

High-Temperature and Short-Contact-Time Oxidative Dehydrogenation of Ethane in the Presence of Pt/Al₂O₃ and BaMnAl₁₁O₁₉ Catalysts

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The oxidative dehydrogenation of ethane over a Pt/ γ -Al₂O₃ catalyst in adiabatic conditions (that is at $T = 800$ – 1000°C and few milliseconds contact time) resulted in the production of ethylene with 50% yield. In order to better elucidate the single roles that gas-phase reactions and heterogeneous phase reactions might play in the high-temperature activation of ethane, a detailed experimental and theoretical investigation was addressed. The results suggested that the performance of the adiabatic reactor relied on a cooperation between catalytic reactions (responsible for deep and partial oxidation of ethane to CO_x, H₂O, and H₂) and homogeneous reactions (responsible for the formation of olefins). In autothermal conditions, thus, the main function of the Pt-catalyst appeared to be that of accelerating ignition of the radical process, through the initial combustion of ethane which can occur at temperatures as low as 200°C . It was demonstrated that the same function can be equally well accomplished by a Pt-free oxidation catalyst like the BaMnAl₁₁O₁₉ which is active in the deep oxidation of ethane. Even in the presence of the hexa-aluminate material, which has no activity in the selective oxidation of ethane to ethylene, yields to ethylene higher than 50% were observed in the autothermal reactor by preheating the ethane/air feed stream at a proper temperature. © 2001

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Key Words: ethane ODH; high temperature and short contact time; Pt/ γ -Al₂O₃ catalyst; BaMnAl₁₁O₁₉ catalyst; homogeneous vs heterogeneous reactions.

INTRODUCTION

High-temperature and short-contact-time oxidative dehydrogenation (ODH) of light alkanes has been proposed as an efficient route for the selective production of short-chain olefins under autothermal conditions (1). Schmidt and coworkers have first shown that total yields to olefins as high as 40% could be obtained via selective oxidation of C₂–C₆ paraffins by running the reaction at few milliseconds contact times over Pt-coated foam monoliths; the reactor operated adiabatically at temperatures of 800 – 1100°C , depending on feed composition (2–5).

The bulk of data reported in the literature on high-temperature ODH of light paraffins show that, among the series of (C_n + $\frac{1}{2}$ O₂) reactions, the oxidative dehydrogenation of ethane is the most selective process and, as a

consequence, the one that might offer a potential for the industrial application. While the published results are stimulating the discussion on the feasibility of novel processes for olefin productions (6, 7), a debate is still open on the roles that homogeneous and heterogeneous reactions have in the short-contact-time catalytic processes.

A few catalysts have been proposed so far for the high-temperature and short-contact-time ODH of ethane and different interpretations on the mechanism of formation of ethylene were given.

Schmidt and coworkers studied several noble-metal-coated ceramic foam monoliths, including bimetallic catalysts (8, 9). Up to 65% ethylene selectivity at 70% ethane conversion and practically complete O₂ conversion were observed over a Pt-coated α -Al₂O₃ foam monolith (2). These results were confirmed also by Flick and Huff (10). In spite of the extremely high reaction temperatures, a heterogeneous reaction mechanism was proposed to explain the formation of olefins on the Pt-surface; the mechanism is based on β -hydrogen or β -alkyl elimination from adsorbed alkyl species (5, 10, 11). Only in the case of higher alkanes, a nonnegligible contribution of homogeneous steam-cracking reactions was supposed (5, 12).

Flick and Huff (13) have recently proposed Cr-containing catalysts for the high-temperature and short-contact-time selective oxidation of ethane to ethylene; they found that a 10% Cr₂O₃–ZrO₂ catalyst outperformed the Pt/Al₂O₃ systems. Also in this case a heterogeneous nature of ethylene formation was assumed and the observed high reactivity of the Cr-containing catalysts was associated to a peculiar dehydrogenation activity of the Cr-oxide.

Bodke *et al.* (14) have recently shown that the selective conversion of ethane to ethylene at high temperature and short contact time can be greatly promoted by adding H₂ to the ethane/oxygen feed stream in the presence of a Pt–Sn catalyst. Ethylene could be produced at 90–95% selectivity with over 60% ethane conversion. Apparently, the whole process was split in two stages: the exothermic oxidation of H₂ and the endothermic dehydrogenation of ethane. The bimetallic catalyst selectively oxidized hydrogen, while presumably homogeneous reactions were responsible for the dehydrogenation of ethane to ethylene.



Pt-Rh gauzes have been applied by Goetsch and Schmidt (15) and by Holmen and coworkers (16, 17) to the selective oxidation of alkanes to olefins. They showed that large amounts of ethylene and ethylene/propylene mixtures could be produced from ethane/air and propane/air feeds, respectively, in the presence of one single gauze at contact times in the order of microseconds. However, Holmen and coworkers (16, 17) proposed that the production of olefins occurred mainly in the gas-phase, since even higher olefin yields could be obtained in the empty reactor when an external heat source was applied; it was also proposed that the main role of the gauze was primarily represented by the rapid ignition of the homogeneous process through initial oxidation reactions.

Recently, theoretical approaches have also been developed to investigate the contributions of homogeneous and heterogeneous reactions in the short contact time partial oxidation of ethane. These are based on the combination of detailed kinetic schemes for the gas-phase and the solid phase, respectively. Huff *et al.* (18) concluded that the role of the catalyst was to initiate by heat release the gas-phase process, while Zerkle *et al.* (19) proposed that catalytic oxidation reactions drove both homogeneous and heterogeneous cracking of ethane to ethylene.

The authors have previously tested a Pt/ γ -Al₂O₃ catalyst in the oxidative dehydrogenation of propane and ethane in adiabatic conditions. At few milliseconds contact time and temperatures of 800–1000°C, the partial oxidation of propane produced 60% total selectivity to olefins (propylene and ethylene) with alkane conversion higher than 50% (20). The oxidative dehydrogenation of ethane resulted in the selective production of ethylene with yields as high as 50% (21). The results of the adiabatic tests were compared with theoretical evaluations on the expected role of gas-phase oxidative pyrolysis of the hydrocarbon; in the cases of both ethane and propane ODH, the measured product distributions were found very close to those characteristic of a purely homogeneous process. This suggested that in the adiabatic reactor gas-phase reactions might control the conversion of ethane and propane.

In order to better clarify the single roles of homogeneous and heterogeneous reactions, the oxidative dehydrogenation of propane was studied by means of an annular reactor wherein very small amounts of catalyst were loaded and tested at high flow rates; temperature was externally controlled and varied from low to high values (22). Experiments with increasing amounts of the Pt/ γ -Al₂O₃ catalyst proved that the catalyst was uniquely active in the production of CO_x, H₂O, and H₂. Conversely, by testing the reactivity of the propane/air mixture in the empty reactor, it was shown that homogeneous oxidative pyrolysis occurred above 600°C and resulted in the selective production of propylene and ethylene. The overall performance of the adiabatic reactor for propane ODH could be thus explained as a combination of heterogeneous reactions (responsible

for rapid ignition) and homogeneous reactions (responsible for the partial oxidation of propane to propylene and cracking to ethylene and methane).

In this work, the same approach was extended to the study of the single roles of homogeneous and heterogeneous reactions in the activation of ethane/air mixtures. The nonadiabatic annular reactor was used to isolate catalytic reactions and homogeneous reactions in the presence of a Pt/ γ -Al₂O₃ catalyst. New pieces of evidence were searched for supporting the correct interpretation of the performance of a short contact time adiabatic reactor, wherein both presumably occur. Also, in order to verify the effective role of Pt as active component, a Pt-free hexa-aluminate catalyst was herein studied for comparison.

EXPERIMENTAL

Catalysts. A commercial Pt/ γ -Al₂O₃ catalyst (Engelhard ESCAT 24) was studied in the present work. It consists of eggshell Pt-coated γ -Al₂O₃ particles with a BET surface area of nearly 95 m²/g and a pore volume of 84 mm³/g (estimated on the basis of Hg-intrusion porosimetry). The powders were ground and sieved with a 325 mesh sieve down to an average particle size of about 15 μ m. Previous studies suggest that the nature of support affects the performance of the Pt-catalyst; Flick and Huff (10) found that γ -Al₂O₃ pellets were less selective to ethylene than α -Al₂O₃ monoliths. In this work, the choice of Pt/ γ -Al₂O₃ catalyst depends on the continuity with previous work, as this is the same catalyst already studied by the authors in the oxidative dehydrogenation of propane.

In order to verify the possible application of a Pt-free oxidation catalyst to the ignition of homogeneous reactions, a Ba-MnAl₁₁O₁₉ catalyst was also tested. The hexa-aluminate catalyst has a proved activity for total oxidation of methane and bio-gas and is characterized by a good thermal stability; it was developed in our laboratory for application to gas turbine catalytic combustors. The preparation and characterization of the catalyst has been reported in detail elsewhere (23). The catalyst powders were ground and sieved with 325 mesh sieve.

Catalyst deposition. The catalyst fine particles were deposited via aqueous slurry onto mullite tubes, thus forming thin (about 50 μ m) and short (1–5 cm) catalyst layers in the central portion of the ceramic supports. Prior to deposition, the mullite tubes were treated in acid bath to increase the surface roughness and enhance the catalyst adhesion. Few milligrams of catalysts are deposited via slurry (10–100 mg) and this allows the realization of experiments at extremely high gas hourly space velocity. The same catalyst slurry was used to deposit the catalyst onto the FeCrAlloy tissue (20); the fibrous metallic support was previously calcined at 1000°C to promote the formation of a superficial layer of inert α -Al₂O₃.

Reactors. Two kinds of reactors were used to realize activity tests at short contact times (20–22): the annular reactor, which is a nonadiabatic reactor wherein heterogeneous and homogeneous reactions could be studied separately, and the adiabatic packed-bed reactor, which is an insulated reactor wherein homogeneous and heterogeneous phases are instead intimately interconnected.

The annular reactor consists of a quartz tube (ID = 0.7 or 0.9 cm), wherein the catalyst-coated mullite tube is inserted. The gas flows in between the tubes and contacts longitudinally the catalyst layer. This reactor configuration is especially suitable to study high-temperature and short-contact-time processes as extremely high space velocities ($>10^6$ L/h/kgcat) can be easily realized with no pressure drop. The catalyst temperature is well characterized, as it can be measured from inside the coated mullite tube by a sliding thermocouple. The reactor is heated by an external furnace; thus experiments can be run at any reaction temperature; the authors were especially interested in performing ethane ODH tests in the temperature range of 200–700°C (that is below the usual operating window of autothermal reactors) in order to isolate the contribution of the single heterogeneous phase. Still, given the high volume/surface ratio of this single-channel reactor, tests in the absence of catalyst were performed for investigating the role of homogeneous reactions.

Adiabatic high-temperature tests were instead performed in an insulated reactor, wherein catalyst-coated FeCrAlloy elements were packed in a quartz tube (0.7 cm i.d.) in between two guard beds of ceramic particles. The external furnace was used to preheat the feed stream and the inlet portion of the reactor. The outlet portion of the reactor, instead, was cooled by an external Cu coil for water circulation. The axial temperature profile was measured by a thin thermocouple sliding inside a $\frac{1}{16}$ " capillary located along the reactor axis.

Analysis of the product mixture was realized by combining the results of three separate gas-chromatographic measurements, obtained respectively from a Molecular Sieve column using He as carrier gas (separating O₂, N₂, CO and CH₄), a Popapak Q column (separating CO₂, H₂O, and hydrocarbons), and a Molecular Sieve column using Ar as carrier gas (for separation of H₂ and N₂). All the columns were connected to thermoconductivity detectors.

ROLE OF HOMOGENEOUS REACTIONS IN ETHANE ODH: TESTS IN THE ANNULAR REACTOR

The gas-phase oxidative dehydrogenation of ethane was studied in the annular reactor in the absence of any catalyst by varying reactor temperature, feed flow rate, and feed composition.

Effects of residence time and temperature. Figure 1 reports the results observed with an ethane/air mixture with

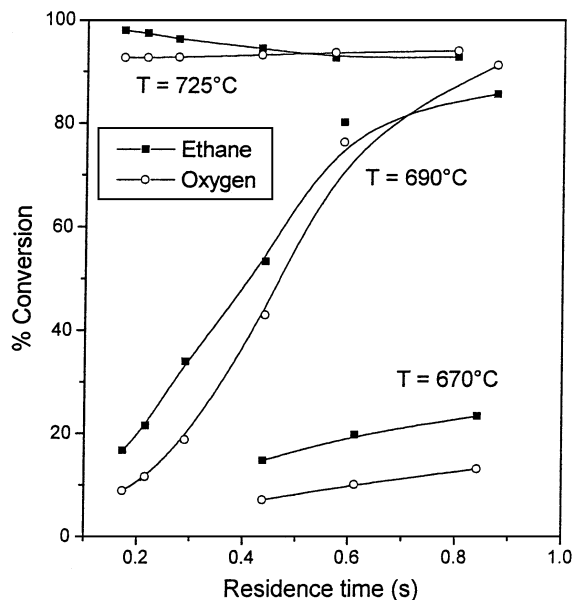


FIG. 1. Homogeneous oxidative dehydrogenation of ethane. Effect of residence time and reactor temperature on ethane and oxygen conversion. Feed composition, C₂H₆/O₂/N₂ = 11/1/4.

1/1 = ethane/oxygen ratio at varying flow rate and oven temperature. Data have been plotted as functions of the reactor residence time (the ratio between the empty reactor volume and the volumetric flow rate, evaluated at the reactor temperature). At the intermediate temperature of 690°C, appreciable conversions of reactants were observed at 0.18 s and they increased rapidly with increasing residence time. At slightly higher temperature (oven $T=725^{\circ}\text{C}$) reaction was so fast that conversion of ethane and oxygen kept over 90% over the whole range of residence times. At the reaction temperature of 670°C, instead, conversion of ethane and oxygen moderately increased with time and amounted to 22 and 11%, respectively, at the contact time of 0.85 s. In all the experiments ethylene was produced in large amounts. For instance, at the intermediate temperature of 690°C, the distribution of the C-containing products (as reported in Fig. 2a) was characterized by extremely high selectivity to ethylene; this decreased from 95% to nearly 60% at increasing contact time. The nonzero selectivity of ethylene at zero ethane conversion clearly shows that ethylene was a primary product of ethane decomposition. CO was produced in much smaller amount and its selectivity increased with increasing residence time in line with the behavior of a secondary product. Methane and CO₂ were also produced and were favored by contact time; they were only minor products as their selectivity maintained below 7 and 4%, respectively. Among the H-containing species (Fig. 2b), water was formed in large quantity while the selectivity of H₂ was below 10%. Concerning the effect of temperature, the process became increasingly selective towards ethylene with decreasing T ,

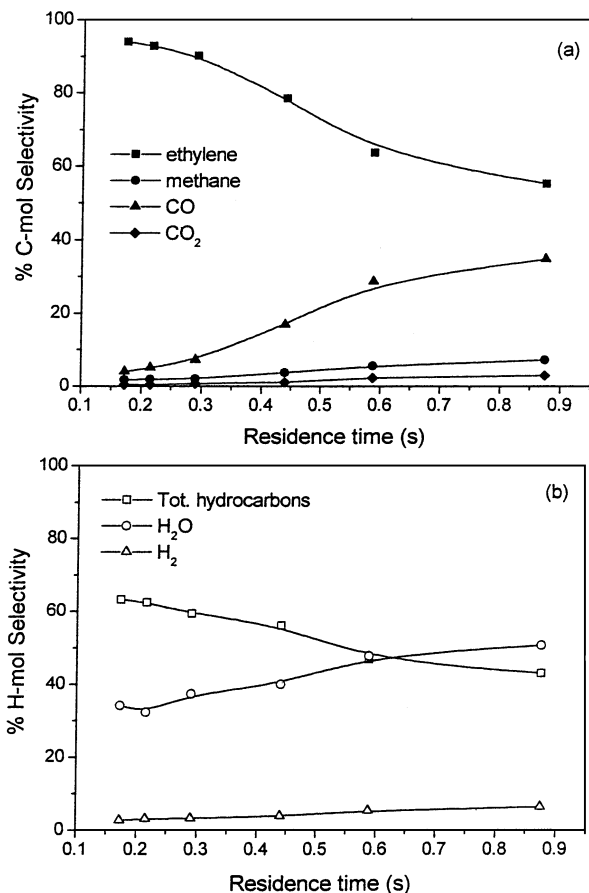


FIG. 2. Homogeneous oxidative dehydrogenation of ethane. Effect of residence time on product distribution at 690°C reactor temperature. Feed composition, $C_2H_6/O_2/N_2 = 1/1/4$.

while the selectivity of CO became larger and larger in the opposite direction. Figure 3 compares the C-selectivity of ethylene at three levels of temperature investigated; it was practically the only reaction product (with water) at 670°C, while its selectivity amounted to nearly 40% (an almost equal selectivity was observed for CO) at 725°C.

Effect of feed composition. At 725°C and 0.4 s contact time, the influence of feed composition was investigated by varying the ethane/oxygen ratio between 1 and 2.6. Figure 4a shows that ethane conversion decreased progressively at increasing feed ratio. However, the converted molar flow of ethane had a net increase. The process became progressively more selective toward the production of ethylene, since the olefin C-selectivity increased from 40 to 65% (Fig. 4b); conversely, CO selectivity was a decreasing function of the feed ratio and amounted to less than 20% at ethane/oxygen = 2.6. Methane selectivity was almost constant around 10%, while CO₂ was detected in small amount. With increasing ethane/oxygen feed ratio, and presumably with increasing ethylene concentration, C₂₊ species were increasingly formed; their contribution

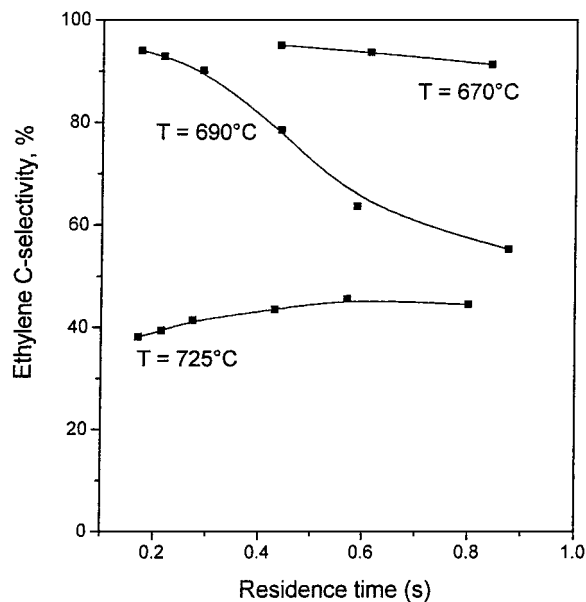


FIG. 3. Homogeneous oxidative dehydrogenation of ethane. Effect of residence time and temperature on ethylene selectivity. Feed composition, $C_2H_6/O_2/N_2 = 1/1/4$.

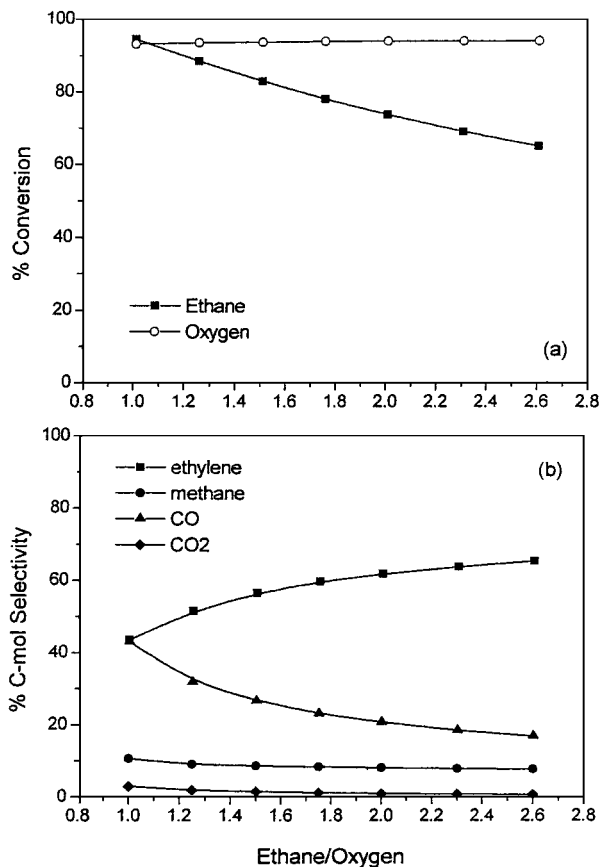


FIG. 4. Homogeneous oxidative dehydrogenation of ethane. Effect of ethane/oxygen feed ratio on ethane and oxygen conversion and on the distribution of C-containing products. Feed, ethane/air; $T = 725^\circ\text{C}$; residence time, 0.4 s.

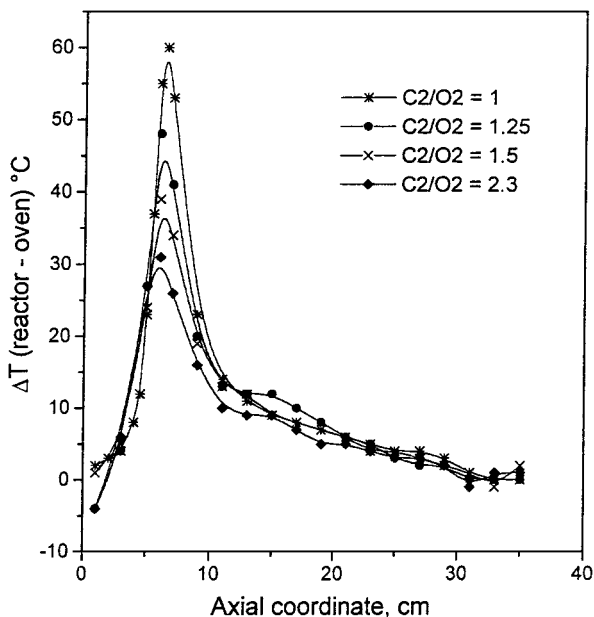


FIG. 5. Measured difference between reactor axial temperature profile and oven wall temperature profile at varying feed composition. Conditions as in Fig. 4.

has been summed up in Fig. 4b and included the production of propylene, propane, and butenes. With increasing ethane concentration in the feed stream, the reaction was less and less exothermic. Figure 5 plots for this set of experiments the measured difference between the reactor axial temperature profile and the oven wall temperature profile. At the entrance of the reactor a hot spot was measured wherein most of the reaction presumably occurred; the hot-spot temperature reduced with increasing ethane/oxygen ratio.

Theory of ethane oxidative pyrolysis. Elsewhere, the authors have simulated the expected behavior of a purely homogeneous plug flow reactor operating under the same conditions as those explored experimentally (21). Simulations were performed by means of a detailed kinetic scheme of homogeneous oxidative pyrolysis of hydrocarbons (24, 25). The data herein reported are fully in line with the theoretical predictions. Experiments and theory concur to evidence that for a given pressure and feed composition, the product distribution is practically a unique function of the degree of ethane conversion, and does not depend on the single values of temperature and contact time. In general, ethylene selectivity is a decreasing function of ethane conversion; for instance, at $C_2/O_2 = 1$, 95% selectivity is measured and calculated at ethane conversions below 10%, and selectivity decreases down to 60% at increasing conversion up to 80%. According to model predictions, such a trend is valid either at intermediate temperature (600°C) and contact times in the order of 0.5–1 s (the operating conditions for the experiments in the annular reactor), either at 1000°C at contact times in the order of 5–10 ms (the operat-

ing conditions of the short contact time adiabatic reactors). The gas-phase process is extremely selective toward the formation of ethylene since the olefin is the primary product of ethyl radical decomposition, while CO_x are terminal products of the radical process. For a given value of ethane conversion, ethylene selectivity is then a slightly increasing function of ethane/oxygen feed ratio (21).

ROLE OF THE $Pt/\gamma-Al_2O_3$ CATALYST: TESTS IN THE ANNULAR REACTOR

Once the important role of gas-phase reactions was verified, attention was then focused on the effective role of the heterogeneous reactions. These were studied through a perturbative analysis, wherein operating conditions were chosen in order to minimize the extent of gas-phase ethane decomposition (high flow rate and low reactant concentrations) and the effect of the addition of increasing amounts of catalysts on the product distribution was analyzed. Experiments were performed at varying ethane/oxygen feed ratio. The results reported in Fig. 6 were obtained in the annular reactor with a total feed stream of 1 L/min (evaluated under Normal conditions, $T = 273$ K and $P = 1$ atm) and molar feed composition ethane : oxygen : nitrogen was 2 : 2 : 96. Three cases were compared: (1) absence of catalyst on the mullite tube (that is the residual contribution of homogeneous reactions in the empty volume of the reactor, as a reference), (2) use of a mullite tube coated with a 1.5-cm-long catalyst layer (catalyst load ≈ 10 mg), (3) use of a mullite tube coated with a 5-cm-long catalyst layer (catalyst load ≈ 35 mg). In the absence of any catalyst, flow rate and feed composition were such that conversion of ethane and oxygen were appreciable over 650–700°C, only, but gas-phase reactions were very fast and conversion of ethane and O_2 amounted to 80 and 60%, respectively, at 770°C oven temperature. In the presence of the Pt/Al_2O_3 catalyst, reactants conversion started already at 250°C. Up to about 600°C oven temperature, reactants conversion did not increase significantly with temperature, but increased with increasing amount of catalyst. Above 600°C, both on the shorter and on the longer catalyst layers ethane conversion had a sharp increase, which could be partly explained by the onset of the homogeneous reactions. Concerning the single reaction products (Fig. 7), CO_2 was only produced in traces in the empty annular reactor; in the presence of the short layer of catalyst CO_2 productivity increased significantly and could completely explain ethane conversion up to 500–550°C. Further increase was caused by the use of a longer catalyst layer. In both cases, the outlet CO_2 flow decreased with increasing temperature above 500°C.

Water was produced in appreciable amounts in the absence of catalyst above 700°C. With addition of a small catalyst load, however, its production initiated at low

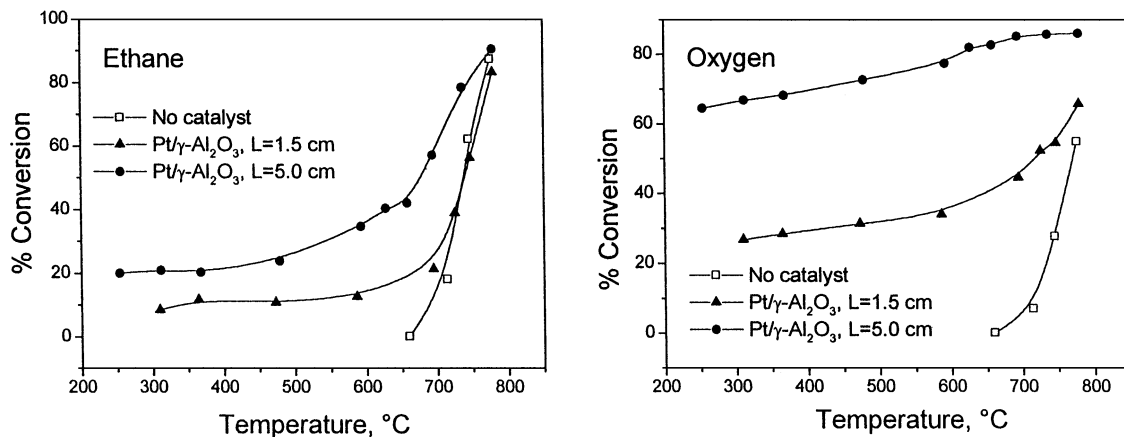


FIG. 6. Ethane ODH in the presence of Pt/γ-Al₂O₃ catalyst at varying catalyst layer length. Conversion of ethane and oxygen. Feed composition, C₂H₆/O₂/N₂ = 2/2/96; flow rate, 1 L/min at 273 K, 1 atm.

temperature and increased with increase of the catalyst layer length. The production of water and CO₂ completely accounted for the conversion of ethane and oxygen observed in the presence of the catalyst in the temperature window between 250 and 500°C; thus deep oxidation of ethane was firstly catalyzed by Pt/Al₂O₃ at low *T*.

Above 500°C, CO was formed in the presence of the short catalyst layer and the production of this species increased significantly with temperature; such a production was higher than that associated to the single contribution of gas-phase reactions. Also, CO molar flow increased with further increase of the catalyst load. A similar trend was

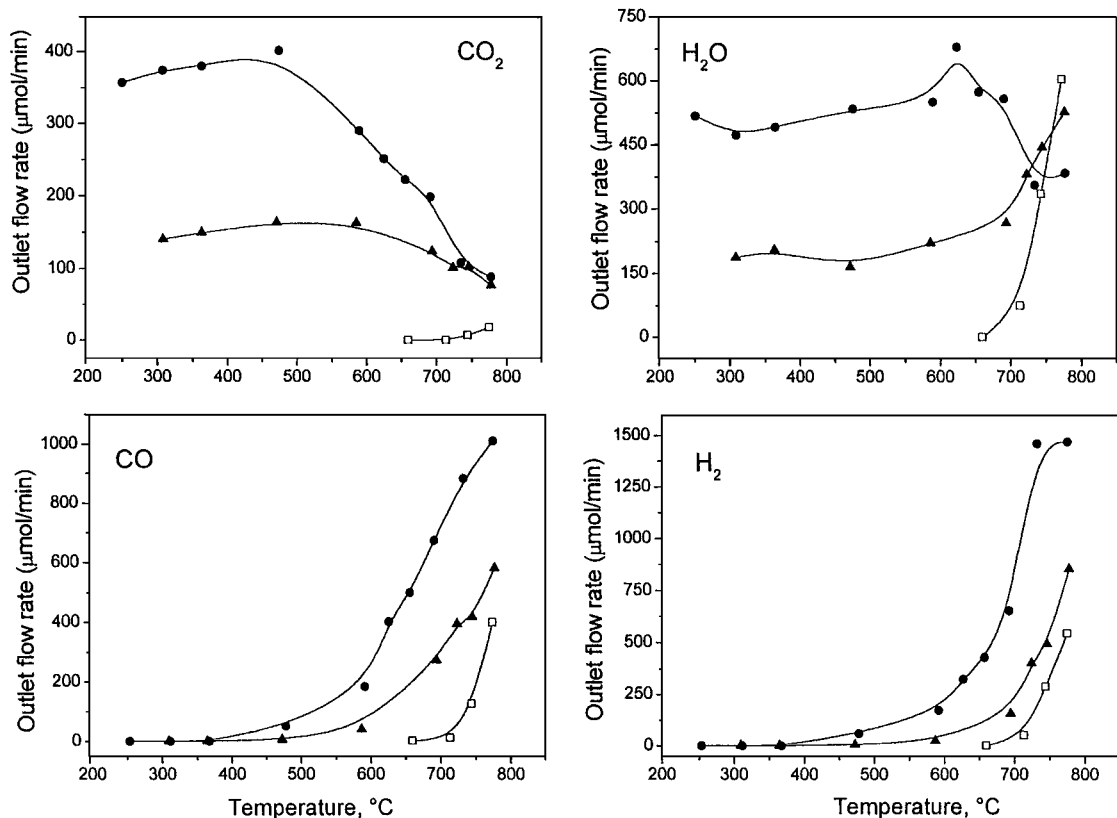


FIG. 7. Ethane ODH in the presence of Pt/γ-Al₂O₃ catalyst at varying catalyst layer length. Outlet flow rate of CO₂, H₂O, CO, and H₂. Conditions as in Fig. 6.

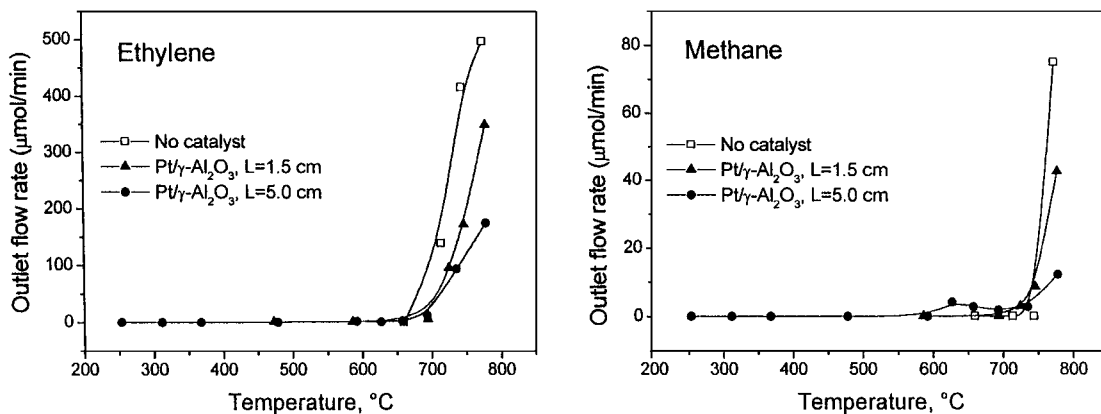


FIG. 8. Ethane ODH in the presence of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst at varying catalyst layer length. Outlet flow rate of ethylene and methane. Conditions as in Fig. 6.

found for the formation of hydrogen: though appreciable at high temperature in the empty reactor, its production was anticipated at 500°C and was progressively enhanced by the addition of increasing amounts of catalyst. In the range of intermediate and high temperature, the catalyst was thus active in the production of synthesis gas, presumably via partial oxidation of ethane. Ongoing research is presently addressing the mechanism and kinetics of CO/H_2 production over the Pt-catalyst.

Concerning the production of ethylene, Fig. 8 shows that the olefin molar flow was maximum, though small, in the empty reactor, while it decreased with increasing catalyst load. The same trend was shown by methane outlet flow. These results suggest that hydrocarbons were formed uniquely in the gas-phase while the catalyst did not contribute to their production. On the opposite the addition of the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst contributed to partly decompose the amount of ethylene and methane produced by the homogeneous reactions.

Analogous experiments were carried out by halving the oxygen feed content. Results are shown in Fig. 9. The decrease of oxygen concentration caused a significant decrease of ethane conversion, but it still grew with the addition of catalyst and the comparison with the tests in the empty reactor showed that ethane conversion up to 600°C could be explained only by the contribution of the catalyst phase. The production of all the species was of course lower than in the previous case. Still, the comparison of the three cases clearly showed the promoting effect of the catalyst addition on the production of CO_2 and H_2O (which were formed only at high temperature in the empty reactor) and on the formation of CO and H_2 , which became important products above 500°C . Concerning the hydrocarbons, also in this case the production of ethylene was maximum in the absence of any catalyst, while it decreased with increasing length of the catalyst layer. A similar trend was shown by methane production.

Additional experiments were then realized in the absence of oxygen. In the three cases of empty reactor, presence of a short catalyst layer and presence of a longer catalyst layer, conversion of ethane was the same in the whole temperature range investigated. The products uniquely observed in the outlet stream were ethylene and hydrogen; the addition of catalyst did not affect the production of these species due to single gas-phase reactions (Fig. 10).

These results were in complete agreement with those obtained from previous experiments with propane/oxygen/nitrogen mixtures (22). Also in the case of propane, in fact, it was observed that the addition of catalyst promoted the formation of the deep oxidation and partial oxidation products, while decreasing the production of ethylene and propylene, which was maximum in the absence of any catalyst layer. Also in that case, then, the oxidation activity of the catalyst decreased with decreasing O_2 feed concentration, and in the absence of oxygen only gas-phase reactions occurred.

ETHANE OXIDATION TESTS OVER $\text{BaMnAl}_{11}\text{O}_{19}$ IN THE ANNULAR REACTOR

The Ba-, Mn-substituted hexa-aluminate catalyst was first tested in the annular reactor, in order to estimate its activity in the oxidation of ethane. A lower activity than that of the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst was expected; thus the experiments were carried out at relatively low flow rate and high reactant concentration. The results reported in Fig. 11 were obtained with a 1.7-cm-long catalyst layer, a total flow rate of 120 cm^3 (NTP)/min and an ethane/air feed with ethane/oxygen ratio = 1. They are compared with the results of experiments which were carried out with the Pt-catalyst under the same operating conditions. The results of blank experiments in the empty reactor are also reported as a reference.

The activity of the noble metal catalyst was so high that the reactant conversions likely underwent mass transfer

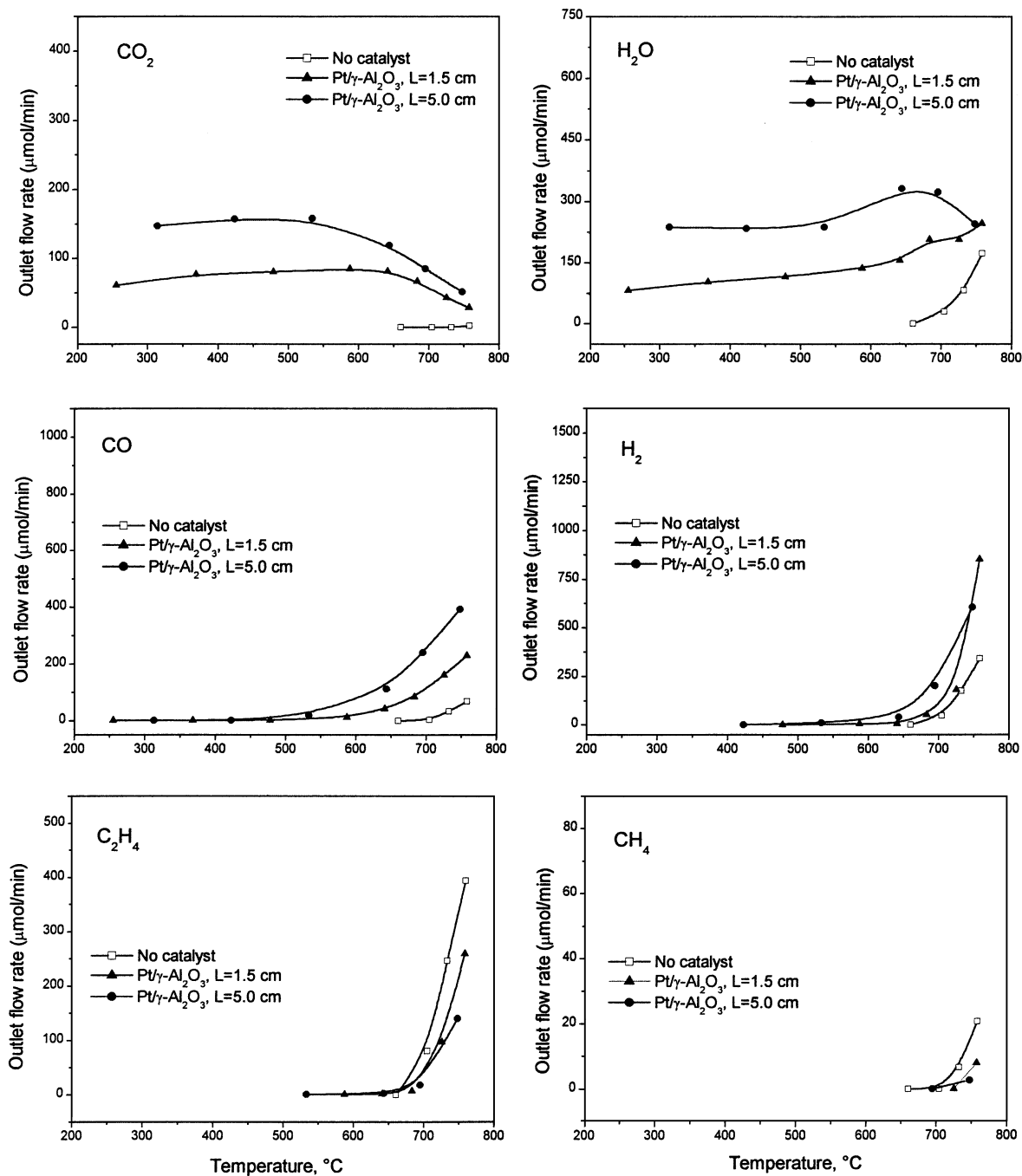


FIG. 9. Ethane ODH in the presence of Pt/γ-Al₂O₃ catalyst at varying catalyst layer length. Outlet flow rate of the single reaction products. Feed composition, C₂H₆/O₂/N₂ = 2/1/97; flow rate, 1 L/min at 273 K, 1 atm.

limitation as soon as reaction started. Instead, the activity of the BaMnAl₁₁O₁₉ catalyst was significantly lower; ethane and oxygen conversions were first observed at nearly 450 °C oven temperature and they increased progressively with increasing *T*. Over 700 °C, the conversion of reactants was complete also in the case of the BaMnAl₁₁O₁₉ catalyst, but comparison with the activity of the gas-phase clearly

indicates that the onset of homogeneous reactions could thoroughly explain the data. The flow rate of the single reaction products are reported in Fig. 12; they refer uniquely to the BaMnAl₁₁O₁₉ which was tested with a 1.7-cm-long and a 5-cm-long catalyst layer. CO₂ and H₂O were the only reaction products observed in the presence of the catalyst and their production increased with increase of

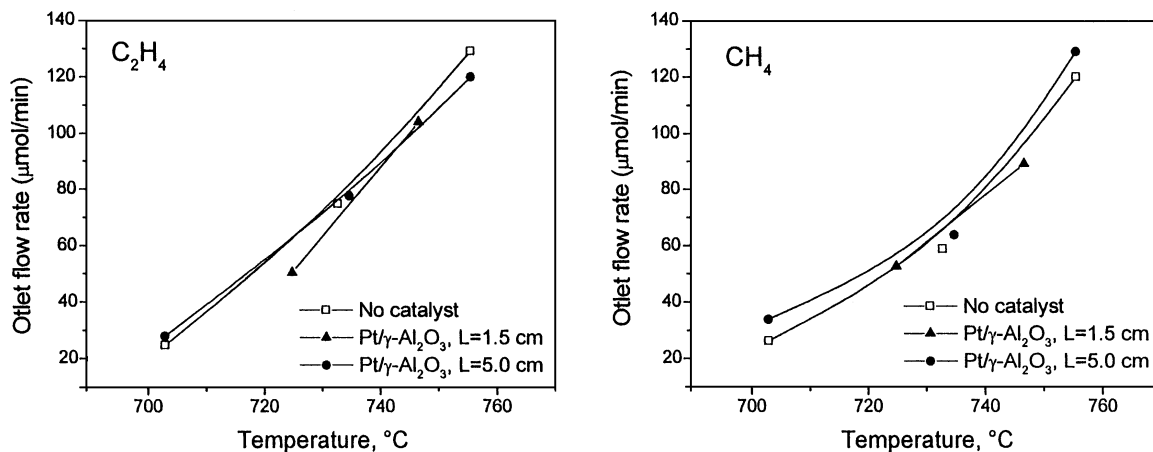


FIG. 10. Ethane ODH in the presence of $Pt/\gamma\text{-Al}_2\text{O}_3$ catalyst at varying catalyst layer length. Outlet flow rate of ethylene and hydrogen. Feed composition, $C_2H_6/N_2 = 2/98$; flow rate, 1 L/min at 273 K, 1 atm.

catalyst load; other species, including CO, H_2 , ethylene, and methane were formed above 650°C but their production was almost entirely accounted for by the contribution of homogeneous reactions. Thus, opposite to the $Pt\text{-Al}_2\text{O}_3$ catalyst, the mixed oxide based catalyst was proven to be uniquely active in the deep oxidation of ethane, while no activity was shown in the partial oxidation to CO and H_2 .

ODH OF ETHANE IN AUTOETHERMAL CONDITIONS OVER $Pt/\gamma\text{-Al}_2\text{O}_3$

Tests of ethane ODH in the presence of the $Pt\text{-Al}_2\text{O}_3$ catalyst were realized in the autothermal reactor at varying inlet temperature and feed composition. Results have been reported in detail elsewhere (17) and are herein summarized in Table 1.

In all the experiments with the Pt -catalyst, reactor light off occurred instantaneously as soon as the ethane/air stream was let in. As an example, Fig. 13 reports the typical

dynamics of temperature. In few seconds the reactor temperature increased up to 900°C , and then the following T increase slowed down and temperature was approximately constant after 30 min from the feed injection.

At varying ethane/oxygen feed ratio, reactor temperature, ethane conversion, and product distribution changed. The maximum temperature of the catalytic portion established close to the theoretical adiabatic temperature and decreased with increasing C_2/O_2 ratio in line with the decreasing exothermic content of the reaction. Conversion of ethane decreased from over 95% to nearly 40%. CO and H_2 were the major products at equimolar feed composition but the production of ethylene prevailed at ethane/ O_2 ratios >1.4 . The olefin selectivity grew to 55%.

At higher preheat temperature, a similar trend was observed. At increasing ethane/oxygen feed ratios, ethane conversion and temperature decreased but ethylene selectivity increased. A larger production of ethylene was

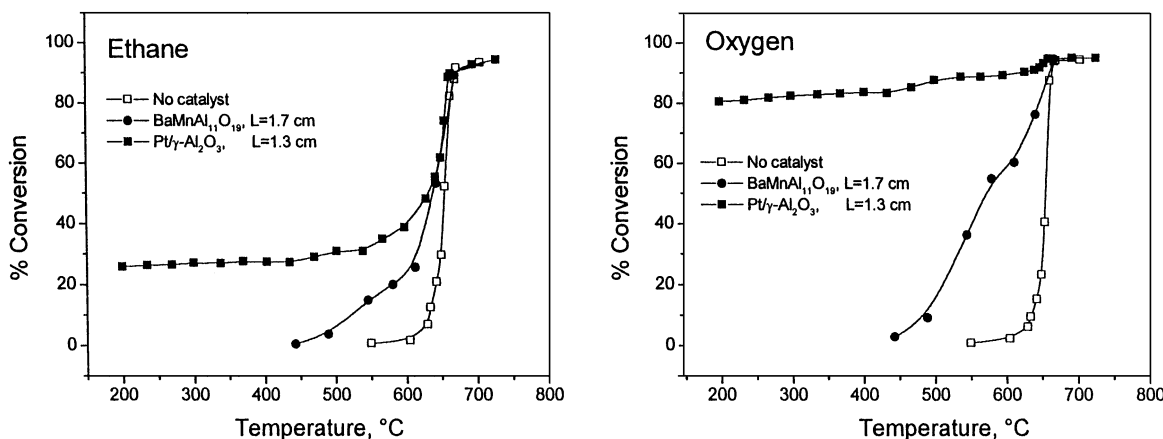


FIG. 11. Comparison of ethane and oxygen conversions in the three cases of absence of catalyst, presence of a 1.3-cm-long Pt/Al_2O_3 catalyst and presence of a 1.7-cm-long $BaMnAl_{11}O_{19}$ catalyst. Feed composition, $C_2H_6/O_2/N_2 = 1/1/4$; flow rate, $120\text{ cm}^3/\text{min}$ at 273 K, and 1 atm.

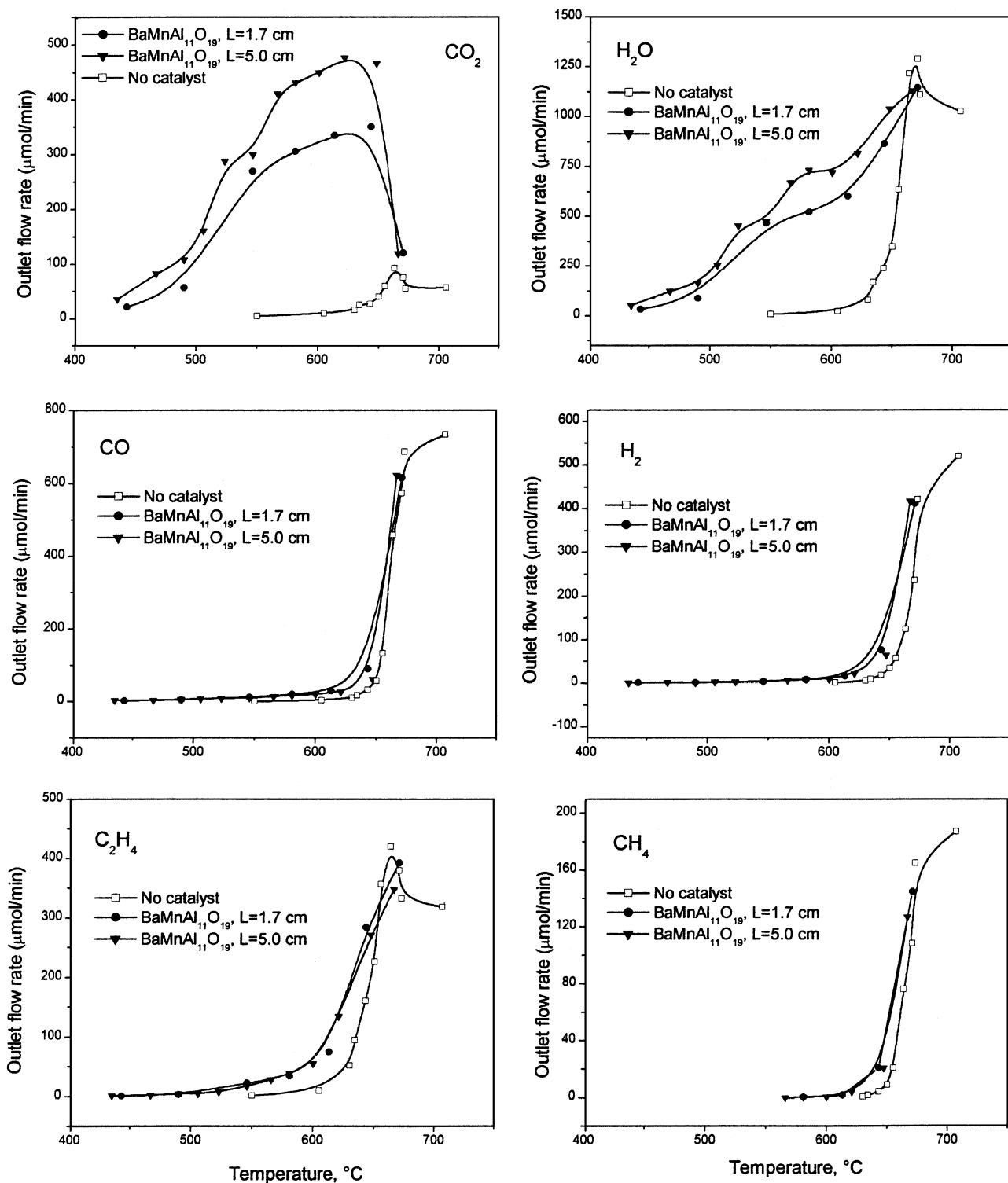


FIG. 12. Ethane oxidation tests over the BaMnAl₁₁O₁₉ catalyst. Outlet flow rate of CO₂, H₂O, CO, H₂, ethylene, and methane over 1.7-cm-long and 5-cm-long catalyst layers and in the absence of any catalyst. Operating conditions as in Fig. 11.

TABLE 1

Performances of the Pt-Containing Autothermal Reactor

% C-mol Selectivity							
C_2/O_2	C_2 conv. (%)	T ($^{\circ}C$)	CO_2	CO	C_2H_4	CH_4	$C_3 + C_4$
$T_{in} = 200^{\circ}C$							
0.98	95.3	998	9.6	47.5	37.4	5.8	0.3
1.36	75.5	960	8.7	28.1	56.4	4.2	2.6
1.43	68.2	947	10.0	30.4	54.2	3.6	1.8
1.74	55.2	924	10.6	27.8	56.6	2.8	2.2
2.12	41.0	890	13.4	30.0	53.4	2.0	1.2
$T_{in} = 400^{\circ}C$							
1.27	92.1	1002	8.3	27.1	53.9	6.7	4.0
1.45	84.6	985	8.1	23.0	59.8	5.7	3.4
1.72	70.7	953	7.9	20.5	63.9	4.4	3.3
2.0	59.9	936	7.9	20.8	64.7	3.6	3.0

Note. Feed, ethane/air; total flow rate, 1 L(NTP)/min; contact time, 5 ms.

observed than at the lower preheat temperature. An ethylene yield as high as 50% was observed at ethane/ $O_2 = 1.45$. Elsewhere (21) these data were compared with the simulations of a purely homogeneous process and it was suggested that, at increasing reactor temperature, the contribution of the catalyst phase to the production of CO_x became less important; this was likely due to the lower sensitivity of heterogeneous kinetics to the increase of temperature, compared with homogeneous kinetics.

The Pt-containing reactor was stable as temperature and product distribution kept constant for several hours, until operating conditions were changed. Light-off of the reactor always occurred very rapidly even after weeks of operation with no need of regeneration. Apparently, the catalyst did not suffer from coking or deactivation.

Preliminary experiments were realized over the Pt/ γ - Al_2O_3 catalyst with the purpose of studying the effect of H_2 cofeed. No significant promotion of ethylene formation was found and this is in line with the same findings of Bodke *et al.* (14); they reported in fact a moderate H_2 effect for the single Pt-coated foam monoliths, while the selective oxidation of H_2 resulted a peculiar characteristic of the bimetallic Sn-Pt system.

ETHANE ODH IN AUTOTHERMAL CONDITIONS OVER $BaMnAl_{11}O_{19}$

The hexa-aluminate catalyst was deposited onto the FeCrAlloy fibrous support and tested in the adiabatic reactor (catalyst load, 90 mg). The purpose of the present experiments was to verify the possible use of a Pt-free oxidation catalyst for realizing the ignition of homogeneous reactions. Preheat temperature for the inlet gas stream was set to the minimum temperature at which the BaMn-catalyst resulted active in the oxidation of ethane, that is 450–500 $^{\circ}C$. Ethane-air mixtures were fed at varying ethane/oxygen ratios with a total flow rate of 1 L(NTP)/min, corresponding to approximately 5 ms contact time in the catalyzed portion of the reactor.

Figure 14 reports an example of light-off of the reactor; while in the presence of Pt/ Al_2O_3 catalyst light-off was instantaneous, in the case of the Pt-free catalyst two distinct phases appeared during reactor ignition. Initially, temperature increased slowly; within several minutes, the reactor temperature grew from the preheat value to nearly 700 $^{\circ}C$ but subsequently a sharp increase of temperature occurred up to the final temperature value which kept constant with time and depended on feed composition. During the initial slow T increase only oxidation products were detected in the outlet product mixture, while after reach of the final

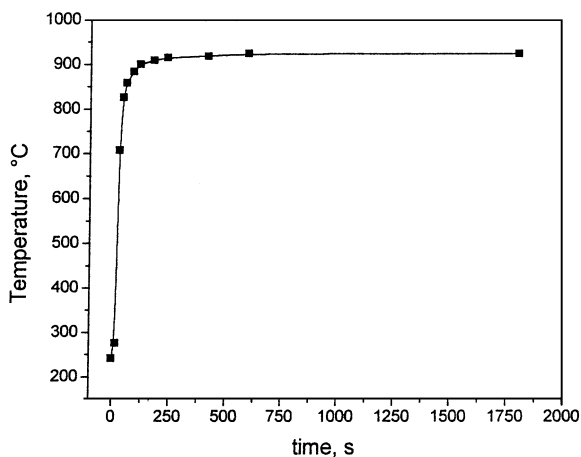


FIG. 13. ODH of ethane in autothermal reactor in the presence of Pt/ Al_2O_3 catalyst. Light-off of the reactor. Flow rate, 1 L/min at 273 K and 1 atm; feed, ethane/air; preheat temperature, 200 $^{\circ}C$.

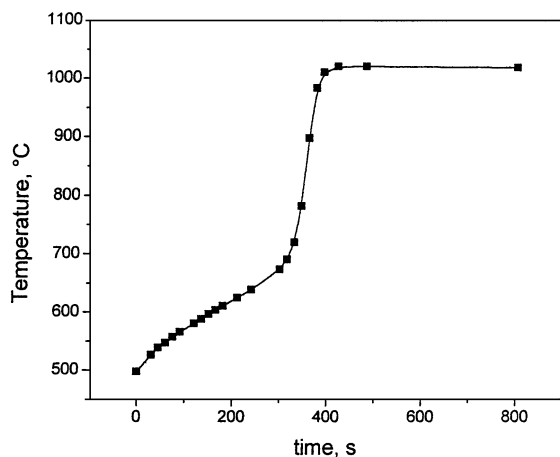


FIG. 14. ODH of ethane in autothermal reactor in the presence of $BaMnAl_{11}O_{19}$ catalyst. Light-off of the reactor. Flow rate, 1 L/min at 273 K and 1 atm; feed, ethane/air; preheat temperature, 500 $^{\circ}C$.

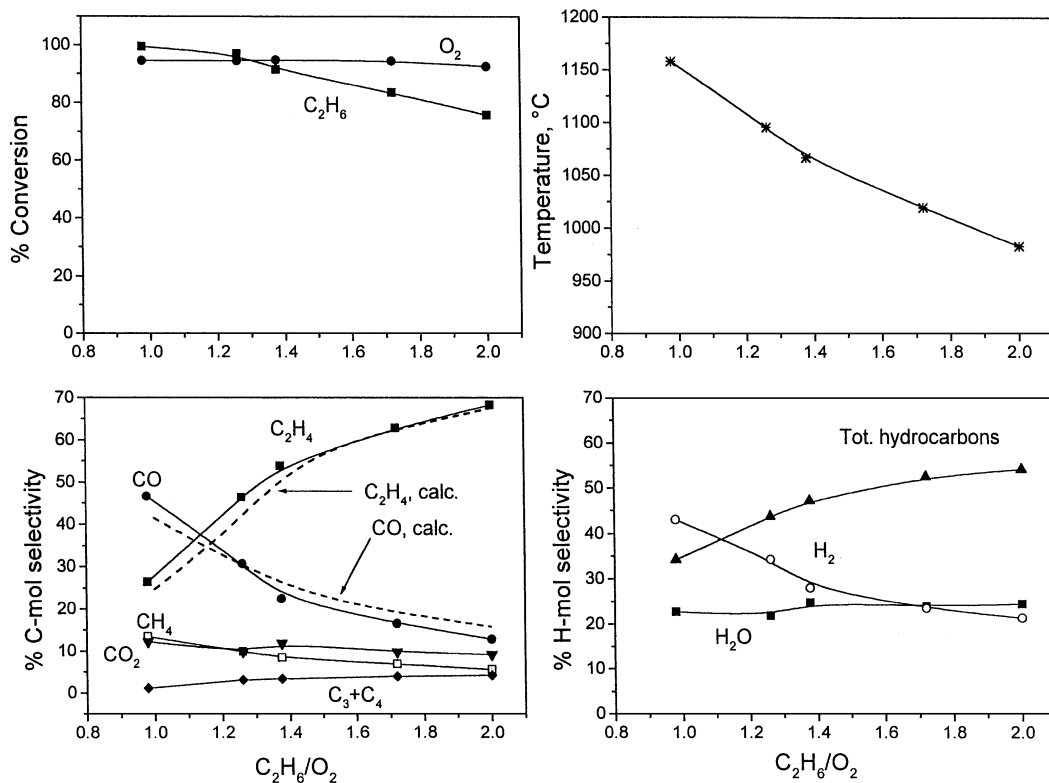


FIG. 15. ODH of ethane in autothermal reactor in the presence of BaMnAl₁₁O₁₉ catalyst. Effect of ethane/O₂ feed ratio on reactants conversion, reactor temperature, distribution of products. Flow rate, 1 L/min at 273 K and 1 atm; feed, ethane/air; preheat temperature, 500°C. Dashed curves, calculated selectivity of ethylene and CO for a purely homogeneous adiabatic reactor, operating at the same inlet temperature and degree of reactant conversion.

temperature level ethylene was also present among the reaction products. The temporal profile of temperature seems to reflect the relative rate and the stepwise onset of heterogeneous reactions and homogeneous reactions; the low oxidation activity of the BaMnAl₁₁O₁₉ catalyst was presumably responsible for the initial slow temperature increase of the reactor, while once the threshold for ignition of homogeneous reactions was reached, then sudden light-off of oxidative pyrolysis occurred.

Once ignited, the Pt-free autothermal reactor behaved similarly to the one with the Pt-catalyst. Temperatures were in general higher likely due to the higher preheat temperature level. As reported in Fig. 15, at equimolar ethane/oxygen ratio, temperature was about 1150°C and it decreased to 980°C at ethane/oxygen ratio = 2. Ethane conversion was also higher than in the presence of the Pt/Al₂O₃ catalyst. As expected, ethane conversion decreased with increasing C₂/O₂ feed ratio; complete conversion was observed at C₂/O₂ = 1 and nearly 75% conversion was obtained at feed ratio close to 2. The product distribution is also shown in Fig. 15. Ethylene selectivity increased significantly with increasing ethane/oxygen feed ratio and amounted to 68% at C₂/O₂ = 2. Accordingly, CO selectivity decreased down to 15%. CO₂ and CH₄ were produced

in low amounts at all composition tested with selectivities in the order of 10% each. Hydrogen was produced in large amount at low ethane/oxygen feed ratios but its H-selectivity decreased with increasing C-feed content. Ethylene yield was over 50% for ethane/oxygen > 1.3.

Experimental results were compared with the simulations of a detailed kinetic scheme of homogeneous reactions and Fig. 15 also shows in dashed lines the calculated C-selectivity of ethylene and CO. Calculations refer to an isothermal adiabatic reactor with inlet temperature of 500°C, which operated at the same conversion level of reactants as measured in the experiments, at few milliseconds contact time. A very close agreement was found between experimental and predicted data.

Indeed the hexa-aluminate catalyst behaved as ignitor of the high-temperature homogeneous process; presumably because of the high temperature level reached and of the low intrinsic activity of the catalyst, homogeneous reactions governed the final performance of the reactor, with consequent minimum production of CO_x and maximum selectivity to ethylene.

Concerning the catalyst stability, after few consecutive cycles consisting of light-off, high-temperature operation, and shut down, the BaMnAl₁₁O₁₉ was unable to activate the

process at the same inlet temperature of 500°C. However, a treatment in air at 500°C for several hours during which CO₂ was formed in traces reestablished the catalyst activity; afterward, in fact, ignition of the reactor occurred with the same dynamics as shown in Fig. 14. The BaMnAl₁₁O₁₉ thus suffered from reversible deactivation, presumably due to coke deposition during the high temperature operation that the lower oxidation activity of the catalyst was not sufficient to prevent. A deeper understanding of the deactivation phenomenon was beyond the scope of the present work, wherein the BaMnAl₁₁O₁₉ catalyst has been simply taken as a model of Pt-free oxidation catalysts.

CONCLUSIONS

Several works in the literature have shown that oxidative dehydrogenation of ethane (and other light alkanes) over Pt-catalysts leads to the selective production of ethylene, when the process is carried out in autothermal reactors at temperatures close to 1000°C and at millisecond contact times. Similar results were obtained by the authors by carrying out the reaction over a Pt/ γ -Al₂O₃ catalyst supported over a metallic tissue under adiabatic conditions. However, in the author's experience the short contact time autothermal reactors are not versatile tools for the kinetic investigation: temperature is not controlled by the operator and cannot be freely varied, high reactant concentrations are needed and the comparison with blank experiments in the absence of catalyst (an important "home-work" when high temperatures are involved) cannot be realized. Furthermore, the short contact times are realized in the adiabatic reactors by supporting the catalyst over high void fraction materials which allow to use high flow rates while minimizing pressure drops (foam monoliths, gauzes, and others); thus, the contribution of homogeneous reactions in the gas volume which is surrounded by the catalyst support should not be excluded a priori.

In this work a nonadiabatic structured reactor was used to investigate separately the single contributions of homogeneous and heterogeneous reactions in the short contact time oxidative dehydrogenation of ethane over the Pt/ γ -Al₂O₃ catalyst. In the absence of catalyst, activity tests showed that the radical gas-phase process was highly selective toward the formation ethylene; theoretical analyses have confirmed the experiments. The study of the single role of heterogeneous reactions showed that from low (200°C) up to high temperatures the Pt/ γ -Al₂O₃ catalyst was active in the deep and partial oxidation of ethane to CO_x, while no positive proof was found of an heterogeneous formation of ethylene. It is thus believed that in the short contact time adiabatic reactor, a synergism between catalytic combustion and gas-phase oxidative pyrolysis is established; the former seems responsible for the rapid light-off of the reactor, while the latter seems to have an important role

in the final performance of the reactor, being responsible of the production of olefins. Indeed, the observed product distributions compared well with the predictions of the expected performance of a purely homogenous adiabatic reactor.

The hypothesis that the main role of the Pt-catalyst was that to accelerate the ignition of homogeneous reactions through oxidation reactions was further verified by testing for comparison a Pt-free oxidation catalyst. The BaMnAl₁₁O₁₉ was proved to be uniquely active in the total oxidation of ethane to CO₂ and H₂O. However, in the adiabatic reactor, at the proper preheat temperature of 500°C, the hexa-aluminate catalyst produced light-off of the reactor and yields over 50% to ethylene were observed from ethane/air mixtures; thus, once ignited the Pt-free adiabatic reactor performed even better than the Pt-containing reactor. The observed product distribution was compared with the predictions of a purely homogeneous reactor and a very good match was found between the measured and predicted ethylene formation. These data suggest that in principle high ethylene yields can be obtained by exploiting the combination of an oxidation catalyst with the fast homogeneous reactions of oxidative pyrolysis.

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