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Production of olefins via oxidative dehydrogenation of light paraffins at short contact times

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Abstract

Experiments of oxidative dehydrogenation of ethane in the presence of a Pt/γ-Al_2O_3 catalyst were performed at high temperatures and short contact times under isothermal and adiabatic conditions. High ethene yields were observed. The comparison of the catalytic data with the results of gas-phase experiments and with the predictions of a detailed kinetic model of homogeneous oxidative pyrolysis of hydrocarbons suggested that radical reactions had a fundamental role in the synthesis of olefins, while the catalyst phase mostly behaved as heat-supplier through combustion routes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; Pt/γ-Al_2O_3 catalyst; High temperature; Short contact time; Annular reactor; Autothermal reactor; Heterogeneous versus homogeneous reactions; Detailed modeling

1. Introduction

Oxidative dehydrogenation (ODH) of light paraffins represents one of the novel routes currently proposed for the conversion of natural gas into valuable chemicals; the synthesis of short chain olefins via the exothermic selective oxidation of ethane and propane is considered in fact a potential alternative to the traditional highly endothermic industrial processes which are based on the pyrolysis of hydrocarbon feedstocks [1].

Very high selectivities to olefins were reported by Schmidt and co-workers [2–6]; they have investigated the selective oxidation of light alkanes over Pt-coated foam monoliths, operating adiabatically at extremely short contact times (1–10 ms). In spite of the high reaction temperatures (700–1000°C), possible contributions from homogeneous reactions were ruled out and a heterogeneous mechanism was proposed to explain the formation of propene and ethene.

In the previous works [7,8], the authors have investigated the role of a Pt/γ-Al_2O_3 catalyst in the selective oxidation of propane to olefins at high temperature and short contact time. It was confirmed that high yields to ethene and propene could be obtained under extreme operating conditions in the presence of the Pt-catalyst. However, the comparison of the catalytic tests with the results of homogeneous experiments and the results of theoretical evaluations about the role of radical reactions indicated that the high-temperature production of olefins could be well explained by the onset of homogeneous reactions; these were in fact extremely active and selective towards the formation of olefins. On the other hand, it was found that the Pt-catalyst was very active in the non-selective oxidation of propane to CO_X. It was thus thought that within an autothermal reactor,

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the Pt-catalyst could be exploited for igniting and thermally supporting the oxidative pyrolysis process. This principle was verified by running adiabatic tests at few millisecond contact time; total yields to olefins up to 50% were obtained, in close agreement with the data already reported in the literature [2,6]. The reactor performance was compared with the expected behavior of a purely homogeneous adiabatic reactor and a close agreement was found between experiments and model predictions.

Additional indications in favor of the importance of gas-phase reactions in the high-temperature selective oxidation of paraffins came from the results reported by Holmen and co-workers [9,10]. They studied the ODH of ethane over Pt and Pt/Rh gauzes and found that the catalyst was purely involved in the ignition of gas-phase reactions; these were instead identified as responsible for the synthesis of olefins.

In this work, the study of the ODH of light paraffins over a Pt/γ-Al_2O_3 catalyst has been extended to ethane. Catalytic tests were performed with short contact time reactors. An annular reactor [11], wherein controlled temperature conditions are realized, was employed for investigating fundamental aspects of the reaction mechanism. An insulated reactor was then used to verify the possibility of producing high ethene yields in adiabatic mode. A metallic high void fraction material was used in the autothermal reactor as catalyst support in order to guarantee rapid light-off and even temperature distribution.

The experimental results were compared with the predictions of a detailed kinetic scheme for hydrocarbon oxidative pyrolysis (previously developed by Ranzi and co-workers [12,13]) about the expected performance of the corresponding purely homogeneous reactors. New pieces of evidence were thus searched about the single roles that catalytic phase and gas phase play in the formation of olefins at high temperature and short contact time.

2. Experimental and modeling

2.1. Catalysts

Tests were performed with a commercial 5% Pt/γ-Al_2O_3 catalyst provided by Engelhard (ESCAT 24). The catalyst was crushed and sieved with a 325-mesh sieve. A fluid slurry was prepared by gradually wetting the fine powders with deionized water; the slurry was dropped onto the central portion of tubular ceramic supports, which were then dried in air and calcined up to 550°C, before being loaded in the annular reactor. Catalyst layers 1–5 cm long and 50–100 μm thick were prepared with this procedure. The same slurry was also dropped, dried and calcined over elements of a Fe–Cr alloy fibrous support; this consists of 1 μm wide fibers which are knitted to form a 1.5 mm thick fabric. The coated metallic elements were utilized for running adiabatic tests at milliseconds contact time. Prior to deposition, the Fe–Cr alloy fibrous mat was calcined at 1000°C for 10 h; the thermal treatment promotes the formation of an inert superficial layer of α-Al_2O_3. Once coated with the catalyst particles, the metallic mat retains its high void fraction; loaded inside the reactor, it realizes a continuum metallic matrix with high thermal conductivity.

2.2. Reactors

A detailed description of the testing unit has been given elsewhere [7,8]. Here are briefly recalled the main characteristics of the reactors used in this work. The *annular reactor* consists in a quartz tube (ID = 7 or 9 mm), wherein a catalyst-coated mullite tube (OD = 4.75 mm) is co-axially inserted. The gas flows in the annular chamber in laminar regime and practically no pressure drop is built along the reactor; together with the possibility of loading very small amounts of catalysts (few milligrams), this allows to realize extremely high gas hourly space velocities, up to $\mathrm{GHSV} = 10^6$–$10^7\ \mathrm{L(NTP)/(kg\,cat)\,h}$. In the annular reactor the catalyst temperature is measured from inside the mullite tube, which is exploited as a thermocouple-well. The reactor is heated by an external carbolite furnace with three independent heating zones.

The autothermal reactor consists of a quartz tube (ID = 7 mm), wherein the catalyst-coated metallic elements are packed for a total bed length of 5–15 mm. Upstream and downstream from the catalytic portion, ceramic particles are packed to form 4 cm long guard-beds in order to minimize axial heat dispersions. Inert material is then wrapped around the reactor, thus insulating it in the radial direction. The axial temperature profile of the adiabatic reactor is measured by means of a thin thermocouple, sliding inside a stainless steel TC-well along the reactor axis. Light-off of the reactor could not be realized in the absence of catalyst, as expected from the inert internal reactor surfaces.

2.3. Homogeneous kinetic model

The detailed kinetic scheme used for the simulation of isothermal and adiabatic homogeneous reactors is the result of a long experience in the pyrolysis and partial oxidation of hydrocarbons. The model involves more than 150 radical and molecular species in about 3000 elementary and lumped reactions. It is characterized by a modular and hierarchical structure, which covers the chemistry of C-species from methane to high molecular weight soot.

The kinetic scheme has been widely validated for partial oxidation and combustion processes, and more recently it has been successfully applied to the analysis of selective oxidation tests which were performed under extreme operating conditions (high temperature and ultra-short contact times) [14].

3. ODH of ethane in the annular reactor: effect of temperature

Most of the data reported in the literature refer to reaction temperatures close to 1000°C only, as autothermal operation is usually preferred in order to evaluate the process performance under conditions of industrial relevance. However, fundamental information are thus missed on the kinetic dependence of the reaction rate and product distribution on temperature. The annular reactor was herein applied to better investigate such dependence, by spanning from low to high reaction temperatures.

Experiments of ODH of ethane were realized at short residence time, with a total feed stream of 120 $\mathrm{cm^3}$(NTP)/min (normal conditions, i.e. $T = 273\,\mathrm{K}$ and $P = 1\,\mathrm{atm}$) and molar composition $C_2H_6/O_2/N_2 = 1/1/4$. The catalyst layer was 13 mm long, which corresponded to a load of nearly 15 mg; the gas hourly space velocity (referred to the catalyst load) was 480,000 L(NTP)/(kg cat) h.

Figs. 1 and 2 report the results of the experiments. Already at 200°C oven temperature, conversion of

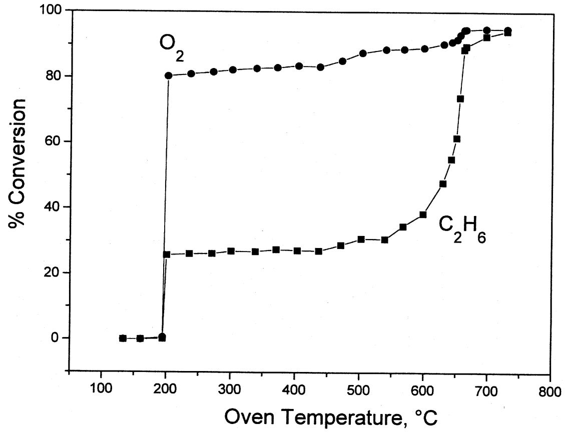

Fig. 1. ODH of ethane over Pt/γ-Al_2O_3 catalyst in annular reactor. Effect of temperature on ethane and oxygen conversion. Feed: $C_2H_6/O_2/N_2 = 1/1/4$. Flow rate: 120 $\mathrm{cm^3}$(NTP)/min. Catalyst layer length: 13 mm (15 mg).

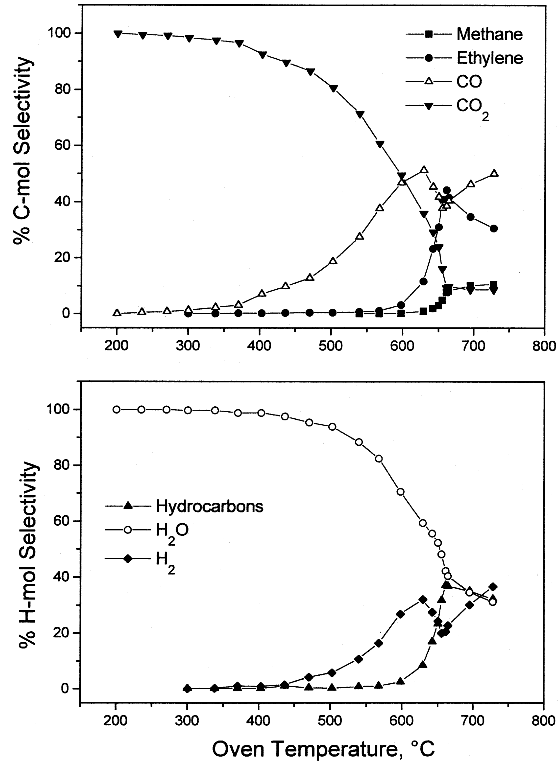

Fig. 2. ODH of ethane over Pt/γ-Al_2O_3 catalyst in annular reactor: product distribution. Operating conditions as in Fig. 1.

reactants was observed: about 25% conversion for ethane and more than 80% conversion for oxygen. These values kept almost constant up to 550–600°C heating temperature; above this temperature ethane conversion had a sharp increase and at 700°C conversion of both reactants was almost complete.

At the lowest oven temperature at which reaction initiated, production of CO_2 and water was uniquely observed. Total combustion of ethane was thus active at low temperature. An a posteriori analysis has shown that the deep oxidation reaction was so fast, that the process underwent interphase mass-transfer limitations, which explains the almost constant trend for the conversion curves. The 80% conversion of oxygen (the limiting reactant) corresponds in fact to a Sherwood number close to 3, which is in line with the estimate of the mass-transfer coefficient in the annular reactor [11].

Above 400°C the selectivity of CO_2 and H_2O partly decreased, as CO and H_2 were progressively formed with increasing heating temperature. Deep oxidation was thus accompanied by partial oxidation or steam/dry reforming of ethane.

In the temperature window where the sharp increase of ethane conversion occurred, the selectivity of CO_2 had a dramatic decrease, while ethene and methane were formed. Ethene selectivity passed through the maximum value of nearly 50% in correspondence with 650°C heating temperature and decreased at the higher T values. Methane selectivity was instead an increasing function of temperature, but kept below 10%. The selective oxidation of ethane and the cracking to methane were thus active only in the range of high temperatures.

Important pieces of evidence were provided by the axial temperature profiles, measured during the activity tests. At the low temperature at which conversion of reactants started and oxidation products were only produced, the axial temperature profile of the annular reactor showed a pronounced hot-spot located in correspondence with the catalyst layer (between 40 and 41.3 cm); this is shown in Fig. 3a, where the profile of the reactor is compared with the profile of the heating furnace wall. At 200°C oven temperature, the catalyst temperature was above 400°C.

The hot-spot in correspondence with the catalyst decreased progressively with increasing furnace temperature; at about 575°C oven temperature, the catalyst temperature was nearly 650°C (Fig. 3b). It must be considered that with increasing temperature up to 600°C, conversion of the reactants kept almost constant, while the production of CO_2 and H_2O was accompanied and gradually replaced by the production of synthesis gas and a strong reduction of the overall exothermicity occurred.

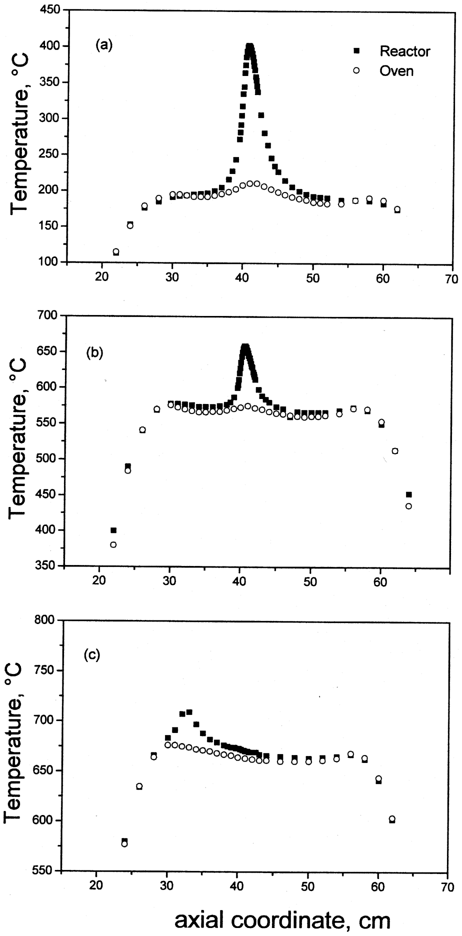

Fig. 3. Temperature profiles of the annular reactor. Solid symbols: temperature profile along the reactor axis. Open symbols: temperature profile of the oven wall. Operating conditions as in Fig. 1.

Remarkably, at the highest furnace temperature at which conversion of reactants was complete and ethene and methane were present in the product mixture, the hot-spot over the catalyst layer disappeared and a new hot-spot grew upstream from the catalyst in the entry empty volume of the reactor (Fig. 3c). This was of course interpreted as an evidence of the onset of gas-phase reactions; blank experiments were thus carried out for comparison.

4. Comparison with experiments in the empty reactor

Tests of the reactivity of the empty reactor volume were performed under the same operating conditions as those of Fig. 1, by simply replacing the coated mullite tube with a bare mullite tube. The results of catalytic and blank experiments are compared in Figs. 4–6.

Fig. 4 shows that up to 600°C oven temperature, the conversion of ethane and oxygen observed in the presence of the Pt/γ-Al_2O_3 catalyst was essentially bound to heterogeneous reactions. However, above 650°C the contribution of the homogeneous reactions to ethane decomposition was increasingly important, and could entirely explain the high values of reactants conversion observed in the presence of the Pt-catalyst at the highest temperatures.

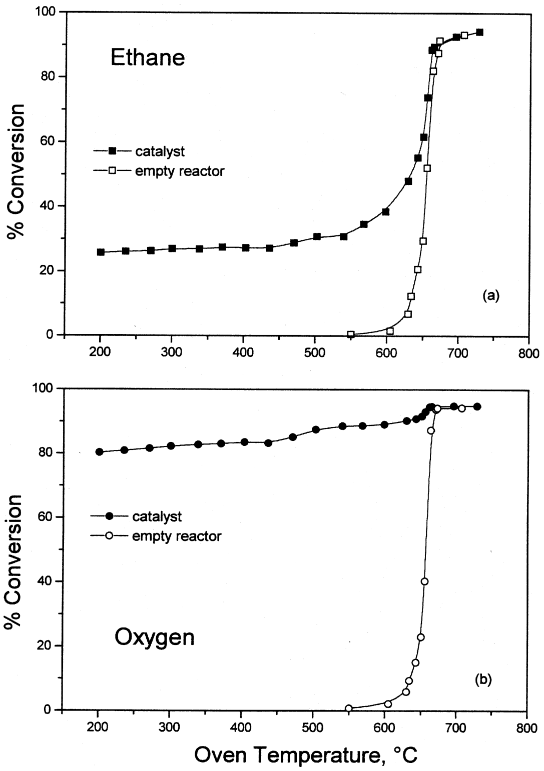

Fig. 4. Comparison of ODH tests in the presence and in the absence of the Pt-catalyst. Conversion of ethane and oxygen versus heating temperature. Operating conditions as in Fig. 1.

Concerning the single reaction products, it was confirmed that the production of CO_2 and water in the T ranges 200–600°C could be attributed to a catalytic oxidation reaction, as negligible amounts were detected in the empty reactor (Fig. 5). However, at higher temperatures the outlet flow rates of these species were comparable either in the presence or in the absence of catalyst.

Also the production of CO and H_2 in the catalytic tests was significantly higher than that associated with the empty reactor up to 650°C; above this threshold, the formation of synthesis gas in the homogeneous phase became instead important (Fig. 5).

Finally, what was most interesting, the comparison of catalytic tests and blank experiments showed that the production of ethene observed in the presence of the Pt-catalyst could be well explained by the single contribution of the gas-phase reactions (Fig. 6); these were presumably active at high temperature upstream from the catalytic layer. An analogous trend was observed for methane production.

Analogous comparisons between catalytic and blank tests have been performed in the annular reactor at much higher flow rates and lower reactant concentrations in order to verify the possible effect of contact time on the catalyst performance. These experiments are not reported in the present paper for brevity. GHSV values were explored in the range 1×10^6–5×10^6 L(NTP)/(kg cat) h and ethane and oxygen concentration as low as 2% (in N_2) were adopted to the minimized exothermal effects. Still in all the experiments ethane conversion initiated approximately at 200°C oven temperature and gave rise to the initial unique formation of deep oxidation products. Production of CO and H_2 was observed beyond 400°C oven temperature. Comparison with blank experiments gave qualitatively the same results as those herein illustrated.

5. Investigation on the homogeneous oxidative pyrolysis of ethane

A number of tests were performed in the absence of catalyst in order to better evaluate the characteristics and the extent of homogeneous reactions. The

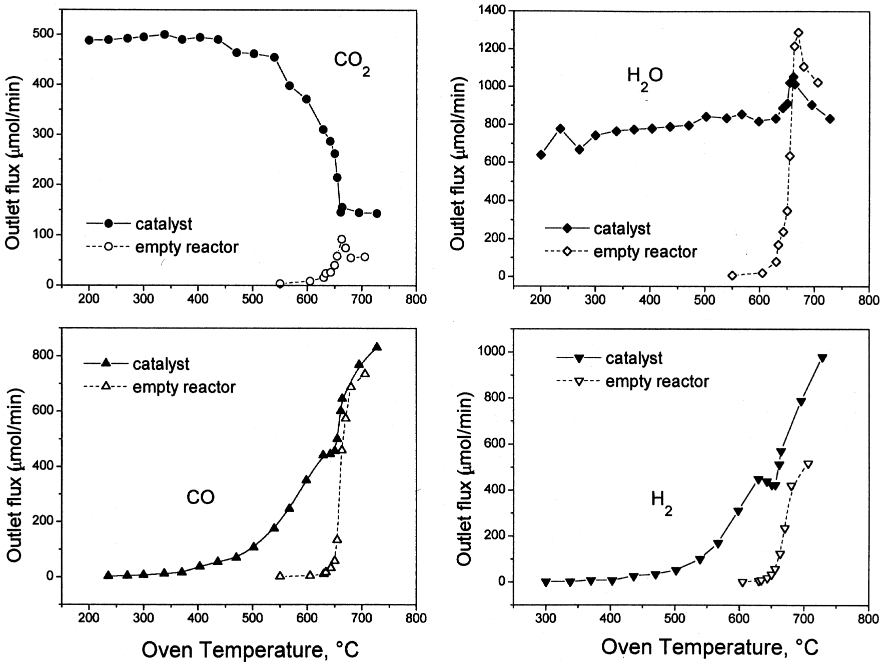

Fig. 5. Comparison of ODH tests in the presence and in the absence of the Pt-catalyst. Flow rate of CO_2, CO, H_2O and H_2 versus heating temperature.

effects of temperature, contact time, and feed composition were explored and a detailed report of the results will be given in a forthcoming paper. These tests confirmed that already above 600°C gas-phase reactions were active in the annular reactor at contact times in the order of 0.1 s. Ethene was the most important reaction product in several experiments and its selectivity decreased with increasing ethane conversion; CO was the most abundant reaction by-product in correspondence with high reactant conversions. These observations were fully confirmed by the theory of ethane oxidative pyrolysis. Data and simulations showed a very good agreement on a quantitative basis and both concurred to evidence that selectivities higher than 60% could be obtained with conversions up to 80% in a homogeneous reactor fed with ethane/air mixtures and ethane/oxygen = 1/1 ratios.

6. Autothermal production of ethene: tests and model simulations

All the experimental and theoretical indications seemed coherent with a homogeneous mechanism for the formation of ethene; this is fully in line with the conclusions of a previous investigation on the ODH of propane over the Pt/γ-Al_2O_3 catalyst [7,8].

No positive proof was found that the Pt-catalyst contributed to the selective oxidation of ethane with formation of ethene. On the opposite, strong proofs were collected that the catalyst was active in non-selective oxidation reactions, and that gas-phase oxidative pyrolysis was a fast process with very high ethene selectivities.

These partial conclusions suggested that catalytic phase and homogeneous phase could cooperate in an adiabatic reactor, wherein the catalytic combustion reactions might ignite the gas-phase oxidative pyrolysis reactions. In order to demonstrate this principle, experiments were performed with the Pt-Al_2O_3 catalyst supported on Fecralloy mat in the autothermal reactor, operating at 5 ms contact time. The procedure of light-off consisted in pre-heating the catalytic bed and the feed stream at the minimum temperature necessary for activating the combustion reactions, i.e. 200–250°C (based on the tests in the annular reactor); afterwards the ethane/air stream was fed to the

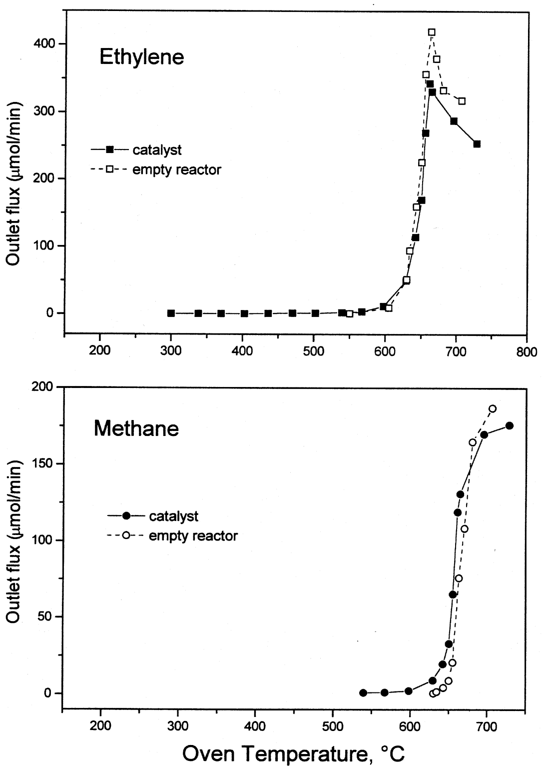

Fig. 6. Comparison of ODH tests in the presence and in the absence of the Pt-catalyst. Flow rate of ethene and methane versus heating temperature.

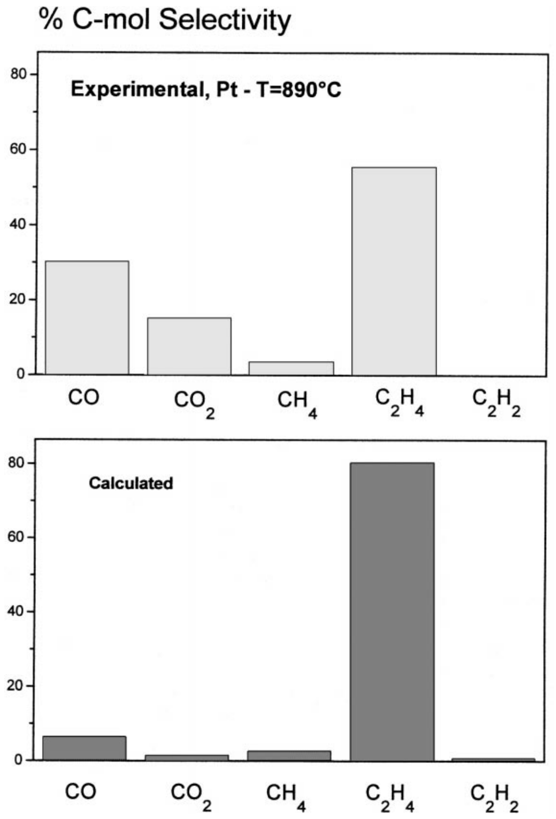

Fig. 7. ODH of ethane in the presence of Pt/γ-Al_2O_3 catalyst in adiabatic reactor. Feed composition: ethane/air with $C_2/O_2 = 2/1$. Contact time: 5 ms. Pre-heat temperature: 250°C.

reactor. The temperature of the catalytic portion had an instantaneous increase from the pre-heat value up to a final steady-state value which ranged between 800 and 1100°C depending on the feed composition.

Fig. 7 reports the results obtained with a 2:1 ethane: oxygen feed ratio, in correspondence with a preheat temperature of 250°C. The final reactor temperature was about 890°C and ethane conversion amounted to 40%. Ethene was the most abundant product in the outlet stream with a C-selectivity of 55%. The total selectivity to CO_X (mostly CO) amounted to nearly 45%, while methane was produced in small amount.

Fig. 7 also reports for comparing the simulation of a purely homogeneous adiabatic reactor operating under similar operating conditions (about 900°C and 6 ms contact time), for an equal value of ethane conversion as that observed experimentally. The simulation refers to an *isothermal* adiabatic reactor, i.e. regardless of the modality for light-off. Ignition of the ethane/air mixture could not occur spontaneously at such low inlet temperature and short contact time. However, once ignited, the homogeneous process guarantees high ethane conversions and high selectivity to olefins within a few milliseconds. In the present case, it was found that the production of ethene obtainable from a purely homogeneous reactor at few milliseconds contact time was significantly higher (nearly 80% selectivity) than that obtained in the catalytic autothermal reactor.

These indications seemed to suggest that: (1) the presence of the catalyst provided the mean for ignition and allowed for ethane activation even at low inlet temperature and small reactor volume; (2) the combustion reactions which are active over the Pt-catalyst likely favored a partial decomposition of the olefin produced and a consequent increase of CO and CO_2 production.

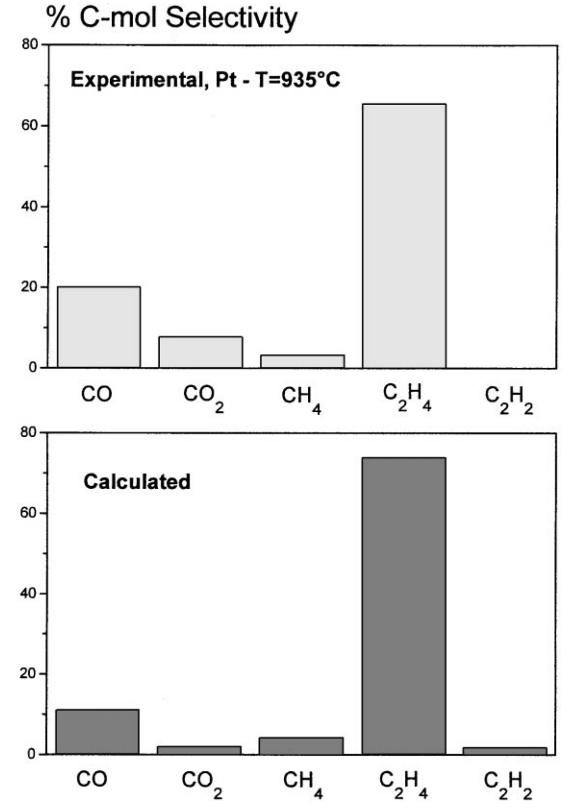

Fig. 8. ODH of ethane in the presence of Pt/γ-Al_2O_3 catalyst in adiabatic reactor. Feed composition: ethane/air with $C_2/O_2 = 2/1$. Contact time: 5 ms. Pre-heat temperature: 450°C.

Different results were obtained when preheating the inlet feed stream at 450°C; results are reported in Fig. 8. The reactor final temperature and the corresponding level of ethane conversion were higher than in the previous case and corresponded to 935°C and 60%, respectively. The observed product distribution was characterized by an increased amount of ethene, whose selectivity grew up to 65%. Again, Fig. 8 also shows the results of the simulation of a homogeneous adiabatic reactor, at the same operating conditions and same degree of ethane conversion. A much closer match was found in this case between experiments and calculations. The experimental ethene yield was closer to the maximum obtainable yield, i.e. the yield of a purely homogeneous reactor. Apparently, at such higher temperature the undesired decomposition of ethene was much less important compared with the faster homogeneous reaction rates. It was thus believed that in the present high-temperature experiment the role of the catalyst had been essentially that of accelerating the reactor light-off, providing for a rapid ignition of the oxidative pyrolysis process.

7. Conclusions

A novel annular reactor was applied to the study of the ODH of ethane over a Pt/γ-Al_2O_3 catalyst. The reaction was studied at very high space velocity on a wider temperature window than that usually associated to the operation of adiabatic reactors. Also, catalytic tests were compared with the results of a campaign of gas-phase experiments, as well as with the theoretical predictions on the expected role of homogeneous reactions. The bulk of data suggested that the production of ethene can be largely explained by the single contribution of radical reactions. The Pt-containing catalyst seemed to be mainly active in the total oxidation of ethane to CO_X.

Tests were also carried out in an autothermal reactor, wherein a cooperation of catalytic combustion and gas-phase oxidative pyrolysis was likely realized. It is believed that the presence of the catalyst accelerated ignition, while ethene production proceeded in the gas-phase.

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