catalyst surface, leading to the formation of CO_2 and H_2O. CO_2 and H_2O grow very rapidly for $x < 0.02$ mm and then they change mainly due to diffusion in the channel. Ethylene is formed only for $x > 0.02$ mm, suggesting that gas-phase reactions are ignited, and for $x < 0.1$ mm its formation occurs mainly near the wall where the maximum temperature is attained. When the temperature becomes uniform along the radius, also the fraction of ethylene grows more uniformly in the channel. The concentration of CO (not shown in the figure), rapidly grows in the vicinity of the hot spot, whereas H_2 concentration profile is more uniform, due to its higher diffusivity. Also, 35% of total acetylene is produced in the first 0.2 mm (where the average gas temperature is still relatively low), with a higher rate in the vicinity of the hot reactor walls.

In the first 0.1 mm of the reactor most of the reactions of interest occurred, with ~53% of C_2H_6 and ~75% of O_2 reacted, and most of ethylene formed (52% of the overall C_2H_4), as shown in Figure 4, where the profiles of the section-averaged values of conversion, gas temperature and yield of the main species, calculated according to Eq. 9, are reported along the axial distance of the entire channel (10 mm) for the same conditions of Figure 3.

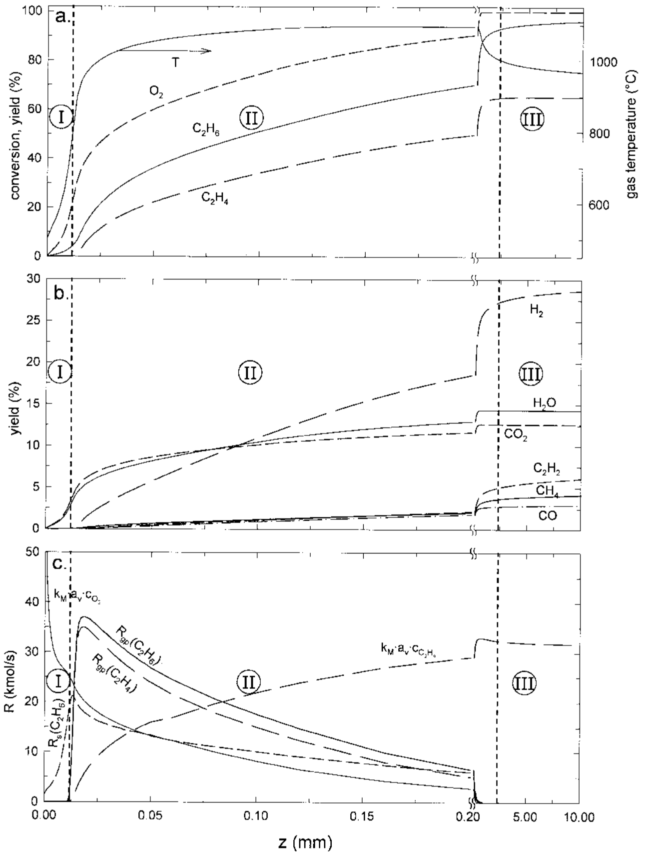

Figure 4. Calculated (a) profiles of temperature, C_2H_6 and O_2 conversion and C_2H_4 yield (b), profiles of the yields of the main products and (c) rates of surface reaction (R_s) of C_2H_6 consumption, of homogeneous reactions (R_{hom}) of C_2H_6 consumption., and of C_2H_4 formation, and of the rate of mass transfer at the surface of O_2 ($k_M \cdot a_v \cdot c_{O2}$), and of C_2H_4 ($k_M \cdot a_v \cdot c_{c_2H_4}$) along the catalytic reactor for the conditions of Figure 3.

Three zones of reaction are identified.

Figures 4a and 4b confirm that at the inlet of the reactor surface reactions are strongly dominant, leading to a rapid increase of temperature. As soon as T_{th} is reached, also homogeneous reactions occur with a significant rate, with the formation of C_2H_4 and of the other compounds produced in the gas phase. When oxygen is completely consumed only homogeneous reactions of decomposition of ethane and ethylene to acetylene and methane occur (Figure 4b).

Remarkably, Figure 4a shows that most of ethylene is formed when the oxygen is not completely consumed, in agreement with a previous work (Donsì et al., 2002), where we claimed that the presence of O_2 in the gas phase is fundamental for obtaining high ethylene yields at short contact times.

The average rates of heterogeneous and homogeneous reactions of ethane consumption are also reported along the channel (Figure 4c). These reaction rates are compared with the rate of mass transfer of oxygen, which is the limiting reactant, from the bulk gas to the catalyst surface, evaluated according to the correlation of Grigull and Tratz (1965) that takes into account also the entrance effects. For $x < 0.01$ mm, only the surface reaction occurs under a heterogeneous kinetic regime, since mass transfer is always faster than the rate of reaction. As temperature increases above 850°C, gas-phase reactions become relevant, and very quickly overcome the rate of the surface reaction. In Figure 4c it is shown that under the conditions examined the rate of gas-phase consumption of ethane and formation of ethylene are twice faster than the surface reaction of consumption of ethane for $x > 0.02$ mm.

Deeper in the reactor, the rates of ethane consumption and oxygen mass transfer decrease with the reactants depletion. The rate of mass transfer of ethylene to the catalyst wall (also shown in Figure 4c) increases as ethylene is formed along the reactor, but becomes significant only when oxygen is largely consumed, thus preventing the oxidation of ethylene on the surface (which however is not predicted by the model). Moreover, the characteristic time-scale of mass transport from the bulk gas to the catalytic surface ($1/k_M$) can be assumed to be longer than the reaction time in the homogeneous phase under fully ignited reactor conditions. The comparison is specifically conducted in Figure 4 for the consumption of O_2, but can be expected even more relevant in the case of much more reactive radical species, thus supporting our assumption of modeling the role of the catalyst only related to the promotion of ethane deep oxidation.

In the reactor channel three zones of the reactor are identified. In the first zone (I), which extends from the inlet temperature to the threshold temperature of gas-phase reactions, ethane and oxygen are consumed almost exclusively on the catalyst surface to give the required temperature increase. The second zone (II) is characterized by a concurrence of surface and homogeneous reactions, with the rate of the latter becoming increasingly fast as the temperature increases. In the third zone (III) extinction of surface reactions occurs due to the exhaustion of oxygen, and thermal dehydrogenation reactions are controlling, mainly leading to degradation of ethylene.

Understanding the behavior of the catalyst in zone 1 and zone 2 is hence important in order to control the ODH performances.

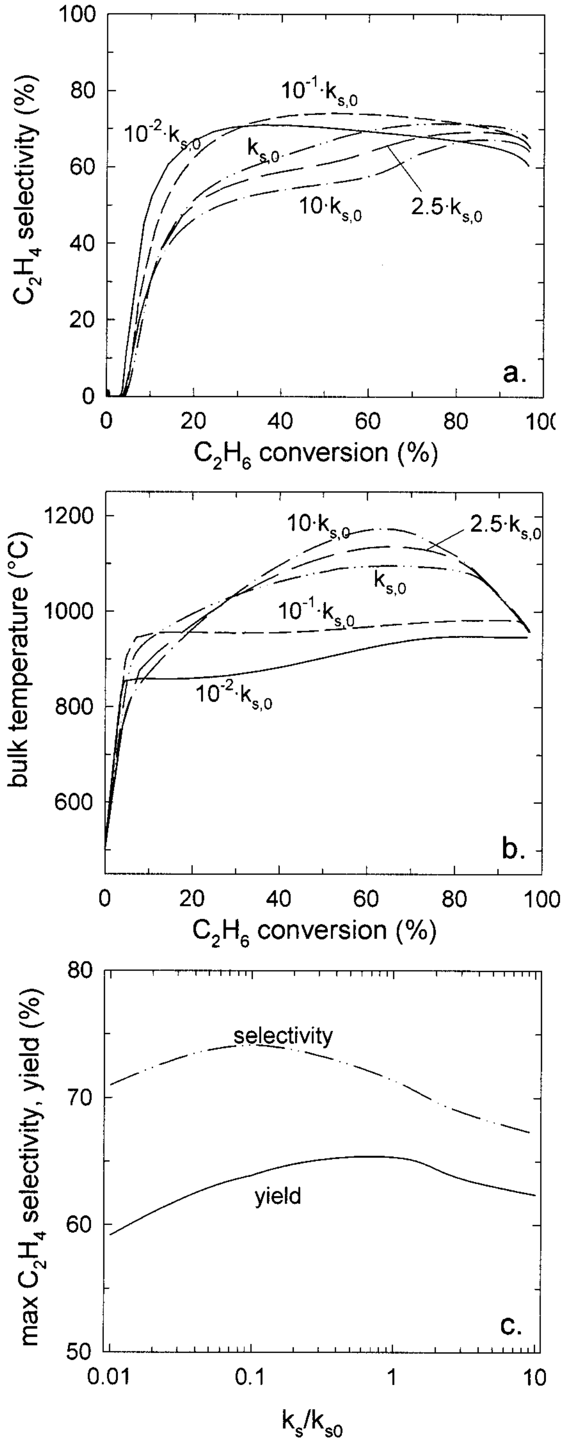

Figure 5. Calculated average (a) C_2H_4 selectivity and (b) gas temperature along the reactor as a function of C_2H_6 conversion at varying the pre-exponential factor for T_{in}=500°C, $C_2H_6/O_2/N_2$=46.7/23.3/30, (c) maximum values of C_2H_4 yield and selectivity attained for any pre-exponential factors.

Effect of changing the catalyst activity

The catalyst activity was affected by varying the pre-exponential factor and the activation energy of the heterogeneous reaction rate in the model. Figure 5 shows the effect of varying of 3 orders of magnitude the original value of the pre-exponential factor (which will be referred as $k_{s,0}$) for the same inlet temperature.The highest values of the maximum achievable ethylene selectivity and yield are attained for intermediate activity of the catalyst (Figure 5a). A pre-exponential factor of $10^{-1} \cdot k_{s,0}$ seems optimal for obtaining the highest ethylene selectivity, whereas a pre-exponential factor of $k_{s,0}$ is suitable for the maximum yield, under the conditions examined.

As shown in Figure 5a, at low ethane conversion ($X_{C2H6} <$ 30%), ethylene selectivity is the highest for the least active catalyst. At higher ethane conversion ($X_{C2H6} <$ 30%), for the least active catalyst, ethylene selectivity shows a constantly decreasing trend, whereas it is increasing in a wider range of ethane conversion for the case of higher activity.

Similarly to the results of Figure 2 this behavior can be explained by looking at the competition between the chemical and the thermal role of the catalyst. If the chemical were the only effect, the optimal catalyst would have been the most active one, which catalyzes the formation of the largest amounts of CO_2, saving more carbon for ethylene production. However, the thermal of the catalyst turns negative at high surface activity, wasting the carbon saved in CO_x to C_2H_2 and CH_4, because the reactor becomes exceedingly hot (Figure 5b). The competition between the chemical, and the thermal role gives rise to an optimum value of $k_{s,0}$ (Fig. 5c).

The effect of the activation energy of the surface reaction on the performance of the process is investigated by changing simultaneously two parameters: the activation energy and the pre-exponential factor of the surface reaction in such a way that the value of the kinetic constant at 850°C is maintained constant. Consequently, the catalyst with the highest activation energy ($\Delta E_a = +40$ kJ/mol) turns out to be the most active above 850°C.

In this case the differences among the maximum attainable values of ethylene selectivity and yield, reported in Figure 6c, are smaller. The general trend reveals that the highest values are obtained for the lowest activation energy, and, hence, when the contribution from the catalyst is the lowest (Figure 6a). In particular, ethylene selectivity becomes higher and higher along the whole reactor length at lowering the activation energy. To explain this result, it is worth noting that, for higher activation energies, the temperature of the gas phase increases (Figure 6b). Unlike what observed by varying the pre-exponential factor, in this case the maximum ethylene selectivity is not attained for an intermediate activity value of the parameter changed because the gain in carbon at higher activity (larger E_a), is always lower than the carbon loss to C_2H_2 and CH_4 due to the higher attained temperature.

Discussion

In this study, it is shown that the use of a catalyst exclusively able to oxidize ethane to CO_2 and H_2O can significantly improve the ethylene selectivity in the ODH process. Actually, the combustion catalyst may interact with gas-phase reactions by selectively subtracting oxygen to form CO_2 (chemical role), thus leaving more carbon for the formation of ethylene with respect to a pure homogeneous case (where CO is the most relevant byproduct), and releasing heat (thermal role) to ignite gas-phase reaction and significantly accelerate all reactions.

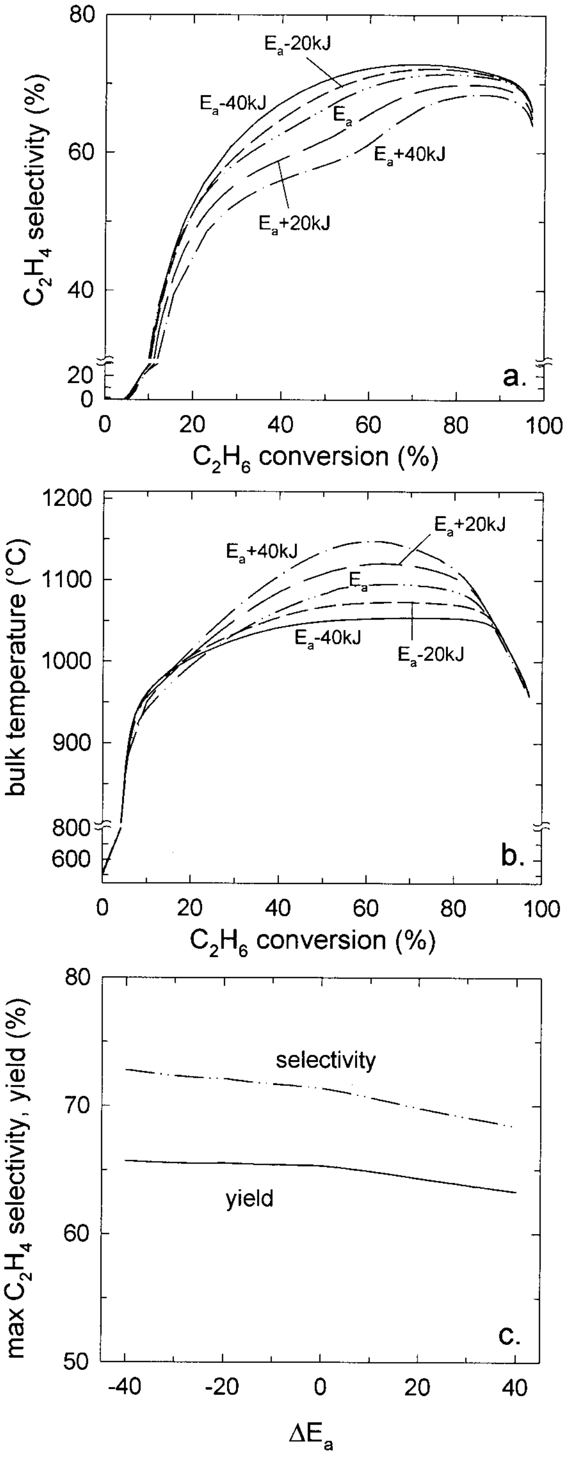

Figure 6. Calculated average (a) C_2H_4 selectivity and (b) gas temperature along the reactor as a function of C_2H_6 conversion at varying the activation energy for T_{in}=500°C, $C_2H_6/O_2/N_2$=46.7/23.3/30, (c) maximum values of C_2H_4 yield and selectivity attained for any activation energies.

The results of our modeling may be more conveniently discussed if a description of the main homogeneous paths yielding to ethylene formation, according to Marinov et al.

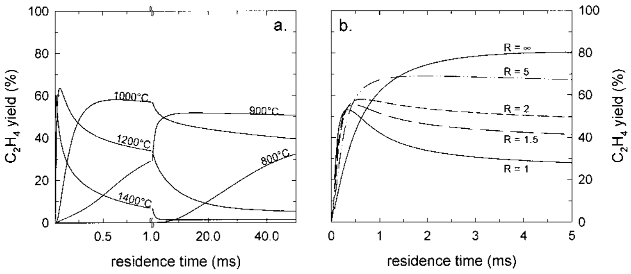

Figure 7. Calculated C_2H_4 yield as a function of residence time in a purely homogeneous isothermal reactor (a) for different temperatures at $C_2H_6/O_2/N_2$=46.7/23.3/30 and (b) for different C_2H_6/O_2 ratios (R) at N_2=30%vol, and T=1,000°C.

(1998), is given. Figure 7 shows the simulations of an isothermal reactor with a purely homogeneous process. It is quite evident that the content of oxygen in the feed mixture (reported as the ratio R = C_2H_6/O_2 in Figure 7b) affects not only the maximum ethylene yield, but also the time required for attaining such maximum. When oxygen is not fed to the reactor (R = ∞) the maximum C_2H_4 yield is attained for residence times of the order of 0.1 s as in the steam-cracking process. The addition of O_2 to the feed greatly reduces the residence time required for attaining the maximum ethylene yield down to 5 ms for R = 1, but has also a negative effect on such maximum.

The trend of the C_2H_4 yield is also dependent on temperature, as shown in Figure 7a, where numerical simulations in an isothermal reactor operated at different temperatures are reported. As the temperature increases from 800 to 1,200°C, the maximum ethylene yield is increased and is attained at shorter residence times.

It is worth saying that in such conditions, ethylene is not a product of thermodynamic equilibrium. For $R = 2$ and $T =$ 1,000°C (Figure 7b), the most favored products at equilibrium are H_2 (45%), CH_4 (20%), and CO (25%), whereas the ethylene yield and the ethane conversion are, respectively 0.5 and 100%, as calculated according to the module EQUIL of the CHEMKIN™ software. Also a low fraction of acetylene is formed (0.7%) but it increases on increasing temperature.

The reaction mechanism used in this work (Marinov et al., 1998) is consistent with the calculated conditions of thermodynamic equilibrium, which are reached at T = 1,000° C, with a residence time of the order of 100 h. Consequently, in short contact time reactors, the predicted reaction products are completely controlled by kinetics.

According to the mechanism implemented (Marinov et al., 1998), the initiation reactions in the gas phase under ODH conditions are represented by the reaction steps 12 and 13, and involve exclusively ethane, which is decomposed to C_2H_5 and CH_3

$$C_2H_6(+m) \rightarrow CH_3 + CH_3(+m) \tag{12}$$

$$C_2H_6 \rightarrow C_2H_5 + H \tag{13}$$

As pointed out in the work of Taylor and Kulich (1973), O_2 is not involved in the initial stages of the process, until a pool of H radicals is formed (mainly via reaction 13). For this reason, the reaction of consumption of oxygen (step 14) is delayed with respect to ethane, and the formation of dehydrogenation products (that is, ethylene) occurs before the oxygenated ones (CO_x)

$$O_2 + H \rightarrow O + OH \tag{14}$$

The reactions of propagation occur with a significant rate via C_2H_6 consumption, involving radical species, such as H · and OH according to step 15 and 16

$$C_2H_6 + H \leftrightarrow C_2H_5 + H_2 \tag{15}$$

$$C_2H_6 + OH \leftrightarrow C_2H_5 + H_2O \tag{16}$$

As concerns the reactivity of the radicals in the consumption of C_2H_6 to C_2H_5, it can be roughly ordered as follows: H > OH $\geqslant$ CH_3 > O. In particular, at the inlet section of the reactor ethane conversion occurs mainly according to step 15, due to the larger amount of H formed in the initiation in step 13. Once a pool of H radicals is formed and, thus, step 14 is activated, OH radicals are produced and quickly react with ethane according to step 16. The main product of the reactions of propagation from ethane is the ethyl radical (C_2H_5), which is formed primarily according to steps 15 and 16 (although, there are also many other and much less relevant reaction steps for the production of C_2H_5), and is very rapidly consumed via both oxygen-assisted (step 17) and pure dehydrogenation (step 18) steps. Alternatively, the main and most representative side-reaction consuming C_2H_5 and not yielding ethylene is the step 19 reported below, which is responsible of the production of CH_3 and CH_2O

$$C_2H_5 + O_2 \leftrightarrow C_2H_4 + HO_2 \tag{17}$$

$$C_2H_5(+m) \leftrightarrow C_2H_4 + H + (m) \tag{18}$$

$$C_2H_5 + HO_2 \leftrightarrow CH_3 + CH_2O + OH \tag{19}$$

Under fuel-rich conditions, the rate of reaction 18 is faster than 17 and 19.

The yield of C_2H_4 exhibits a maximum for contact times of the order of milliseconds. Indeed, the rate of consumption of C_2H_4 becomes faster than that of production, once a significant concentration of C_2H_4 and radicals is achieved. The radicals consuming C_2H_4 are in the order of reactivity OH, CH_3, O, H, mainly leading to C_2H_3, which further reacts toward acetylene, or toward the formation of CO or PAH via a complex mechanism. Under oxygen-lean conditions, CO is the main stable oxidation product, whereas CO_2 is produced in small amounts.

In an adiabatic reactor, both in the presence and in the absence of catalyst the effect of the oxygen content and temperature overlap each other and partially compensate. At lower values of R, higher temperatures compensate the effect of the larger oxygen content in the ethylene selectivity. Nevertheless, when R is too low, a negative effect due to the exceedingly high-temperature is added to the negative effect due to the large oxygen content.

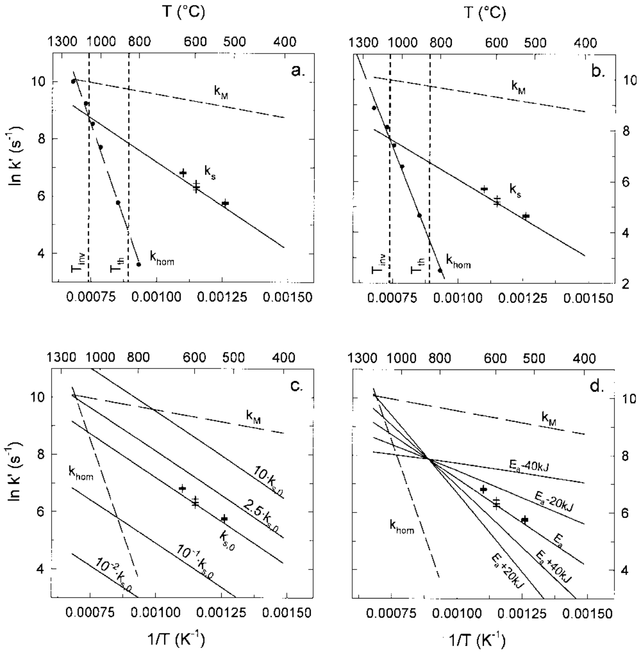

Figure 8. Normalized (s$-^1$) mass-transfer coefficient (k_M) in the modeled channel, the kinetic constant of the surface reaction (k_s, symbols: experimental values from Donsi et al., 2002; lines: this work), and the kinetic constant (k_{hom}, symbols: extended mechanism from Marinov et al., 1998; lines: lumped mechanism from Marinov et al., 1998) of the homogeneous reactions of ethane consumption for (a) C_2H_6/O_2=2 and C_2H_6=46%vol, and (b) C_2H_6/O_2=2 and C_2H_6=5%vol, and at varying (c) the pre-exponential factor, and (d) the activation energy.

Moreover, in the heterohomogeneous adiabatic reactor different phenomena coexist. In order to compare them, the order of magnitude of the kinetics of the homogeneous reaction, mass transfer and heterogeneous reaction have been evaluated, and the mutual interaction among the different phenomena occurring in the reactor, the actual relative weight of each of them and the effective proceeding of gas phase and catalyzed reactions was roughly assessed. To this purpose, Figure 8 reports the kinetic constants and the mass-transfer coefficient as functions of temperature.

The rates of the homogeneous reactions of consumption of ethane, as described in the Marinov mechanism (Marinov et al., 1998), have been empirically lumped into a single reaction, whose overall kinetics has been modeled with a power law equation, characterized by a reaction order of 0.5 for ethane and 1 for oxygen (Eqs. 20 and 21). Such power law expression is quite accurate in describing the overall rate of consumption of ethane in the range of operating conditions of interest for the process under examination, and can, hence, be used to predict characteristic reaction times

$$r_{C_2H_6} = -k_{hom} \cdot c_{C_2H_6}^{0.5} \cdot c_{O_2} \quad [\text{mole/s} \cdot \text{m}^3] \tag{20}$$

$$k_{hom} = k_{hom,0} \cdot e^{-(E_{a,hom}/R_gT)} = 1.50 \cdot 10^{12} \cdot e^{-(217020/R_gT)} \quad [\text{m}^{1.5}/\text{s} \cdot \text{mole}^{0.5}] \tag{21}$$

The order of magnitude of the global coefficient of mass transfer among the bulk gas and the catalyst surface (k_M) is evaluated from the correlation reported by Hawthorn (1974), whereas the kinetic constants of both homogeneous and heterogeneous reactions reported in Figure 8 are normalized by multiplying for $c_{C_2H_6}^{0.5}$, in order to be comparable with the mass-transfer coefficient. The rate of surface reaction is reported in Eq. 10, that of homogeneous reaction in Eq. 20.

In Figure 8, it appears that the mass-transfer coefficient is high in comparison to the value of surface reaction rate ($k_{s,o}$) in the temperature range of interest (between 400 and 1,200°C), both at high (Figure 8a) and especially at low ethane concentration (Figure 8b): mass transfer is not controlling the overall rate of ethane consumption on the catalyst surface.

Figure 8 also shows that at low-temperature a heterogeneous kinetic regime rules, as the surface reaction is much faster than the reactions occurring in the gas phase. According to the homogeneous model simulations, the homogeneous reactions resulted to occur with a significant extent in the range of short contact times investigated (between 5 and 100 ms) for temperatures higher than 850°C, which has been considered as the threshold temperature of gas-phase reactions (T_{th} in Figure 8). The temperature at which the rate of gas-phase reactions reaches that of surface reactions is here referred as the inversion temperature (T_{inv}) as shown in Figure 8. Due to the efficiency of mass transfer along the reactor in the temperature range of interest, heterogeneous and homogeneous reactions coexist until the extinction of surface reactions occurs, as a consequence of the complete consumption of oxygen (since our model does not consider nonoxidative reaction paths catalyzed by the surface), thus leading to a purely homogeneous regime in the reactor.

Actually, for a catalyst activity increased of a factor 2.5, the inversion temperature (T_{inv}) rises from 1,050°C to ~1,200°C, whereas decreasing $k_{s,0}$ it decreases down to about T_{th}. At higher activity ($10 \cdot k_{s,0}$) the superficial reactions are controlled by mass transfer from the bulk gas phase to the surface, as shown in Figure 8c. Starting from this value, any increment of the catalyst activity will not have any effect on ethylene selectivity because the competition between heterogeneous and homogeneous reactions is controlled only by the mass fluxes. This result suggests that in the presence of the most active oxidation catalysts (such as Pt) a detailed description of surface chemistry could be quite useless, being the reaction rate at surface controlled by diffusion of reactant toward the catalytic surface. Hence, for the most active catalysts, all the results for ODH performances should be the same, whatever the catalyst used, under the hypothesis that the effects of the presence of catalyst other than the activity in the deep oxidation are not very relevant in the determination of the overall performances of short contact time reactors.

In the case of low catalyst activity ($10^{-1} \cdot k_{s,0}$ and $10^{-2} \cdot k_{s,0}$) the inversion temperature is very close to the threshold temperature of gas-phase reactions (Figure 8c), and the point of ignition of the homogeneous reactions is over-imposed to the inversion point. For higher activity, instead, the change in slope takes place for ethane conversion increasing with the catalyst activity.

Figure 8d shows that when the activation energy is changed, the range of variation of T_{inv} is much narrower than that attained varying the pre-exponential factor and, also, the differences among the maximum attainable values of ethylene selectivity and yield are thus smaller.

According to these results, it is possible to better define three zones in the reactor. The inversion temperature T_{inv} at which gas phase reactions become faster than the surface reaction is comprised in the second zone and marks the boundary between the dominant role of heterogeneous and that of homogeneous reactions.

The extension of the first zone of the reactor depends on the inlet temperature, which determines the amount of oxygen and ethane to be consumed to raise the temperature up to 850°C. According to the stoichiometry of ethane combustion (Eq. 22), oxygen conversion at the exit of the first zone (X_{I,O_2}) is much higher than ethane conversion (X_{I,C_2H_6}), as shown in Eq. 23, where it is reported as a function of ethane conversion and feed ratio at the inlet (R_I)

$$C_2H_6 + 3.5\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O \tag{22}$$

$$X_{I,O_2} = 3.5 \cdot X_{I,C_2H_6} \cdot R_I \tag{23}$$

The consumption of larger amounts of oxygen than ethane determines that the fuel-to-oxygen ratio at the inlet of the second zone (R_{II}) is higher than the one at the inlet of the reactor (R_I). The new C_2H_6/O_2 ratio at the inlet of the second zone is given in Eq. 24

$$R_{II} = R_I \cdot \frac{1 - X_{I,C_2H_6}}{1 - 3.5 \cdot X_{I,C_2H_6} \cdot R_I} \tag{24}$$

From what was said above, it results that, at a fixed value of the gas inlet temperature, the activity or the specific surface of the catalyst does not seem likely to influence the composition of the gas mixture at the exit of the first zone, as R_{II} and X_I are independent on catalyst activity, but they can influence only length of such a zone. However, also in the first zone, some products of gas-phase reactions can be obtained, due to the presence of hot spots, more relevant if the catalyst is too active.

Figures 5 and 6 have shown that when the catalyst is exceedingly active, or the inlet temperature is high, hot spots can be formed on the surface, increasing gas temperature, and other species, such as C_2H_2, CH_4 and higher hydrocarbons are formed. Figure 8c showed that mass transfer (and heat transfer shows a similar trend) becomes slower than the rate of surface reaction at large pre-exponential factors. Thus, surface temperature becomes much higher than the bulk gas temperature (up to 1,500°C), and leads to fast reactions of ethylene decomposition in the close proximity of catalyst. Figure 9 shows that for the lowest-activity catalyst, temperature is uniform along the radius for the entire length of the reactor. Also, at a pre-exponential factor of $10^{-1}\cdot k_{s,0}$, the temperature difference between the surface and the bulk is limited to less than 100°C. For further increasing pre-exponential factor, the formation of a thermal boundary layer can be observed, which thickens and becomes increasingly hotter. The highest temperature attained near the wall grows from 1,200°C (for $k_{s,0}$) to 1,500°C (for $10\cdot k_{s,0}$), concurrently to the growing of the thickness of the hot spot, thus favoring ethylene decomposition to other products (C_2H_2 and CH_4) in the vicinity of the surface.

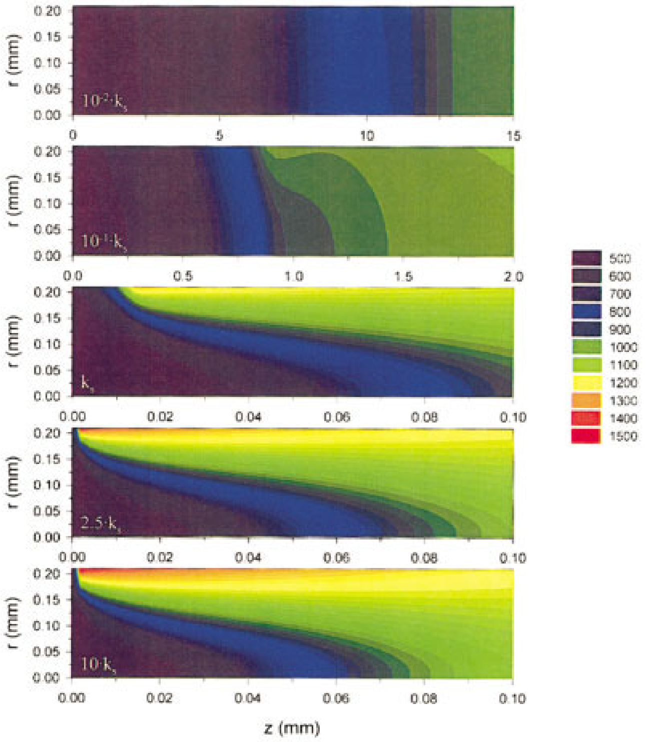

Figure 9. Contour plots of temperature for different channel lengths between the center (r=0) and the wall (r=0.21) of the channel at varying pre-exponential factor.

Conditions of Figure7.

This situation is clarified in Table 1, where a comparison is drawn between the characteristic timescales of heat transfer, that is, the time required to transfer the heat produced on the surface to the bulk gas phase, and the characteristic times of heat production, at different values of $k_{s,0}$. As the catalyst activity is increased, the characteristic timescales of the surface reactions decrease and become comparable with those of heat transfer, leading to the formation of hot spots. Concurrently, as temperature rises, it is observed a significant reduction of the characteristic times of ethylene decomposition, which means that the degradation of a fraction of ethylene formed in the local hot spots is likely to occur.

From the results in Table 1, it appears that $10^{-1}\cdot k_{s,0}$ is the optimal value for ethylene selectivity (Figure 5a) because $\tau_s \gg \tau_H$, thus suggesting that local hot spots are absent. By increasing catalyst activity ($> 10^{-1}\cdot k_{s,0}$), heat transfer and heat production become comparable, and local hot spots are possible: ethylene selectivity decreases due to high-temperature.

Conclusions

In this work a 2-D mathematical model was used to investigate the main effects of the presence of a catalyst not able to promote ethylene formation, but only active in the total oxida-

Table 1. Comparison of the Characteristic Times (s) of Heat Transfer ($\tau_H = \rho c_p/ha_v$) of the Rate of Homogeneous Reaction of Consumption of C_2H_4, $\tau_{hom}(C_2H_4)$, and of the Rate of the Surface Reaction τ_s at Varying the Pre-exponential Factor, for Some Typical Temperatures of the Reactor

T (°C)	τ_H	$\tau_{hom}(C_2H_4)$	$\tau_s(10^{-2}k_{s,0})$	$\tau_s(10^{-1}k_{s,0})$	$\tau_s(k_{s,0})$	$\tau_s(2.5 \cdot k_{s,0})$	$\tau_s(10 \cdot k_{s,0})$
850	$5.3 \cdot 10^{-5}$	—	$3.8 \cdot 10^{-2}$	$3.8 \cdot 10^{-3}$	$3.8 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$3.8 \cdot 10^{-5}$
900	$4.9 \cdot 10^{-5}$	—	$3.0 \cdot 10^{-2}$	$3.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$3.0 \cdot 10^{-5}$
1000	$4.3 \cdot 10^{-5}$	—	$2.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-4}$	$8.1 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$
1100	$3.8 \cdot 10^{-5}$	1.6	$1.4 \cdot 10^{-2}$	$1.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$5.8 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$
1200	$3.4 \cdot 10^{-5}$	$3.0 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$	$1.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-4}$	$4.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$
1300	$5.9 \cdot 10^{-5}$	$7.5 \cdot 10^{-3}$	$6.7 \cdot 10^{-3}$	$6.7 \cdot 10^{-4}$	$6.7 \cdot 10^{-5}$	$2.7 \cdot 10^{-5}$	$6.7 \cdot 10^{-6}$
1400	$7.8 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	$5.6 \cdot 10^{-3}$	$5.6 \cdot 10^{-4}$	$5.6 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	$5.6 \cdot 10^{-6}$
1500	$9.2 \cdot 10^{-5}$	$9.0 \cdot 10^{-4}$	$4.7 \cdot 10^{-3}$	$4.7 \cdot 10^{-4}$	$4.7 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	$4.7 \cdot 10^{-6}$

tion of C_2H_6 in the oxidative dehydrogenation of ethane at short contact times. Such a catalyst was shown to be not only able to ignite and sustain gas-phase reactions, but also important in improving the maximum attainable ethylene yield, by optimizing the sacrifice of ethane for producing heat, due to a larger selectivity to CO_2, than a purely homogeneous process.

From the computational results, a schematization of the reactor into three zones is derived. In the first zone only surface reactions occur, in the second surface and gas-phase reactions are concurrent, whereas in the third only homogeneous reactions take place in the absence of molecular oxygen. Two competitive roles of the catalyst are identified: the chemical role and the thermal role. The chemical role consists of catalyzing the consumption of oxygen toward CO_2, thus reducing the sacrificial ethane. The thermal role consists of heating the surface in the first zone, thus igniting the gas phase reactions and producing heat in the second zone, with the drawback of the generation of local hot spots. The competition between the chemical role and the thermal role is crucial for the ethylene selectivity. The extension of the second zone is fundamental in determining the performance of the system, and is determined by the catalyst activity. Strong catalyst activity, investigated varying parametrically the pre-exponential factor, and the activation energy of the surface reaction, resulted to be beneficial to ethylene selectivity as the chemical role of the catalyst is reinforced, until hot spots are formed on the catalyst surface. Indeed, the presence of hot spots determined by a too fast production of heat in the heterogeneous reaction leads to undesired products of C_2H_4 degradation. Consequently, from our investigation, intermediate values of activity turned out to be optimal for maximizing ethylene selectivity, and increase the yield to the C_2H_4 with respect to a purely homogeneous process.

Notation

a_v = specific geometric surface, m^{-1}
c_i = concentration of species i, mol/m^3
c_p = specific heat, J/kg K
D_i = diffusion coefficient of species i, m^2/s
d_c = channel diameter, m
E_a = activation energy, J/mol
h = heat transfer coefficient, J/m^2 s K
h_i = enthalpy of species i, J/kg
$J_{r,i}$ = radial mass flux of species i, m/s
k = kinetic constant, mol, m, s
k_0 = pre-exponential factor, mol, m, s
P = pressure, Pa
r = radial coordinate, m
R = C_2H_6/O_2 ratio
R_g = gas constant, J/mol K
r_i = gas-phase reaction rate of species i, mol/m^{3}s
r_i^r = surface reaction rate of species i, mol/m^2 s
T = temperature, K
V_0 = space velocity, m/s
v_r = radial velocity, m/s
v_z = axial velocity, m/s
$\bar{W}$ = average molar weight, kg/mol
w_i = mass fraction of species i
W_i = molar weight of species i, kg/mol
X = conversion
Y_i = molar fraction
z = axial coordinate, m

Greek letters

λ = thermal conductivity, W/m K
μ = viscosity, Pa s
ρ = density, Kg/mol
τ = characteristic time, s
ϕ = any intensive variable

Subscripts and superscripts

av = average
H = heat
hom = homogeneous
in = inlet
m = mixture
s = surface
T = temperature
I = at the inlet of the first zone
II = at the inlet of the second zone

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