Journal of Catalysis **209,** 51–61 (2002)
doi:10.1006/jcat.2002.3636

Oxidative Dehydrogenation of Ethane over a Perovskite-Based Monolithic Reactor

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Received September 17, 2001; revised March 15, 2002; accepted April 11, 2002

The oxidative dehydrogenation (ODH) of ethane has been investigated in a short-contact-time reactor consisting of a $LaMnO_3$-based monolithic catalyst with a honeycomb morphology. Using an ethane/air mixture with a C_2H_6/O_2 ratio $= 1.5$ and a preheat temperature ranging from 250 to 400°C results in a 55% ethylene yield, a value even higher than those reported in the same experimental conditions over Pt-based catalysts. By investigating the effect of the experimental conditions, we found that the major role of increasing the feed flow rate and decreasing the C_2H_6/O_2 ratio is to raise the degree of adiabaticity of the reactor and, consequently, ethane conversion and temperature. The selectivity to ethylene also seems to increase with increasing temperature, but only up to about 950°C. At higher temperatures, further degradation of ethylene to C_2H_2 and CH_4 occurs. We also found that, unlike Pt monoliths, the perovskite catalyst is intrinsically active in ODH.

Key Words: **ethane; ODH; ethylene; short contact time; monolith; oxidative dehydrogenation; autothermal reactor.**

INTRODUCTION

The abundant availability of natural gas stimulated the study of novel and more efficient processes for its exploitation. Although combustion processes for thermal energy production represent the most practised way of utilysing natural gas, the chemical transformation of small alkanes into more valuable or transportable compounds is also a matter of intensive and interesting research (1–3). Extensive work has been devoted to studying oxidative processes for ethylene production, owing to the potential advantages of exothermic and thermodynamically unlimited reactions, coupled with the possible reduction of coke deposition in the furnaces. Specifically, the catalytic oxidative coupling of methane (OCM) and the oxidative dehydrogenation of ethane (ODH) have been investigated thoroughly, but among all catalysts considered, none seems to exhibit promising performance for large-scale applications in conventional reactors (4).

In recent years, a renewed interest towards partial oxidation processes of light alkanes has been sparked by the results of the group of Prof. Lanny Schmidt at the University of Minnesota. Since 1993, they have demonstrated that olefins can be efficiently produced by the autothermal oxidative dehydrogenation of ethane over Pt containing structured reactors at short contact times (milliseconds) and temperatures in the range of 900–1000°C (5). Under such reaction conditions, it was shown that feeding a mixture C_2H_6/O_2 in a molar ratio slightly lower than 2 (namely, the stoichiometric value for ethane ODH) makes the ethylene yield high enough to be compared with the existing cracking processes.

The choice of platinum-based catalysts for this process resulted from the investigations of Schmidt *et al.* (6), who compared the activity of different noble metals in short-contact-time reactors for partial oxidation processes, reporting Pt as the best catalyst for ethane ODH and Rh as the most suitable in partial oxidation to syngas. The other noble metals tested for CH_4 partial oxidation did not show promising performances or enough stability. Pd, for instance, quickly deactivated due to coke formation (7). Moreover, doping Pt with tin or copper resulted in improved performance for ethane ODH, with a significant increase in ethylene yield (8), which was even greater as a result of H_2 addition (9).

The nature of these results remains disputed. Until recently, it has been reported that processes occurring in this kind of reactor are purely heterogeneous (5, 10, 11) and can be regulated by the appropriate choice of the active component (12), support morphology (11), and reaction mixture composition (5). This seems to be true only at moderate temperatures, while above 800°C, it has been shown, both experimentally (13–17) and theoretically (18–20), that the kinetics of homogeneous reaction paths is not negligible, even for millisecond residence time scales.

The alternative possibility to a purely heterogeneous mechanism of ethylene production is a hetero-homogeneous reaction path. As proposed in recent works (13), the catalyst could be assumed to act mostly as an igniting agent, active for total oxidation reactions, while ethylene-forming reactions mainly occur in the gas phase.

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In the same way, Bodke *et al.* (9) sketched a short-contact-time reactor as a two-zone reactor where in the first zone oxygen depletion occurs through C_2H_6 oxidation to CO_x and H_2O with consequent temperature increase, while in the second zone, where O_2 is absent, the endothermic dehydrogenation of ethane to ethylene and H_2 takes place. Moreover, Bodke *et al.* (9) also reported that the use of hydrogen co-feeding allows a minor ethane consumption in the first zone of the reactor, with H_2 being oxidised more easily than ethane over the Pt–Sn surface, and consequently C_2H_6 dehydrogenates in the second zone with very high selectivity (>80%) and yield (about 60%) to ethylene. Detailed heterogeneous and homogeneous chemical kinetic mechanisms employed in the two-dimensional computational fluid dynamics model developed by Zerkle *et al.* (20) confirmed the main scheme of Bodke *et al.* (9) and showed that the relative contributions of heterogeneous and homogenous reactions to the ethane overall consumption are strongly dependent on C_2H_6/O_2 feed ratio. More specifically, they reported that the formation of ethylene must be mainly attributed to heterogeneous dehydrogenation paths, especially when H_2 is added to the feed.

The use of materials other than noble metals has been considered by some authors (16, 21, 22). Flick and Huff proposed the use of Cr_2O_3-based foam monoliths in ethane ODH (21), showing that they exhibit very promising performance, even better than Pt-based monoliths, but with a strongly limited catalyst lifetime, likely due to the well-known deactivation processes occurring on transition metal oxides in the catalytic combustion of hydrocarbons (i.e., under operating conditions characterised by high temperatures, oxidising atmosphere, and the presence of water and CO_2).

$BaMnAl_{11}O_{19}$ hexa-aluminate, characterised by a high thermal stability, was investigated by Beretta and Forzatti under autothermal conditions (22). In comparison with Pt/α-Al_2O_3 catalyst, hexa-aluminate showed better performance, even though the higher preheat temperature required caused coke deposition. However, the authors did conclude that the presence of any catalyst could be useful in making the process autothermal but reduces the maximum yield attainable in the homogenous phase by only heating the C_2H_6/O_2 mixture. In particular, they clearly evidenced that Pt catalysts under controlled isothermal conditions, namely, in the absence of any homogeneous contribution, do not exhibit any intrinsic activity in ethane ODH to ethylene, and in short-contact-time reactors the Pt catalysts are hence responsible of the higher amount of ethane oxidised to CO_x compared to a pure homogeneous process (15, 22).

The morphology of the catalyst used for such processes has also been under investigation. Foams have been thoroughly studied since 1992 by Hickman and Schmidt (23), who found clear evidence that extruded honeycombed monoliths performed worse than foams in partial oxidation of methane over Pt-based monoliths (23). Since then, foams have been mainly investigated for ODH reactions (5, 9, 21). Sadykov *et al.* (24) used honeycombed monoliths in oxidative dehydrogenation of propane to reduce secondary catalytic reactions of propylene through the straight channels of the monolithic support. Only limited interest has been devoted to noble metal gauzes (13), because of the large Pt consumption due to volatilisation at the high temperature of operation of gauze reactors. FeCr alloy elements packed in a quartz tube were used as an alternative to foams, because of their high void fraction and large thermal conductivity (15, 19). However, there is no assurance that foams are more useful than honeycomb-type monolith catalysts in ethane ODH, as the conclusions of the work of Hickman and Schmidt (23) can be strictly applied only to the partial oxidation of CH_4, in which the role of homogeneous reaction paths is much less relevant, if not negligible, than in the case of ethane. ODH is different from partial oxidation to syngas, because the latter is a process that is widely accepted to occur to a larger extent on the catalytic surface and is then more influenced by the larger geometric surface of foam monoliths. As a consequence, we think that honeycombed monoliths for the application of the short-contact-time concept in ethane ODH could be preferable, as their straight channels could better preserve ethylene from further reacting in secondary paths.

Finally, we have considered the study of non-noble-metal-based catalysts in the oxidative dehydrogenation of ethane in short-contact-time reactors with a honeycomb-type morphology. In this field, we have recently developed novel structured catalytic systems, active in hydrocarbon deep oxidation processes as an alternative to noble metals (25). Specifically, the activity of a $LaMnO_3$-based monolithic catalyst has been proven to be stable in the catalytic combustion of methane under 100 h of operation in ignited conditions at 1000°C (26). To test the applicability of such a catalyst in ethane ODH at short contact time, we have performed reaction tests under a wide range of experimental conditions with the aim of both assessing the ultimate role of the catalyst properties in the reaction paths leading to olefins and of evaluating the possibility of using a significantly cheaper catalyst (compared to Pt-based ones) in the development of a novel and more efficient process of olefin production.

EXPERIMENTAL

Catalyst Preparation

The preparation of perovskite-based honeycomb monoliths via active phase deposition on cordierite is essentially identical to that previously described (25). The ceramic substrates (Corning) with a cell density of 400 cpsi (cells per square inch) were washcoated with alumina by repeated dipping in a slurry of finely grounded γ-Al_2O_3 powder, diluted nitric acid solution, and pseudobohemite. La_2O_3 (5% wt) was added to the washcoat by impregnation, followed by calcination at 800°C for 3 h. The $LaMnO_3$ active phase (30% wt) was added to the monolith using the wet impregnation method.

Autothermal Reactor Configuration

Catalytic activity measurements of ethane ODH at short contact times were carried out by placing two blank cordierite monoliths, 2 cm long, upstream and downstream of the catalytic monolith, in order to limit as much as possible heat losses by radiation, and sealing all three with quartz wool in a steel tube. The whole system was placed in an electric furnace to preheat the gas and solid. The annular gap between the steel tube and the furnace walls was completely filled with ceramic wool to limit as much as possible heat losses from the laboratory-scale reactor under ignited conditions.

The monolith employed in autothermal tests was characterised by an open cross section of 7×7 channels and a length of 40 mm. The central channel was blocked for wall temperature measurement at four different locations (upstream cordierite monolith, inlet and outlet of the catalytic monolith, and downstream cordierite monolith) using K-type thermocouples ($d = 0.5$mm), two of which enter from the top and two from the bottom of the reactor. As a consequence, the number of working channels for the catalysts was 48. A high value of ethane concentration was used in such tests to achieve a large heat production rate from the chemical reactions.

Isothermal Reactor Configuration

A smaller catalytic monolith, characterised by eight working channels, was employed in isothermal tests. In contrast to the autothermal measurements, in this case quartz wool was removed from the gap between the steel tube and the furnace walls. To carry out a correct characterisation of catalyst performance in ethane partial oxidation, experimental conditions have been adjusted to exclude the onset of gas-phase reactions. The system can be considered isothermal for a mixture with an inlet molar fraction of ethane as low as 0.5%. By reducing heat production on the surface, the difference between catalyst and oven temperature can be maintained to within a few degrees Celsius. In this way gas-phase temperature can be kept to less than 600°C, which was considered the threshold temperature for homogeneous reactions.

Gas flow into the reactors was controlled by three Brooks mass flow controllers, respectively, for ethane, oxygen or air, and nitrogen. GHSV (Gas Hourly Space Velocity) was varied from 18,000 up to 480,000 h^{-1} as evaluated at standard conditions on the basis of monolith volume, corresponding to residence times ranging from 4 and 50 ms. Feed gas composition was varied with a C_2H_6/O_2 ratio between 1 and 2. Product gases were fed to a $CaCl_2$ trap to selectively remove water, prior to splitting to an on-line gas chromatograph and to a Hartmann & Braunn Caldos analyser, which was employed to measure H_2 concentration.

RESULTS

We carried out ODH tests under different experimental conditions in both autothermal and isothermal reactor configurations, as described in the previous section. In autothermal tests, the high temperature attained, together with the presence of a large amount of water produced by the reaction, generated conditions strongly favourable to sintering phenomena. Moreover, the temperature spatial gradients as well as the thermal shocks undergone by the catalyst in start-on/shut-off operations were also relevant and potentially capable of deactivating the catalyst. Nevertheless, the same monolithic sample used in the whole investigation resulted in very stable and repeatable experiments for about 90 h of operation. Similar performances of thermal stability properties of this catalyst were already demonstrated in a previous investigation on methane catalytic combustion (26).

Representative results of the experimental campaign are reported here. In all the autothermal runs, the conversion of O_2 was complete in the steady state, independently of operating conditions, while the values of selectivities, yields, and temperatures were significantly variable. The maximum reactor temperature seems to be the key factor in determining the catalyst performance. The higher the temperature of the reactor, the higher the ethane conversion achieved. Nevertheless, the highest selectivity to ethylene seems not to be reached at the highest temperature attained but lies in the range of 850–950°C, as already reported by Flick and Huff (27). Indeed, below this temperature range ethylene is not significantly produced, while above 900°C acetylene, CH_4, and CO are favourably formed. The main parameters of the process (ethane/oxygen ratio, total flow rate, and preheat temperature) had to be tuned to keep the temperature in the optimal range.

Flow Rate

The effect of space velocity was investigated using a $C_2H_6/O_2/N_2 = 24/16/60$ mixture (ethane in air) at a preheating temperature of 400°C. Space velocity was changed by varying feed flow rate between 35 and 90 Nl/h (l/h measured at 273 K and 1 atm), i.e., the contact time between 77 and 200 $ms \cdot cm^3/Ncm^3$. Under the actual operating conditions this corresponds to an interval from 20 to 50 ms, evaluated at an average temperature of 900°C.

Figure 1a shows that ethylene yield reaches a maximum value for a total flow rate of about 70 Nl/h. Such a maximum

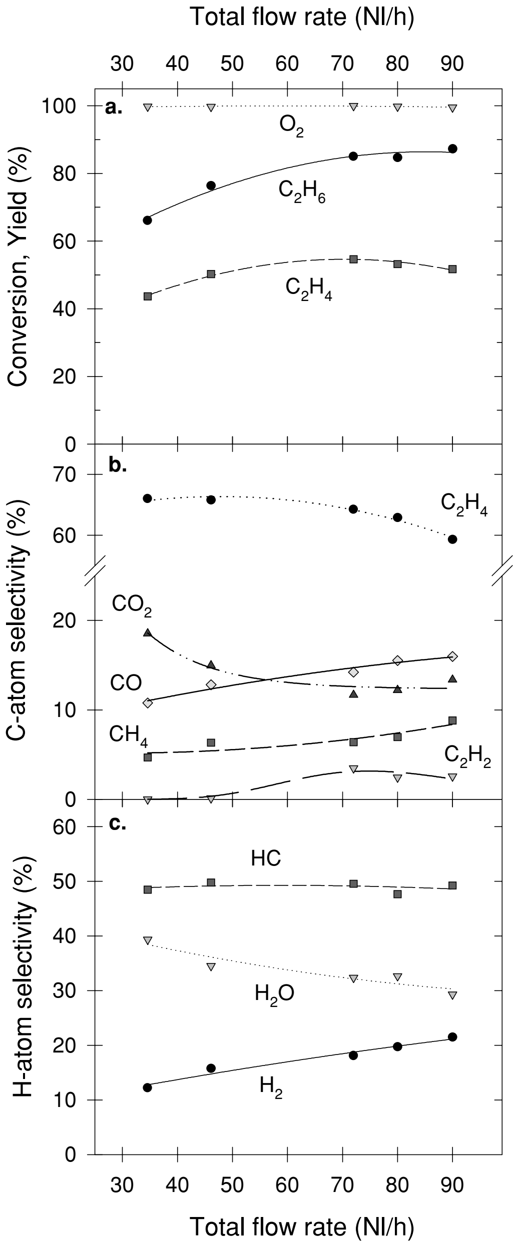

FIG. 1. O_2 and C_2H_6 conversion and C_2H_4 yield (a), C-atom selectivity (b), and H-atom (c) selectivity at varying total inlet flow rate. Operating conditions: $C_2H_6/O_2/N_2 = 24/16/60$; $T_{\text{preheat}} = 400°C$.

occurs because ethane conversion increases (from 66 to 87%) at increasing flow rate, while the selectivity to ethylene is observed to decrease from 66 to 59% (Fig. 1b). Actually, while the production of CH_4 and C_2H_2 is more favoured at the highest velocities explored, the overall selectivity to hydrocarbons remains constant (Figs. 1b and 1c), suggesting that these species are formed via in-series mechanisms of ethylene degradation.

In Fig. 2, the temperature profiles for the three highest flow rates investigated are shown. At 90 Nl/h, the maximum temperature was 1000°C, while at 72 Nl/h it was 50°C lower. Nevertheless, in the upstream radiation shield the highest temperature was observed in the case of the lower flow rate, because of both the higher retro-diffusional effects and the lower extent of cooling of the solid.

Higher flow rates lead to higher temperatures and ethane conversions, because the system becomes more adiabatic, as already shown in a previous investigation (28). In the energy balance, indeed, the heat generation term is bound to the total flow rate and the amount of ethane converted, while the heat dissipation term depends only on the geometry of the system and on the maximum temperature. Around 1000°C, radiation becomes the major dissipation route, and this feature leads also to a self-adjusting maximum temperature. With this in mind, it seems better to correlate the observed variation of conversion and selectivities with the temperature profile established in the reactor, rather than with the change in contact time. Actually, the singular increase of reactant conversion with decreasing contact time appears very reasonable, taking into account the contemporary temperature increase.

On the other hand, the selectivity to ethylene weakly decreases with increasing space velocity, mainly due to the appearance of other hydrocarbons, produced by C_2H_4 degradation favoured at higher temperature.

Similar results were also reported on Pt-based foam monoliths (5), where the increase of ethane overall conversion and ethylene yield with increasing feed gas rate was shown for contact times between 20 and 100 ms · cm^3/Ncm^3. Such results were discussed by means of a completely heterogeneous reaction mechanism; the authors argued that "the conversion increases at high flow rates because short contact times favour partial oxidation products." More specifically, they explained that "At long contact times, the reactants remain on the catalyst surface long enough to produce complete combustion products, CO_2 and H_2O. This quickly consumes all of the O_2 so oxidative dehydrogenation is greatly reduced; thus some C_2H_6 remains unreacted" (5). However, the authors reported that the exit temperature increases with the flow rate from 750 to 900°C, thus supporting our assumption that reactor temperature plays the major role in determining conversion and selectivites, as revealed by the measurements of axial temperature profile established in the monolith (Fig. 2).

C_2H_6/O_2 Ratio

The C_2H_6/O_2 ratio plays a significant role in determining the reactor temperature and affecting the selectivity. Figure 3 reports the behaviour of reactant conversion and product selectivity as functions of C_2H_6/O_2 ratios and constant feed flow rate. The experiments were carried out at constant ethane concentration (24%), enriching air with oxygen at lower ratios and with nitrogen at higher ones. The nominal contact time of the runs was 96 ms · cm^3/Ncm^3, which under real operating conditions corresponds to about

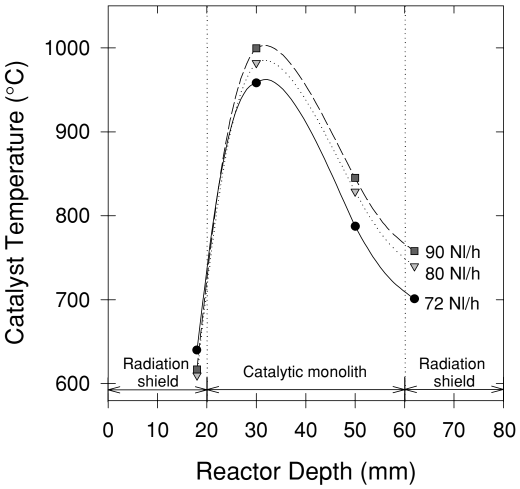

FIG. 2. Temperature profiles in the reactor at varying total inlet flow rate as a function of reactor depth. Catalytic monolith is placed between 20 and 60 mm. Radiation shield monoliths are placed upstream and downstream. Operating conditions: $C_2H_6/O_2/N_2 = 24/16/60$; $T_{\text{preheat}} = 400°C$.

24 ms (by assuming a uniform gas temperature of 900°C; see Fig. 2).

Ethane conversion was observed to decrease with increasing C_2H_6/O_2 ratio, while the selectivity to ethylene was significantly enhanced by the defective oxygen, growing from 50% at the lower ratio investigated up to 70% at the higher one (Fig. 3b). Nevertheless, ethylene yield exhibited a maximum (Fig. 3a), since conversion decreased in the same conditions from 93 to 58%.

Oxygen conversion was always complete, but product distribution markedly changed. At $C_2H_6/O_2 = 1.3$, larger amounts of CO_2, CH_4, C_2H_2, and H_2 were measured than at higher ratios, while an increase of C_2H_4, CO, and H_2O was observed on increasing the C_2H_6/O_2 ratio to 2.

We reckon that the defective oxygen content plays an important role in changing ethane conversion and ethylene selectivity. Nevertheless, the formation of CO, CH_4, C_2H_2, and H_2 is more reliably bound to the reactor temperature, which is higher at lower C_2H_6/O_2 ratios due to the higher exothermicity of the mixture.

Flick and Huff (27) pointed out that since the adiabatic temperature is higher at lower C_2H_6/O_2 ratios, this has a strong influence on product distribution and above all on products formed in the gas phase, for instance acetylene, but also CH_4, CO, and H_2, which are enhanced by high temperature. Such findings are confirmed by the results reported over different active phases, such as Pt (5), Pt–Sn and Pt–Cu (8), Pt–Cr_2O_3 (21), and $BaMnAl_{11}O_{19}$ (22), and also by a detailed computational study (20). Accordingly to our results, over these catalysts it was reported that, at increasing C_2H_6/O_2 ratio, ethane conversion decreases while ethylene selectivity increases, corresponding to a decrease in reactor temperature. This gives rise to a maximum yield around $C_2H_6/O_2 = 1.6$–1.7, which in our experiments is shifted towards a slightly lower value (the optimal ratio C_2H_6/O_2 was equal to 1.5), probably due to the higher amount of CO_2 generally found among reaction products in our tests and consequent higher O_2 demand.

Preheating Temperature and Transient Behaviour

The best performances in terms of ethylene yield have been reached at a C_2H_6/O_2 ratio of 1.5 and a flow rate of 72 Nl/h. Under these conditions, we investigated the effect of the preheat temperature. The experiments have been carried out by repeatedly increasing the temperature of the system by 20°C and waiting for the establishment of steady-state conditions.

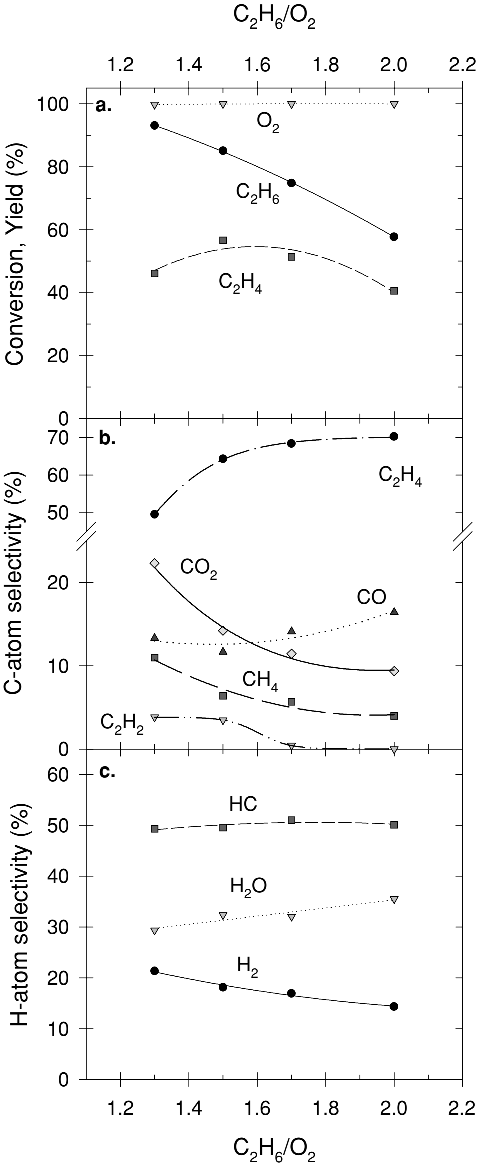

FIG. 3. O_2 and C_2H_6 conversion and C_2H_4 yield (a), C-atom selectivity (b), and H-atom selectivity (c) at varying C_2H_6/O_2 ratio. Operating conditions: C_2H_6 : 24%; total flow rate: 72 Nl/h; $T_{\text{preheat}} = 400°C$.

At lower temperature (200–360°C), the system reaches the stationary condition at very low conversion of ethane (lower than 1%) and oxygen (lower than 4%) and solid temperatures slightly higher than the preheating one (within 5°C). Under those conditions, CO_2 was the only product of ethane oxidation. In the range of preheat temperature around 380–400°C, the ignition of the monolith, characterised by large conversions and temperatures raises, was observed.

Figure 4 presents the behaviour of reactor temperature profile and outlet gas composition during the ignition transient period, as functions of time after a step change of ethane concentration in the feed. The behaviour of the four temperatures measured in the different axial positions shows that light off occurred in the exit sections of the catalyst; subsequently, the reaction front moved towards the inlet. The downstream monolith was heated by the catalyst exit section and its temperature (T_4) was always 100°C lower than catalyst T_3 temperature. Stationary conditions were reached in about 2 h. A similar behaviour was observed on the same catalytic system during the transient of CH_4 combustion under lean conditions (26). The time needed to stabilize temperatures and consequently stabilize conversion and product distribution is probably determined by the large thermal capacity of the solid, as recently described and evaluated (28). The maximum temperature reached in the inlet sections of the catalytic monolith was 960°C; this sharply decreased to 800°C in the exit sections within 2 cm distance, due to either the occurrence of endothermic dehydrogenation reactions of ethane (20) or to the defective insulation of the system (28). Indeed, these values are significantly lower than T_{adiab} reported in Fig. 4a, which is the value expected after an adiabatic temperature rise (1250°C at steady state). A rough estimate of the adiabaticity degree under the experimental conditions of Fig. 4 is 65%, i.e., not very different from the value of 75% reported by Huff *et al.* for foam monoliths (18).

The concurrent behaviour of the gas-phase composition is also shown in Fig. 4: in the first minutes of the run, O_2 very quickly reached 100% conversion, while ethane was mostly converted to CO_2 and water. When the solid temperature profile assumed values comparable to those reached in the stationary regime, the distribution of products slowly changed, with the selectivities of CO_2 and H_2O decreasing and those of CH_4, H_2, and CO increasing in time. Moreover, also ethane conversion and, consequently, the yield to ethylene significantly increased in the transient period before steady state.

In the ignited state, O_2 was completely consumed while ethane conversion reached about 84%. The main C-containing product was C_2H_4 with a selectivity of about 65% (the overall yield was 55%); also CO_2, CO, and in lower extent CH_4 and C_2H_2 were produced. Moreover, H_2O and H_2 were also formed, with the former exhibiting a concentration about double with respect to the latter in the steady state.

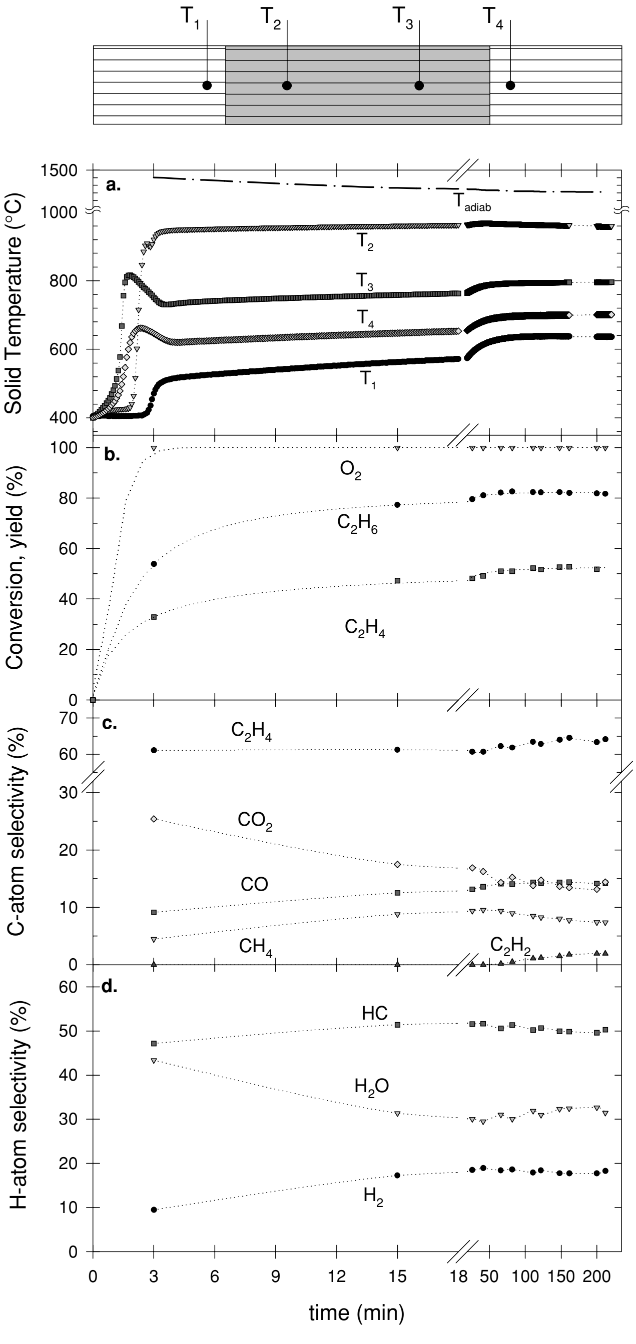

FIG. 4. Thermal profiles at the light off (a). T_1 and T_4 are placed in the upstream and downstream shield monolith, respectively (at 0.5 cm from the catalyst); T_2 and T_3 are placed in the catalyst monolith at 1 cm from the inlet and 1 cm from the outlet, respectively; T_{adiab} is the expected value of temperature for the outlet gas under adiabatic conditions. O_2 and C_2H_6 conversion and C_2H_4 yield (b), C-atom selectivity (c), and H-atom selectivity (d). Operating conditions: $C_2H_6/O_2/N_2 = 24/16/60$; flow rate: 72 Nl/h; $T_{preheat} = 400$°C.

Once the reactor was ignited, the preheat could be lowered to 240°C before extinction occurred. Figure 5 shows

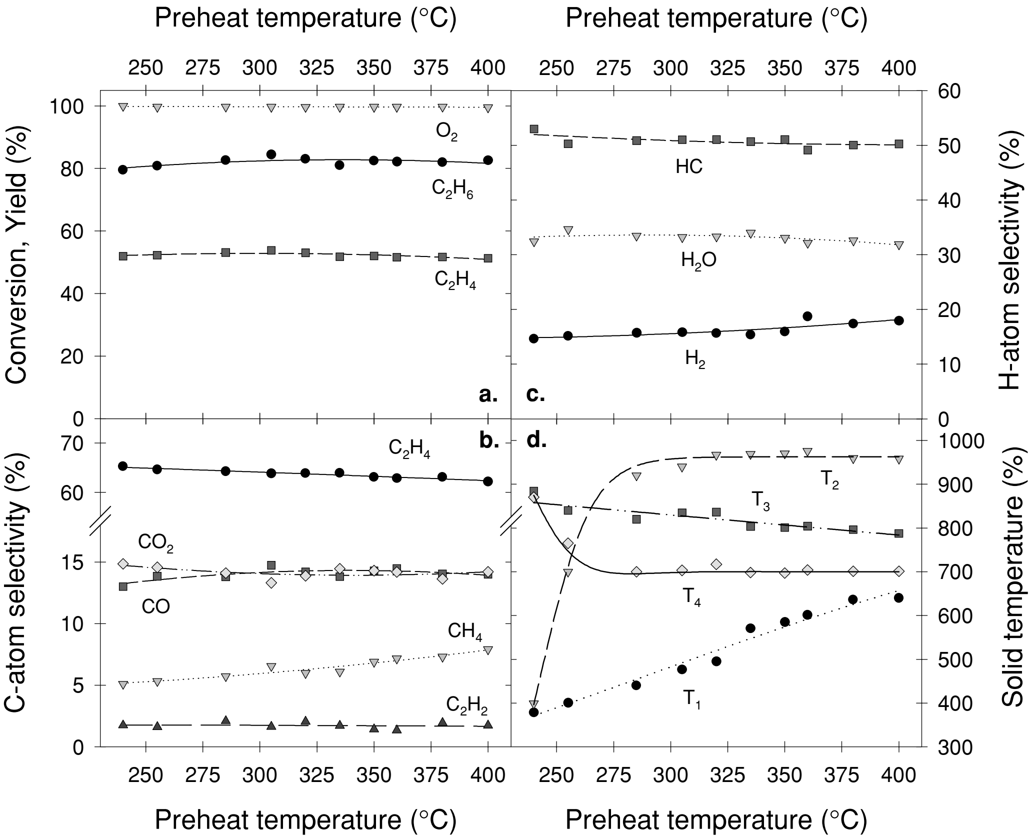

FIG. 5. O_2 and C_2H_6 conversion and C_2H_4 yield (a), C-atom selectivity (b), H-atom selectivity (c), and solid temperature profiles (d) at varying preheat temperature. T_1, T_2, T_3, and T_4 as in Fig. 4. Operating conditions: $C_2H_6/O_2/N_2 = 24/16/60$; flow rate: 72 Nl/h.

that conversions and product distribution were not severely affected by a 150°C decrease in preheat temperature. Indeed, there is no clear evidence that preheat affected the maximum temperature of the system. It can be supposed that the maximum temperature was self-adjusted to about 1000°C, because at this temperature heat dispersion becomes much more efficient due to radiation. Temperature T_1 in the radiation shield, instead, diminished uniformly with decreasing preheat temperature.

When the preheat was reduced, a longer distance of the reactor worked as a gas preheater, until the threshold temperature of the exothermic reactions was reached. Extinction occurred when the exothermic reactions took place over a distance that was too short in the catalytic monolith, since the entrance sections were too cold and heat production was no longer able to balance heat losses.

On reducing preheat, ethane conversion weakly decreased from 83 to 80%, while selectivity to ethylene slightly increased. This is possibly due to a positive effect of temperature on ethylene selectivity, even if different factors can influence it. As preheat temperature is varied, indeed, not only do maximum temperature and temperature profile change but also contact and residence time and ethane conversion.

Even though reactor extinction occurred for a preheat below 240°C, Fig. 6 shows that already from $T_{\text{preheat}} = 255°C$ the reaction front moved towards the exit of the reactor. Moreover, notice in Fig. 6 that the temperature T_1, which is the most affected by the decrease in preheat

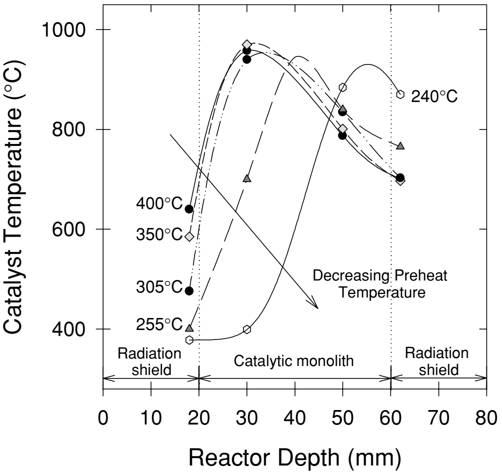

FIG. 6. Temperature profiles in the reactor at varying preheat temperature. Operating conditions as in Fig. 5.

temperature, is reduced to about 400°C, i.e., very close to the light-off temperature. So, feeding the C_2H_6/O_2 mixture at temperatures lower than this value made the system unable to self-sustain the ignited state, as already observed during the heating cycle.

In contrast, Yokoyama *et al.* (8) found a strong dependence of conversion and selectivities on preheat temperature. Ethane conversion and C_2H_4 selectivity were enhanced by preheated feed mixture, since preheat raises the autothermal reaction temperature and provides heat for thermal dehydrogenation reactions. Results not comparable with ours were reported in the study of ethane ODH in an autothermal conventional fixed-bed reactor (16). It was found that reactor temperature increased from 850 to 950°C as oven temperature was increased from 300 to 500°C. This leads to increased ethane conversion, from 62 to 79%, but not ethylene selectivity, which did not change significantly. However, operating a packed-bed reactor can be difficulty under autothermal conditions, since the high reactant flow rates needed to achieve quasi-adiabatic conditions lead to unsustainable pressure losses and, consequently, the lower adiabaticity must be compensated by a larger preheat.

Experimental data (5) reported for an ethane/oxygen mixture in Pt-based foam monoliths were similar to our results, with conversion and selectivities that did not change markedly by lowering the preheat. This can be attributed to the maximum temperature, which, when around 1000°C, is not affected by further preheat, due to the very effective radiative heat transfer mechanisms. Nevertheless, the whole reactor is slightly hotter and this influences the thermodynamically favoured products, such as CO, CH_4, and H_2.

In conclusion, a general statement on the effect of preheat temperature cannot be expressed. The influence of this parameter seems to be strongly connected to the degree of adiabaticity of the laboratory-scale reactor.

With an ethane/air mixture, perovskite-based catalysts seem to perform much better than Pt-based foams, with the same preheat temperature. Under similar conditions Huff and Schmidt (5) reported less than 55% selectivity to ethylene and an ethane conversion slightly higher than 80%. Only by reducing N_2 dilution to 20% and consequently raising ethane concentration from 25 to 50%, probably due to a strong temperature increase, could conversion and selectivity be significantly increased to values close to ours.

Perovskites also seem to exhibit better performance in comparison to active phases other than Pt. In experiments performed over $BaMnAl_{11}O_{19}$ catalyst Beretta and Forzatti (22) always obtained ethylene selectivity and ethane conversion lower than ours, with a preheat temperature of 500°C. In a rare earth oxide packed bed Mulla *et al.* (16) were able to reach an ethylene yield higher than 50% ($S_{C_2H_4} = 66\%$) for a C_2H_6/O_2 ratio of 2, but had to compensate for the lower exothermicity of their fuel-rich mixture with very low N_2 dilution (25% vol) and high preheat (500°C). At the same feed ratio, even though at lower conversion, due to lower preheat (400°C) and high dilution ($N_2 = 60\%$), we obtained 70% ethylene selectivity. Chromium-based monoliths, although tested under different conditions (21), showed performances worse than ours in terms of yield and selectivity, with scarce stability under reaction.

ISOTHERMAL MEASUREMENTS

Preliminary blank tests in a 7-cm-long cordierite monolith, carried out under experimental conditions identical to those investigated in the presence of the perovskite monoliths, allow us to exclude any reaction from proceeding up to 600°C, either in steel tubes or in cordierite shields. Similar tests were performed by Beretta *et al.* (15) on uncoated mullite tubes and confirmed a range of temperatures for the occurrence of gas-phase reactions very close to what we found. Products of ethane homogeneous oxidation were mainly ethylene and carbon monoxide, as already put into evidence (15, 17).

In order to characterise the properties of perovskite catalysts in the absence of any other chemicophysical effect or homogeneous reaction, a smaller monolith was tested under almost isothermal conditions. For this purpose, a 0.5% ethane mixture, with $C_2H_6/O_2 = 1.7$, was fed into the reactor. As shown in Fig. 7, the solid temperature was kept below 600°C in all runs, and traces of H_2,which indicate a homogeneous phase chemistry, were never detected.

It is worth noting that C_2H_4 is also produced at low temperature, when O_2 is not yet completely consumed and under conditions that allow homogeneous reactions to be excluded. The amount of C_2H_4 produced is very low, because both inlet concentration of ethane and conversion and selectivity are low. The sensitivity of the GC apparatus used for the analysis of gas-phase composition is high enough to detect parts per million of ethylene with good confidence.

The comparison with experimental data reported by Beretta (15, 19) over a Pt catalyst under similar controlled conditions shows that the properties of our catalyst are significantly different, since it results intrinsically active in ethane ODH, even if ethylene selectivity is low in this range of temperature. Actually, perovskites are known to be potential catalysts for the oxidative dehydrogenation of light alkanes, due to the capability to promote the formation of alkyl radicals on their surface, rich in structural oxygen defects (29). Over Pt, indeed, only CO_2 at low temperature and CO at higher temperature are produced, while ethylene is formed above 650°C, at the onset of homogeneous reactions.

This allows us to draw the conclusion that also under autothermal conditions, characterised by high reactant concentrations, good insulation, and consequently high temperatures, the catalyst should contribute to the formation

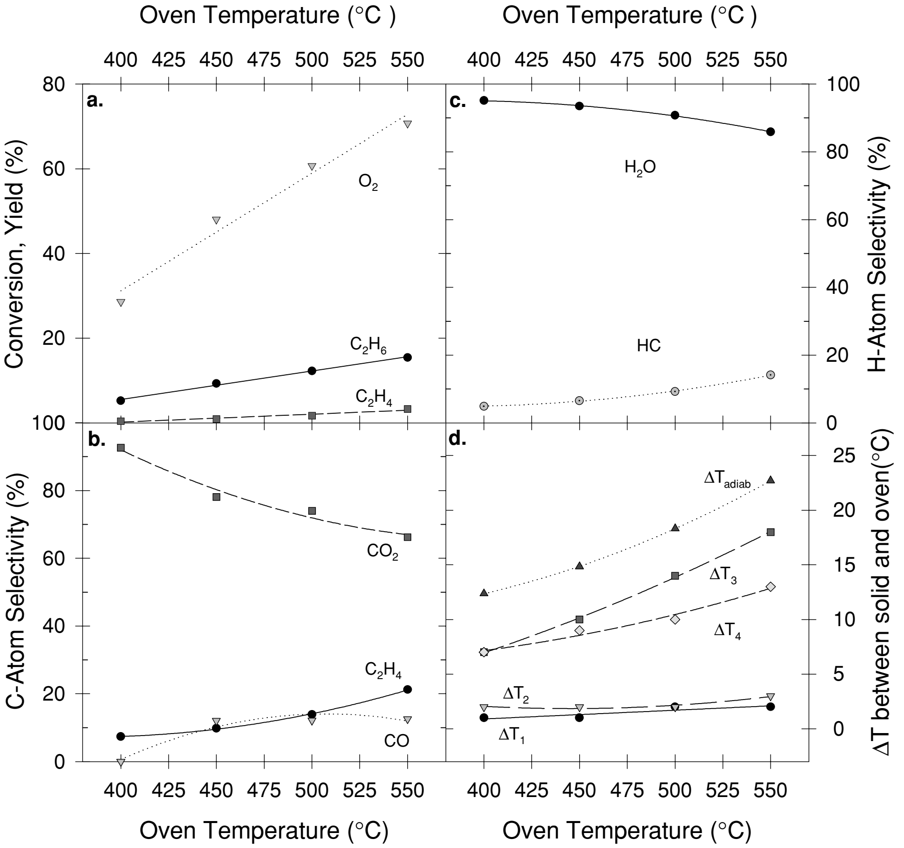

FIG. 7. O_2 and C_2H_6 conversion and C_2H_4 yield (a), C-atom selectivity (b), H-atom selectivity (c), and difference between solid and oven temperatures (d) at varying preheat temperature. T_1, T_2, T_3, and T_4 as in Fig. 4. Operating conditions: $C_2H_6: 0.5\%$ vol; total flow rate: 86 Nl/h; $C_2H_6/O2: 1.7$.

of ethylene, even if it seems clear that a large fraction of it is produced via gas-phase reaction paths. Hence the weak activity of perovskites could be beneficial to ethylene formation by a mechanism that can be purely heterogeneous or hetero-homogeneous, through ethylene formation in the gas phase, following ethyl radical desorption from the catalytic surface.

DISCUSSION

The behaviour of short-contact-time reactors for the oxidative dehydrogenation of ethane has been discussed in both experimental (5, 8–16, 21, 22) and theoretical (18–20, 23) works. Most recent investigations reveal that homogeneous reaction paths cannot be neglected (18–20), even at very short reaction times. Ethylene production in Pt-based foam monoliths seems to occur via a hetero-homogeneous reaction mechanism, in which the catalyst should act as an igniting agent, active for total oxidation reactions, while ethylene-forming reactions mainly occur in the gas phase (9, 15, 18, 19).

On the other hand, Beretta *et al.* (15) showed that appropriate preheating of the C_2H_6/O_2 mixture in the absence of the catalyst led to even higher C_2H_4 yield than in the presence of Pt. These results were also supported by the kinetic modelling of gas-phase reactions, which demonstrated that in a purely homogeneous reactor the selectivity to ethylene is even higher than in the catalytic tests at the same level of ethane conversion (19).

As reported in a recent paper (30), we have already experienced homogeneously controlled reaction systems. The investigation of ethane ODH in a packed-bed reactor filled with different basic oxide catalysts (promoted and unpromoted MgO, Sm_2O_3, and La_2O_3) showed that ethylene selectivity was largely independent of the catalyst composition and mainly determined by gas-phase reactions, even at a temperature as low as 700°C. In a very recent work, Mulla *et al.* (17) clearly confirmed that a high ethylene yield is obtainable both in the presence and in the absence of a packed bed of $Sr_{1.0}La_{1.0}Nd_{1.0}O_x$ particles. Nevertheless, the development of a completely homogeneous process is inhibited by the formation of coke in the temperature range of interest, notwithstanding the mild oxidising conditions adopted. As a consequence, it may be argued that the presence of any catalyst could be useful in driving an autothermal process but that it reduces the maximum yield attainable through heating a C_2H_6/O_2 mixture in the absence of the catalyst.

If all this is true, use of very expensive noble-metal-based catalyst should not be necessary. Nevertheless, previous studies carried out on materials other than noble metals (16, 21, 22, 29) did not produce any relevant results since the significant limitations encountered, such as the very poor stability of Cr_2O_3-based foam monoliths (21) or low activity of $BaMnAl_{11}O_{19}$ hexa-aluminates (22), prevented any future application. Instead, the use of honeycomb-type $LaMnO_3$-based catalyst allowed us to obtain stable and even higher ethylene yield than those reported on Pt-containing foams under the same experimental conditions (5, 22). This led to two main consequences.

First, testing a reacting system, with a behaviour comparable to that of Pt in terms of performance, but where the most significant parameters, such as the active phase and the reactor morphology, have been changed, confirms that in short-contact-time reactors for ethylene production the role of the catalyst is not in catalysing the ethylene formation, but rather in thermally igniting the hydrocarbon/oxygen mixture, via the combustion of a fraction of ethane to CO_x and water (13, 15, 16). In this way, the system can autothermally reach the range of temperatures in which gas-phase reactions favourably occur to transform ethane into ethylene without coke formation, probably due to a positive effect of the presence of catalyst and/or the very low residence time of hydrocarbons in the high-temperature zone.

Second, it can be argued that the main reason why noble metals, and in particular platinum, have been thoroughly investigated is likely that they are very active catalysts in the total oxidation of hydrocarbons. Combustion catalysts other than noble metals, such as the significantly cheaper transition metal oxides, suffer poor thermal resistance above about 800°C (21) but are conceptually as able as Pt. As previously demonstrated (25, 26, 28), perovskite-based catalysts show, together with a good oxidation activity, an excellent thermal stability and are competitive with more expensive noble-metal-based catalysts.

Moreover, in comparison with most of the results reported on Pt-based catalysts (5, 9–12), we found in our experiments not only a higher ethylene yield (comparing the results obtained under the same experimental conditions) but also a larger CO_2 selectivity (always above 10%). This difference appears relevant, as at the reactor temperature (between 800 and 1000°C) the formation of CO as a product of ethylene oxidation is largely favoured amongst CO_x by homogeneous kinetics (18–20). Following the concepts proposed by Bodke *et al.* (9), Zerkle *et al.* (20), and Huff *et al.* (18) of a two-zone reactor and "sacrificial ethane," it now seems that our catalyst plays the same role of platinum but with higher efficiency, since it sacrifices less ethane than over Pt-based and hexa-aluminate catalysts (9, 21, 22), provided that its catalytic oxidation mainly proceeds to CO_2, with the consequent maximum production of heat and lower reactant consumption. Moreover, in contrast to what was shown by Beretta *et al.* (15, 19) for Pt over perovskite-based waschcoated monoliths, it is also possible to hypothesise that a nonselective ethylene formation is catalysed (about 25% selectivity measured at 550°C, Fig. 7). Both reactions of ethane catalytic oxidation (leading to CO_2 and ethylene as products) contribute to sustain reactor temperature levels. Nevertheless, the perovskite-based catalyst exhibits a quite negligible activity towards the weakly exothermic partial oxidation of ethane to CO and H_2, in contrast to what is observed over Pt catalysts (9, 21, 22).

We believe gas-phase reactions play the main role in the production of ethylene. At this stage, determining the proportion between homogeneous and heterogeneous contributions to the formation of C_2H_4 is difficult, but we are convinced that the yields attained in the presence of any catalyst are of the same order of magnitude as those expected in a pure homogeneous phase, as proposed or shown by others (15, 17, 19). However, in contrast with the assumptions of Bodke *et al.* (9), we think that the main pattern of ethylene formation in the gas phase is the oxidative pyrolysis of ethane, as it is known to proceed with a higher rate than the dehydrogenation into ethylene and hydrogen. More specifically, it seems certain that the ultimate step in ethylene formation in the gas phase is the decomposition of the ethyl radical:

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot. \qquad [1]$$

Under the presence of oxygen, ethyl radicals are more quickly formed via an oxidative pyrolysis step,

$$C_2H_6 + OH\cdot \rightarrow C_2H_5\cdot + H_2O, \qquad [2]$$

than via thermal dehydrogenation,

$$C_2H_6 \rightarrow C_2H_5\cdot + H\cdot. \qquad [3]$$

In the stationary regime the ethane/oxygen mixture enters the reactor relatively cold but, as evaluated by Zerkle *et al.* (20), very quickly reaches the high solid temperature, at which reaction [2] is much faster than reaction [3].

As a consequence, under the examined reaction conditions, we think that sketching the reactor as consisting of two consecutive zones, characterised by the presence or absence of O_2, as proposed by Bodke *et al.* (9), and accepted with minor modifications by Zerkle *et al.* (20), is not a thorough description of the system. Rather than a scheme of in-series reactions, we think that a mechanism of parallel steps of catalytic and homogeneous oxidation of ethane is more reliable, where the role of the catalyst, in the case of perovskite oxides, could be significant not only in igniting gas-phase reactions but also in forming a fraction of ethylene.

CONCLUSIONS

The oxidative dehydrogenation of ethane to ethylene in a short-contact-time reactor can be successfully carried out over catalysts other than Pt or Pt–Sn. Use of much cheaper honeycomb-type cordierite monoliths consisting of a $LaMnO_3$ active phase supported onto a La-stabilised γ-Al_2O_3 washcoat allowed us to obtain even higher ethylene yield than those reported under the same experimental conditions over noble-metal-based foams.

These results can be explained in terms of the role of the catalyst, which is mainly to thermally ignite the hydrocarbon/oxygen mixture, via the combustion of a fraction of ethane to CO_2 and H_2O. In addition, we also showed that the perovskite-based catalysts we have proposed, in addition to their good oxidation activity and excellent thermal stability, are also intrinsically active in the ethane ODH.

Under the examined reaction conditions, the formation of ethylene can be considered to occur through two different parallel mechanisms, one catalysed by monolith surfaces and the other proceeding through gas-phase radical reactions.

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