Journal of Catalysis **184,** 469–478 (1999)
Article ID jcat.1999.2447, available online at http://www.idealibrary.com on IDEAL®

Production of Olefins via Oxidative Dehydrogenation of Propane in Autothermal Conditions

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Received November 9, 1998; revised January 29, 1999; accepted January 31, 1999

It was demonstrated experimentally that yields as high as 50% to olefins can be obtained from propane/oxygen mixtures into an adiabatic reactor wherein a Pt-catalyst (active in the oxidation of propane) likely served as ignitor of the gas-phase oxidative pyrolysis. By comparison of the experimental results with the simulations of a purely homogeneous reactor obtained by means of a detailed kinetic scheme, it was found that the addition of the Pt catalyst accelerated ignition and allowed the realization of the same propane conversions of a homogeneous reactor at shorter contact times.

Key Words: **oxidative dehydrogenation; autothermal reactor; homogeneous oxidative pyrolysis.**

INTRODUCTION

In the preceding article (1), some of the authors analyzed the behavior of a commercial Pt/γ-Al_2O_3 catalyst in the oxidative dehydrogenation of propane (a review of the published literature is provided in (1), especially on the results obtained by Schmidt and co-workers by using Pt/α-Al_2O_3 foam monoliths (2)). Briefly, it was found that the Pt-based catalyst was highly active in the oxidation of propane to CO_x, H_2O, and H_2. No evidence was found in favor of the existence of heterogeneous routes to the formation of propylene. Also, gas-phase experiments showed that the homogeneous oxidative pyrolysis of propane could produce ethylene and propylene with a total carbon selectivity higher than 50–60% even at the highest temperatures and propane conversions; the analysis of the dependence of the product distribution on the reaction parameters showed that the total yield to olefins increases by increasing the reaction temperature and by decreasing the contact time.

These pieces of evidence seemed to suggest that an autothermal reactor configuration could realize a synergism between heterogeneous phase and gas phase; in principle, in fact, the catalytic combustion over the Pt/γ-Al_2O_3 can be exploited for providing the reaction heat necessary to ignite and support the homogeneous radical process.

The aim of the present work was to establish a theoretical background about the chemistry of gas-phase propane oxidation at high temperature and short contact times, and, upon this rational basis, to apply experimentally the concept of coupling of catalytic and homogeneous phases in an autothermal reactor for producing olefins from propane.

In the following, an overview of the reaction mechanism involved in the homogeneous oxidative pyrolysis of propane is first presented. This is based on a consolidated expertise in the field of complex kinetic schemes for pyrolysis and combustion of hydrocarbons developed by Dente, Ranzi, and co-workers (3–5). In a preliminary phase, their kinetic model was applied to analyze the expected dependences of propane conversion and olefin selectivity on the reaction operating variables (contact time, temperature, feed composition) in the absence of catalyst; the performance of a purely homogeneous autothermal reactor was also simulated. General indications were thus gained which served for designing, realizing, and interpreting the results obtained in a millisecond contact time adiabatic reactor, wherein the Pt/Al_2O_3 catalyst was primarily used to ignite the gas-phase process. The catalyst was supported onto a Fecralloy-steel fibrous support, which guaranteed a more even temperature distribution. Runs were performed at varying contact times and feed composition, with the aim of maximizing the total yield to ethylene and propylene.

EXPERIMENTAL

The testing unit has been described elsewhere (1). In the following, details are provided about the adiabatic reactor design and operation, which were specific of the present experiments.

Catalyst and Reactor

The catalyst used in the present study was a commercial 5% by weight Pt/γ-Al_2O_3 (Engelhard ESCAT 24), the same catalyst studied in (1). It was deposited via slurry onto small elements of Fecralloy fibrous support, provided by

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0021-9517/99 $30.00

AEA. Fecralloy is a metallic alloy of Fe, Cr, and Al with thermal conductivity of 15 $W/m^2/K$ and a maximum operating temperature of 1375°C. The fibrous configuration is characterized by a very high void fraction (>80%), so that when it is used as barrier for impacting a gaseous stream no pressure drop is built. Experiments in the absence of catalyst showed that the metallic support alone could not ignite the hydrocarbon/oxygen mixture, when heated at the same preheating temperature as in the catalytic experiments. Besides, it is known that at high temperature Fecrally behaves also as inert material due to the migration of Al which forms a thin and uniform surface α-Al_2O_3 layer.

The coated elements of Fecralloy support were packed in the central portion of a 7 mm i.d. quartz tube. To minimize heat dispersion in the axial directions, guards of ceramic particles (0.8–1 mm particle size) were also packed upstream and downstream from the catalytic portion. The ceramic beds were 4–5 cm long. Quartz wool was used to separate the catalytic zone from the ceramic particles, and at the ends of the whole assemblage. A thick layer of quartz wool was also used to insulate the reactor outlet surface, in order to contain radial heat dispersion. A Cu coil with circulating water was used downstream from the insulated zone to cool more rapidly the outlet reactor gas stream. The reactor was inserted into a cylindrical Carbolite furnace with three independent heating zones.

The experiments reported in the following section were obtained with a catalyst load of about 50 mg and a length of the catalytic reactor zone of 2 or 6 mm. This configuration corresponded to a nominal contact time (referred to the whole volume occupied by the coated Fecralloy support) of 0.5–5 ms at the reference temperature of 800°C and the reference flow rate of about 1 L(STP)/min.

Light-off

The start up of the adiabatic reactor consisted in the initial pre-heating of the quartz reactor upstream from and in correspondence with the catalytic zone at 200–300°C, by using the inlet and central zones of the oven only. Already at this temperature the Pt/Al_2O_3 catalyst had been previously proved to be extremely active in the total oxidation of propane (1). Once the catalyst had reached the desired temperature level, the reacting mixture (propane/air or propane/oxygen/nitrogen), initially flowing in a by-pass line, was fed into the reactor. Instantly, the temperature of the catalytic portion had a sharp increase, which was monitored during time. After 20–30 min a steady-state temperature was usually established, ranging between 750 and 1100°C, depending on the operating conditions.

Analyses

When steady-state conditions were reached, the outlet gas stream was sampled and analyzed: two gas chromatographs (GC) were used in parallel. A Varian GC, equipped with a Molecular Sieve column, a Porapak-Q column (both using He as carrier gas), and a thermo-conductivity detector, was used to analyze CO, CO_2, H_2O, and hydrocarbons. A Carlo-Erba GC equipped with a Molecular Sieve column using Ar as carrier gas and a TCD was used to analyze the concentration of H_2.

Propylene, ethylene, methane, CO_x, H_2O, and H_2 were the most abundant species in the product mixture. Ethane was also observed in lower amounts. Small quantities of other species were also detected; these included C_1 and C_2 oxygenates (mainly formaldehyde and acetaldehyde) and C_4 hydrocarbons and accounted for 2–7% of the total converted carbon atoms depending on the operating conditions. C, O, and H atomic balances (converted vs produced) were verified in each experiment and errors were always within 5%.

THEORY OF PROPANE OXIDATIVE PYROLYSIS

The detailed reaction scheme used herein for analyzing the behavior of propane/oxygen mixtures in the gas phase has been discussed in detail elsewhere (4). In its extensive formulation, the kinetic model includes more than 150 species and over 3000 elementary steps. In the following, the main steps that are specifically involved in the oxidative pyrolysis of propane are first illustrated. Then the predicted effects of contact time, temperature, and propane/oxygen feed ratio on the product distribution are analyzed. The simulation of an autothermal reactor is also addressed and guidelines are drawn for the rational design of an adiabatic reactor wherein the catalytic phase is used for igniting the gas-phase process.

Reaction Mechanism

It is well understood that combustion and pyrolysis processes mainly proceed via a chain radical mechanism (6).

Like in the case of pure pyrolysis, the gas-phase mechanism of propane oxidative pyrolysis always proceeds through the successive reactions of *n*- and *iso*-propyl radicals. When oxygen is present in the reacting mixture, the chain radical initiation step

$$O_2 + C_3H_8 \rightarrow HO_2 + C_3H_7 \qquad [1]$$

requires only 46 kcal/mol, while the chain initiation reaction in case of pure pyrolysis is

$$C_3H_8 \rightarrow CH_3 + C_2H_5 \qquad [2]$$

with an activation energy of about 87.5 kcal/mol. Reaction (1) prevails at low temperature and high oxygen concentrations.

Once the first radicals are formed, chain propagation steps are the H abstraction (or metathesis) reactions,

$$R + C_3H_8 \rightarrow RH + n\text{-}C_3H_7 \quad [3]$$

$$R + C_3H_8 \rightarrow RH + \text{iso-}C_3H_7, \quad [4]$$

and successive reactions of propyl radicals form ethylene and propylene:

$$n\text{-}C_3H_7 \rightarrow C_2H_4 + CH_3 \quad [5]$$

$$\text{iso-}C_3H_7 \rightarrow C_3H_6 + H. \quad [6]$$

The differences between pyrolysis and oxidation reactions rely on the relative reactivity of the different radicals. When oxygen is present in the reacting mixture, OH radicals (R in steps [3] and [4]) become the dominant ones and accelerate the hydrocarbon decomposition path. Instead, in pyrolysis conditions H and CH_3 radicals justify more than 90% of propane decomposition via reactions [3] and [4].

Thus the main effect of oxygen is on the decomposition rate rather than on the olefin selectivities. This is better shown in Fig. 1 where the calculated propane conversion of an isothermal plug flow reactor operating at 900°C is reported versus contact time, in the presence and absence of oxygen, respectively. It was estimated that under oxidative conditions only 3 ms are required to reach 50% propane conversion, while pyrolysis requires about 24 ms. The initial ethylene and propylene selectivities are only marginally affected by the oxidative conditions. Successive oxidation reactions of propylene justify its lower selectivity at high propane conversion in the case of presence of oxygen. A comparison of the complete product distribution at 50% propane conversion is given in Table 1.

Noticeably, oxidative pyrolysis is associated to a lower production of methane than pure pyrolysis. With or without O_2, methyl radicals are mostly formed by reaction [5]. Successive H-abstraction reactions to form CH_4 are the main fate of this radical under pyrolysis conditions, while the formation of methoxy radical CH_3O and its successive decomposition steps to form formaldehyde

$$CH_3 + O_2 \rightarrow CH_3O + O \quad [7]$$

$$CH_3O + M \rightarrow CH_2O + H + M \quad [8]$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad [9]$$

become relevant under oxidative conditions.

TABLE 1

Comparison between the Calculated Product Distribution from Oxidative Pyrolysis (Propane/Oxygen = 1/1) and from Pyrolysis at 50% Propane Conversion

	Oxidative pyrolysis	Pyrolysis
CH_4	33.1	51.2
C_2H_2	1.0	1.8
C_2H_4	54.2	55.5
C_2H_6	4.6	2.2
C_3H_4	0.7	0.3
C_3H_6	27.8	37.9
C_4H_6	0.2	0.7
C_4H_8s (and C_4H_{10} 0.17)	1.4	1.6
C_5s	0.3	0.5
Acrolein and acetone	1.0	—
CH_3CHO (and ketene 1.7)	4.7	—
CH_3OH	2.2	—
CH_2O	13.3	—
CO	21.7	—
CO_2	2.4	—

Note. $T = 900°C$, $P = 1$ bar. Results are reported in terms of % mole selectivity. Mole selectivity of species *i* is defined as the number of moles of *i* produced per mole of propane converted.

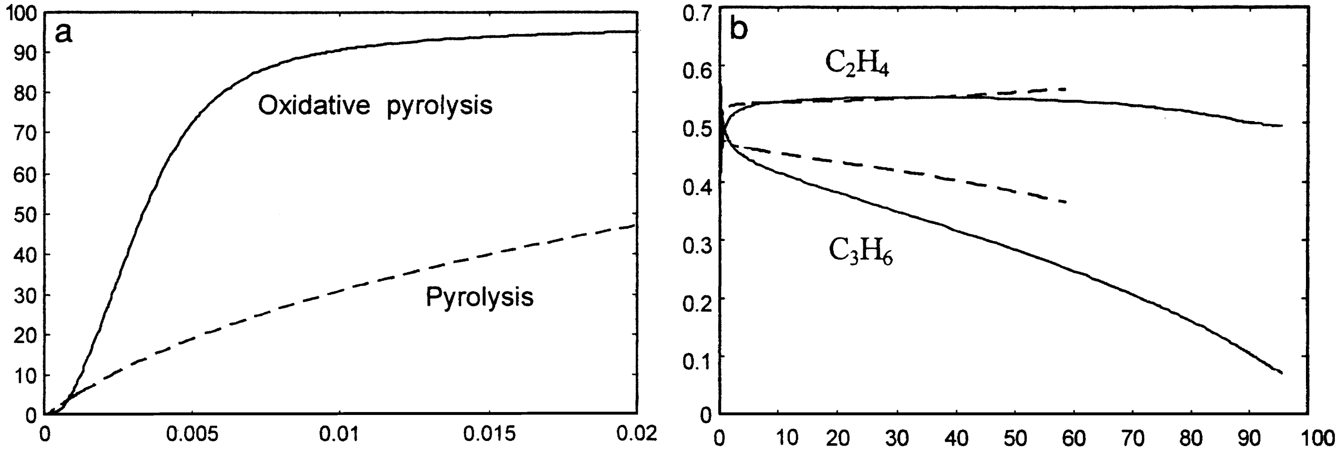

FIG. 1. Model calculations: comparison between pure pyrolysis and oxidative pyrolysis (inlet propane/oxygen feed ratio, 1) in an isothermal plug flow reactor; $T = 900°C$, $P = 1$ bar. (a) % propane conversion vs contact time. (b) Mole selectivity of ethylene and propylene at varying propane conversion.

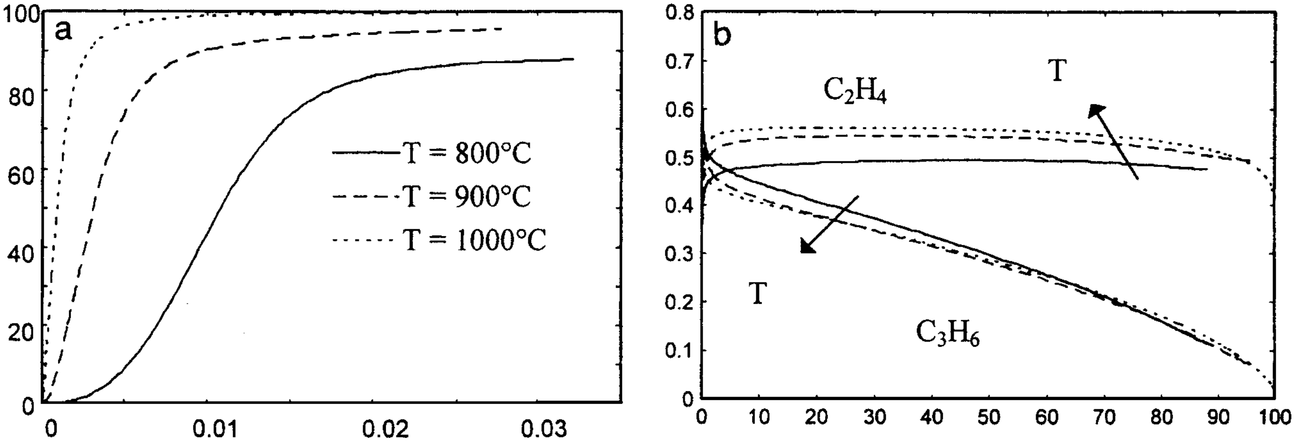

FIG. 2. Model calculations: effect of reaction temperature on (a) propane conversion and (b) ethylene and propylene mole-selectivity. Isothermal plug flow reactor. Propane/oxygen feed ratio, 1; $P = 1$ bar. (a) % propane conversion vs. contact time, s; (b) mole-selectivity vs. propane conversion.

Successive reactions of formaldehyde justify then the formation of CO and CO_2.

$$CH_2O \rightarrow HCO \rightarrow CO \rightarrow CO_2 \qquad [10]$$

Methanol formation can be explained on the basis of the H-abstraction reactions of methoxy radical and the recombination reactions of methyl and OH radicals:

$$CH_3O + RH \rightarrow CH_3OH + R \qquad [11]$$

$$CH_3 + OH + M \rightarrow CH_3OH + M. \qquad [12]$$

Acrolein and acetone as well as C_2 oxygenated species are the major intermediate species in the oxidation processes of propylene and ethylene.

Effects of T and C_3H_8/O_2 Feed Ratio on the Product Distribution

As already mentioned, propane decomposition is mostly justified by the H-abstraction reactions [3] and [4]. As a consequence, the final product distribution is mainly governed first by the relative importance of these reactions, i.e., the relative formation of *n*- and iso-propyl radicals, and then by their successive reactions.

Reactions [3] and [4] involve the H-abstraction respectively of 6 primary and 2 secondary H atoms. Always referring to the previous kinetic scheme (5), the ratio of the kinetic constants *k* of reactions [3] and [4] when OH and H are the attacking radicals is only a weak function of the temperature:

$$k_3/k_{4\text{-OH}} = 4.0\exp(-1650/RT)$$

$$k_3/k_{4\text{-H}} = 4.0\exp(-2550/RT).$$

Accordingly, ethylene and propylene selectivities show only a moderate dependence on temperature at equal propane conversion. As an example, Fig. 2 reports the simulation of oxidative pyrolysis in the three cases of 800, 900, and 1000°C reaction temperature, assuming a propane/oxygen feed ratio of 1. Propylene selectivity is only marginally affected by temperature. Ethylene selectivity tends to decrease at decreasing operating *T*. Such reduction of the olefin yield at low temperature is explained on the basis of the longer contact times (to reach the same conversion) and therefore of the onset of successive condensation reactions.

Always referring to ideal isothermal conditions, the effect of different propane to oxygen ratios was also analyzed; the cases of C_3H_8/O_2 feed ratios 0.5, 1, and 2 in a plug flow reactor operating at 897°C were considered. Figure 3 reports (a) the predicted conversion of propane vs contact time and (b) the selectivity of ethylene and propylene vs propane conversion in the three cases. It can be observed that the feed composition strongly affects the extent of propane decomposition; with increasing O_2 feed content, progressively shorter contact times are necessary to guarantee equal conversion and, for a fixed reaction temperature, the maximum attainable propane conversion increases as well. Instead, olefin selectivity is an almost unique function of the hydrocarbon conversion and is scarcely affected by feed composition. Differences among the curves reported in Fig. 3b can be justified by the different contact times and extent of consecutive reactions.

Simulation of Autothermal Operation

The kinetic scheme was applied to the simulation of the performance of an autothermal reactor with inlet temperature $T_{IN} = 327°C$. Figure 4 reports the calculated propane conversion vs contact time at varying propane/oxygen feed ratio. It was found that reactor light-off is progressively retarded with decreasing oxygen content; for a fixed reactor volume, these profiles indicate that at increasing

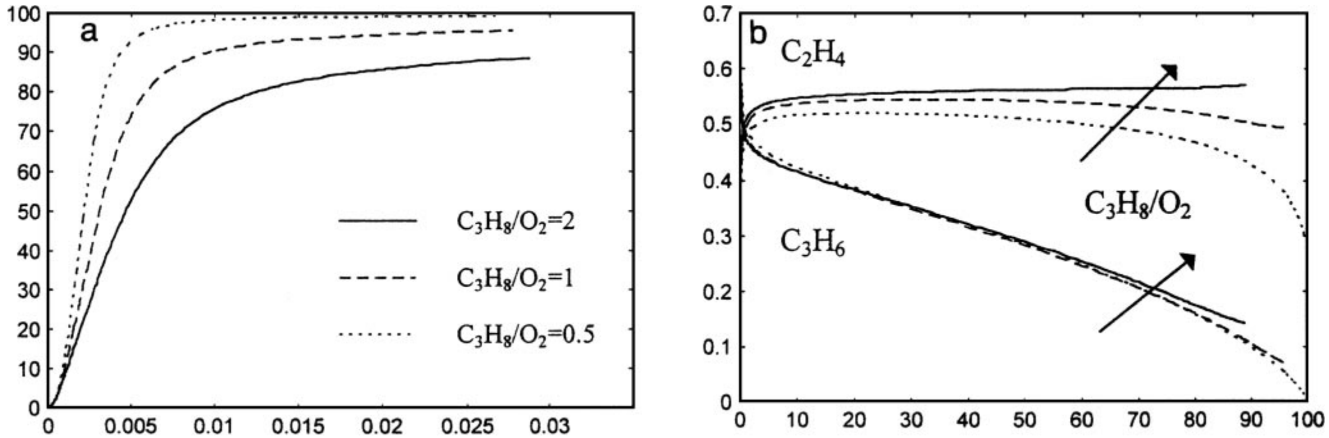

FIG. 3. Model calculations: effect of propane/oxygen feed ratio on (a) propane conversion and (b) ethylene and propylene mole selectivity. Isothermal plug flow reactor. $T = 897^\circ\text{C}$. $P = 1$ bar. (a) % propane conversion vs. contact time, s; (b) mole-selectivity vs. propane conversion.

propane/oxygen ratio a progressively smaller portion of the reactor participates in the reaction and, as a consequence, the final propane conversion and the outlet temperature decrease accordingly. In correspondence with an inlet propane/oxygen ratio of 3, reaction does not ignite within 20 ms and no propane conversion is realized.

In general, it has been verified that a critical propane/oxygen feed ratio exists, above which reaction does not occur. For a fixed reactor volume, such a critical threshold depends on the inlet reactor temperature. An increase in T_{IN} tends to favor the ignition and larger propane/oxygen ratios are allowed. As a comparison, it was estimated that for $T_{\text{IN}} = 127^\circ\text{C}$ the critical C_3/O_2 ratio above which no conversion of propane is realized within 20 ms is about 1.0.

Concerning the predicted product distribution obtainable with an autothermal reactor, the reduction of the severity of the system which accompanies the enrichment of hydrocarbon in the feed (i.e., lowering of the overall exothermicity and consequent decrease of both temperature and propane decomposition) has a beneficial effect on the olefins selectivity. As shown in Fig. 5, the carbon selectivity of propylene increases progressively at increasing propane/O_2 ratio up to about 25%; ethylene selectivity undergoes a significant increase as well and amounts to 35% at the highest propane concentrations. Conversely, selectivity of CO_x is predicted to decrease significantly. Autothermal operation is thus expected to guarantee the realization of total C-selectivities to olefins higher than 55–60%, in correspondence with high propane conversions. In a purely homogeneous adiabatic reactor, contact times within 20 ms seem preferable in order to limit the effect of consecutive reactions and maximize the olefin production.

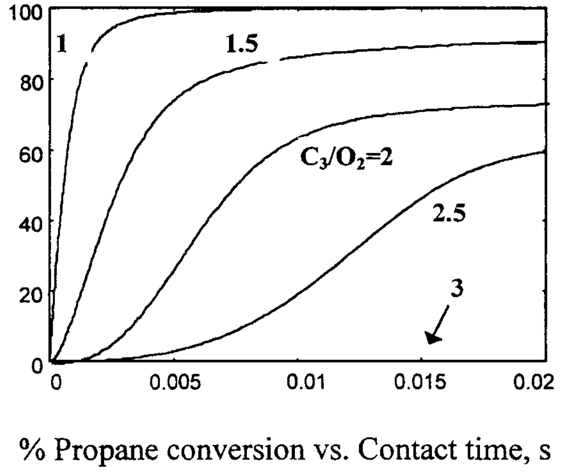

FIG. 4. Model calculations: simulation of an adiabatic plug flow reactor with inlet $T = 327^\circ\text{C}$. Profiles of propane conversion vs contact times at varying propane/oxygen feed ratio.

Guidelines for the Design of an Autothermal Reactor

Major indications from the theoretical analysis of the homogeneous oxidative pyrolysis of propane are as follows.

- Operating conditions affect primarily propane conversion, but only weakly the product distribution.
- The product distribution is mainly controlled by the extent of propane decomposition. In particular, propylene selectivity tends to decrease at increasing propane conversion. As a consequence, the total olefin selectivity increases at decreasing contact time and temperature and at increasing propane/oxygen feed ratio. In other words, the formation of olefins, especially propylene, benefits from a reduction of the severity of the reacting system.
- Opposite to the case of pure pyrolysis, which is highly endothermic, purely homogeneous oxidative pyrolysis can sustain autothermal operation at short contact times, provided sufficiently high pre-heat and oxygen feed content. In adiabatic conditions, the increase of the propane/oxygen

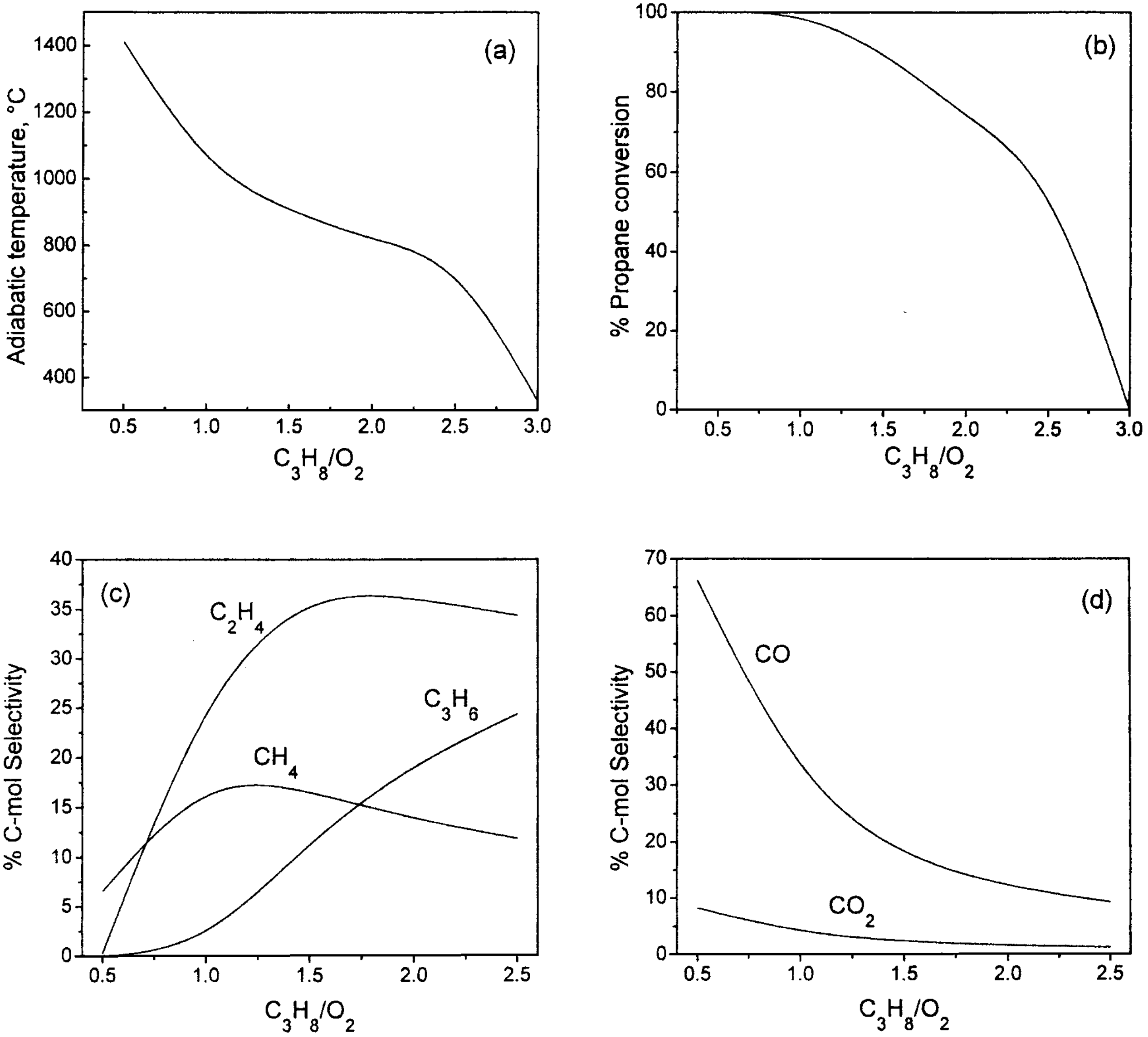

FIG. 5. Model calculations: simulation of an adiabatic plug flow reactor. Effect of propane/oxygen feed ratio on (a) adiabatic temperature, (b) propane conversion, (c, d) distribution of the C-containing products. $T_{IN} = 327°C$; contact time, 20 ms; $P = 1$ bar.

feed ratio lowers the severity of the system and is accompanied by an increase of propylene C-selectivity up to 25%. Ethylene selectivity is also favored by high propane/oxygen feed ratios and amounts to 30–35%. Propane conversions can be obtained ranging between 50 and 100%.

These standpoints were exploited for rationalizing the design of an autothermal reactor for the oxidative dehydrogenation of propane, wherein the Pt-catalyst provided ignition to the gas-phase process. In particular, short contact times and high propane/oxygen feed ratios were looked for in order to enhance the selectivity to olefins. Differences from the calculated product distributions of a purely homogeneous adiabatic reactor were expected, though, due to the presence of the catalyst phase.

LAB-SCALE TESTS IN AUTOTHERMAL REACTOR

Reactor Dynamics

Figure 6a shows the typical dynamics of the reactor light-off observed during the auto-thermal experiments; time $t =$ 0 indicates the instant when the feed stream was switched from the by-pass line into the reactor. Within less than 30 s, temperature (read by positioning the thermocouple at mid length of the catalytic bed) increased over 500–600°C, while after 20–30 min it reached a steady-state level. Actually, a residual increase in temperature of 20–50°C could occurr during the following hours of operation of the reactor.

The temperature reached strictly depended on the operating conditions, and was usually close to the theoretical

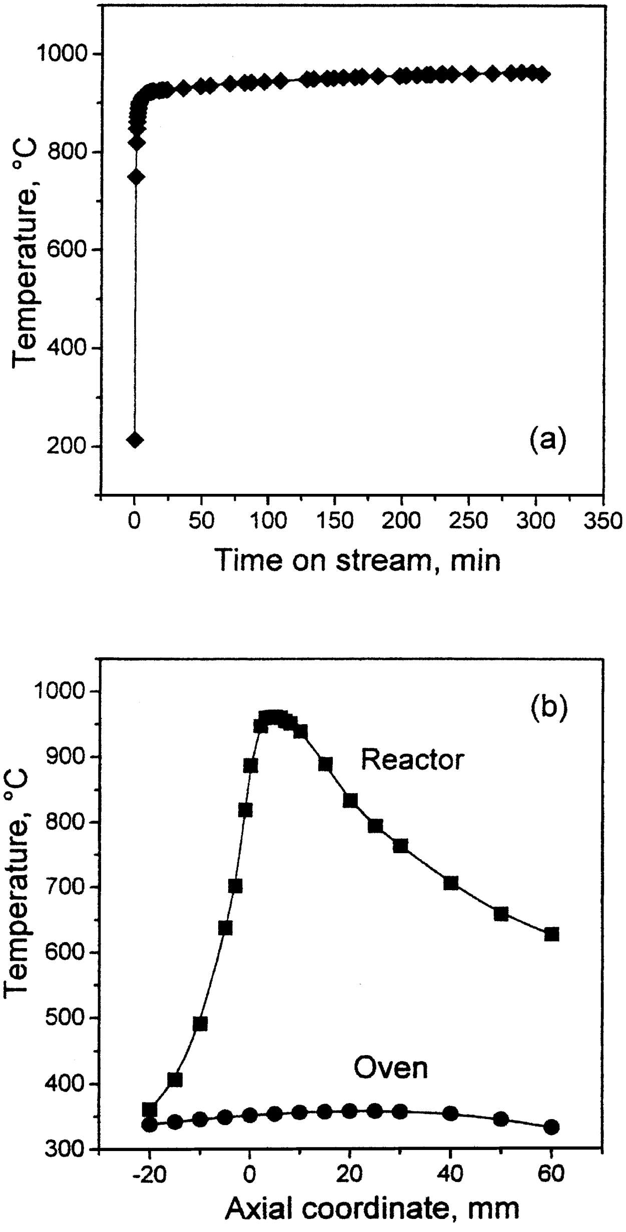

FIG. 6. Experimental. (a) Example of the temperature increase during light-off of the reactor. Time zero corresponds to the instant when the reacting mixture is fed into the pre-heated reactor. Total flow rate, 0.98 L(STP)/min. Propane/oxygen feed ratio, 1. (b) Example of the axial temperature profile under steady-state conditions.

adiabatic temperature with differences lower than 100°C.

It was observed that only when operating at sufficiently high flow rates (higher than 0.5 L(STP)/min in the case of air) did light-off effectively occur with temperatures higher than 750°C reached, onset of gas-phase oxidative pyrolysis and consequent formation of olefins. At flow rates in the range of 0.3 L(STP)/min, temperatures not higher than 500°C were reached in the catalytic portion; only products of combustion were present in the outlet gas stream with a total conversion of oxygen, and 20% conversion of propane but no ignition of the gas phase or formation of olefins occurred. Huff and Schmidt (7) had already observed that only high flow rates guaranteed the desired high-temperature operation of an autothermal foam monolith reactor. The effect of flow rate was attributed to the increase of the rate of heat production from the reaction, which counterbalanced and eventually overcame the reactor heat dispersions. The same interpretation is applied to the present experiments; however, it must be specified that propane combustion over the catalyst particles is herein believed the source of heat production responsible for the reactor ignition.

Steady-State Temperature Profiles

When steady-state conditions were reached, the axial temperature profile of the adiabatic reactor was measured by sliding the internal thermocouple. An additional thermocouple was used to measure the longitudinal profile of the oven wall. Figure 6b shows an example of the two profiles. It is noted that the catalytic portion of the reactor presented the highest temperatures; however, short portions of the reactor upstream and downstream from the catalyst were at high temperature enough to justify a contribution from gas-phase reactions. This evidence suggests that in practice the exact definition of the contact time for an autothermal lab-scale reactor is hardly achievable and that in general contributions from zones close to the catalytic region should be taken into consideration.

Effect of Propane/Oxygen Feed Ratio

Experiments were performed at varying propane/oxygen feed ratio in the range 1–2.4 with a total flow rate of 0.98 L(STP)/min and a constant oxygen flow rate of 163.5 cm^3 (STP)/min. As reported in Fig. 7a, the maximum temperature (located between 2 and 4 mm from the inlet section of the catalytic zone) decreased from 960°C for an equimolar feed to nearly 850°C at propane/oxygen ratio of 2.4. The measured conversions of the reactants are reported in Fig. 7b. Oxygen conversion was always almost complete (95–100%), while propane conversion progressively decreased from 90 to 43% at increasing propane flow rate. The product distribution (represented in Figs. 7b and 7c) was significantly affected by changing the feed composition. A remarkable increase in propylene selectivity from 10 to about 28% was observed. Ethylene selectivity kept almost constant at nearly 30%. CO C-mole selectivity decreased from 37 to 21%. As a total result, thus, by increasing the propane/oxygen feed ratio from 1 to 2.4 the total olefin selectivity grew up to 55–60%, while the total CO_x selectivity decreased from 45 to 28%. Figure 7d also reports the distribution of the H-containing products; water (the co-product of propylene in the oxidative dehydrogenation of propane) was always produced in a much larger

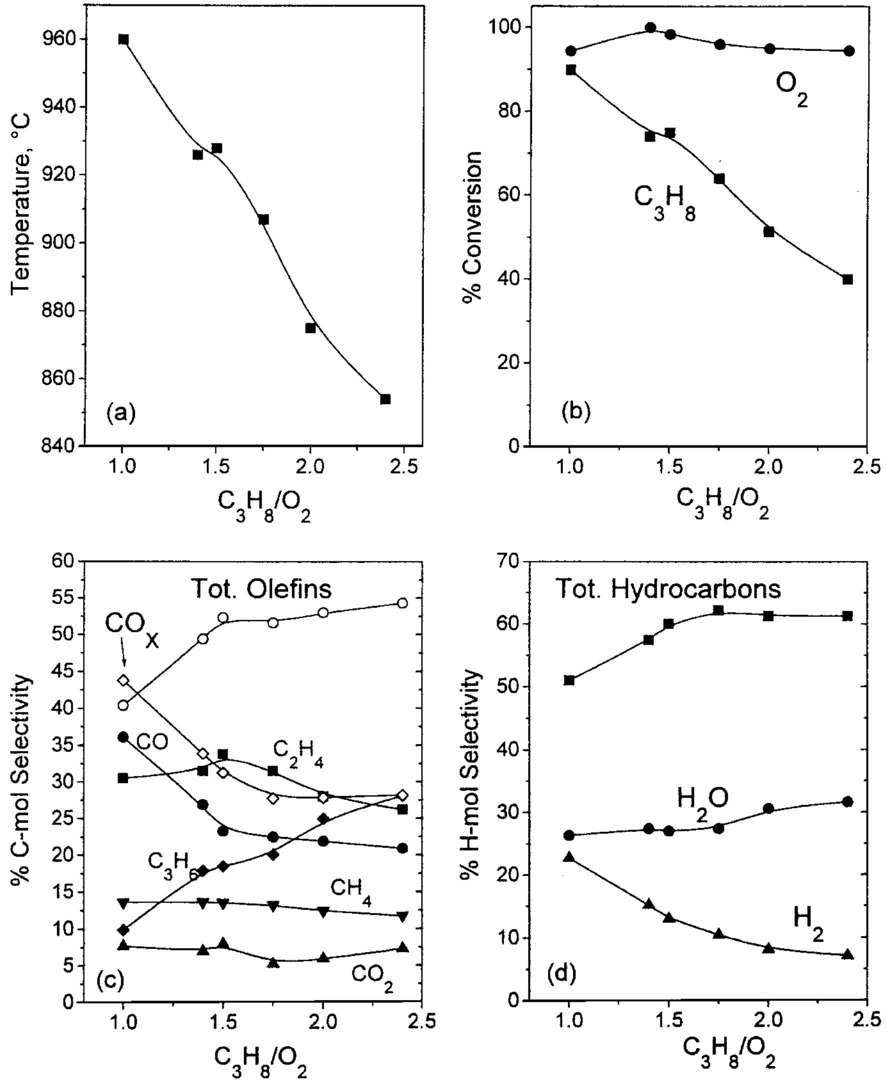

FIG. 7. Experimental: effect of propane/oxygen feed ratio on (a) reactor temperature, (b) propane conversion, (c) distribution of the C-containing products, and (d) distribution of the H-containing products. Catalyst bed length, 6 mm. Total flow rate, 0.98 L(STP)/min, pre-heat $T = 250°\text{C}$, $P = 1.1$ bar.

amount than H_2 and its selectivity increased with increasing propane/oxygen feed ratio, similarly to the increase of propylene selectivity.

The reactor temperature, the extent of propane conversion, and the olefin yield observed in the Pt-containing autothermal reactor were thus in very close agreement with the predictions of the purely homogeneous kinetic scheme reported in Figs. 4 and 5. The experiments were indeed performed in correspondence with operating conditions (pre-heat temperature and range of propane/oxygen feed ratios) which are compatible with the purely thermal activation of propane. However, it seems that the high yield to olefins were realized at shorter residence times than predicted by the model; it is noted in fact that the time (reactor volume) scale of Fig. 4 is at least 2 to 3 times larger than that characteristic of the experiments. This would suggest that the presence of the catalyst (that is the overimposition of a combustion route to the gas-phase process) accelerated the reactor ignition. This is also in line with the observation of higher selectivities to CO_2 and H_2O during the operation of the lab-scale reactor than predicted for the ideal purely homogeneous reactor. Such a higher production of CO_2 was however moderate and the selectivity observed for ethylene and propylene were very close to the maximum attainable values in a purely homogeneous process; this would indicate that under steady-state conditions the combustion kinetics interfered only at a small degree with the gas-phase process. It is beyond the scope of the present paper to find an exact quantification of the extent of propane decomposition due to the combustion over the catalyst phase, given the already mentioned uncertainty in the definition of the reaction volume. However, it seems that the twofold evidence,

(1) the catalyst tended to shorten the contact times necessary for realizing the same propane conversion of a gas-phase reactor and
(2) the yields to olefins obtained with or without catalyst were comparable,

is in agreement with a primary role of the catalyst phase uniquely in the reactor light-off, and with the prevailing role of the sole gas-phase process once the reactor temperature is sufficiently high for activating the self-sustainable oxidative pyrolysis.

Effect of Contact Time

The effect of contact time was studied by reducing the volume packed with the coated Fecralloy elements to 0.03 cm^3 (corresponding to a length of catalytic zone of 2 mm). At the reference flow rate of 983 cm^3(STP)/min and temperature of 850°C this volume corresponded to a *nominal* contact time (see considerations above on the *T* profile) of 0.5 ms. The results obtained with the feed composition $C_3H_8 : O_2 : N_2 = 1 : 1 : 4$ are reported in Table 2 and compared with those obtained, under the same operating conditions, at 3 ms contact time. The maximum reactor temperature was much lower in the smaller reactor; also the conversions of both reactants were significantly lower at the shorter contact time. The total amount of olefin was comparable: however, at the extremely, short residence time, the selectivity of propylene was significantly higher, in line with the theoretical indications about the beneficial effect of less severe conditions (lower *T* and shorter contact time are in fact expected to disfavor propylene cracking).

TABLE 2

Results of Oxidative Dehydrogenation of Propane in the Lab Reactor with 6 and 2 mm Catalytic Bed Lengths

Catalyst bed length (mm)	6	2
Propane conversion (%)	90	42
Oxygen conversion (%)	95	70
Maximum temperature (°C)	960	811
CO C selectivity (%)	36	35
CO_2 C selectivity (%)	8	12
CH_4 C selectivity (%)	13	11
C_2H_4 C selectivity (%)	30	20
C_3H_6 C selectivity (%)	10	17
Others, C selectivity (%)	3	2

Note. The two cases correspond to nominal contact times of 3 and 0.5 ms at 983 cm^3(STP)/min and 850°C. The results are reported in terms of % carbon selectivity. C selectivity of species *i* is defined as: (moles of *i* produced) × (carbon atoms number of species *i*)/(moles of propane converted × 3).

TABLE 3

Effect of Reducing N_2 Flow Rate

N_2 flow rate (cm^3(STP)/min)	654	502	393	284	164
Propane conversion (%)	42	42	43	64	99
Oxygen conversion (%)	70	60	60	70	98
Maximum temperature (°C)	811	850	830	880	1150
CO C selectivity (%)	35	34	30	20	37
CO_2 C selectivity (%)	12	8	11	8	10
C_2H_4 C selectivity (%)	20	22	24	30	30
C_3H_6 C selectivity (%)	17	19	20	17	1

Note. Catalyst bed length, 2 mm. Propane = oxygen flow rate, 164 cm^3 (STP)/min.

Effect of Diluent

The nitrogen flow rate was reduced from 654 to 164 cm^3 (STP)/min, while oxygen and propane flow rates were kept constant at 164 cm^3(STP)/min. The results obtained are reported in Table 3 and refer to the reactor configuration with small catalytic portion (0.03 cm^3). As expected, the reactor temperature increased progressively with decreasing N_2 concentration from 811 to 1150°C. An increase in the propane conversion was observed; conversion of oxygen and conversion of propane were complete at the highest temperature investigated. The decrease in nitrogen flow rate and the increase in propane conversion initially resulted in a decrease of CO_x selectivity and an increase of propylene selectivity. Ethylene selectivity progressively increased from 20 to 30%. However, in agreement with the general indications provided by the model analysis, at very low N_2 concentration and extremely high reaction temperature propylene selectivity had a dramatic drop in favor of an increase of CO_x selectivity.

Experiments with an increase of the propane/oxygen feed ratio were repeated with the small volume adiabatic reactor at low N_2 concentration. The results are reported in Table 4.

TABLE 4

Effect of Propane/Oxygen Mole Feed Ratio

C_3H_8/O_2 feed ratio	1.0	1.5	1.8	2.0	2.3
Maximum temperature (°C)	1132	968	909	872	868
Propane conversion (%)	99	90	70	64	57
Oxygen conversion (%)	94	99	99	99	95
CO C selectivity (%)	37	20	16	14.5	9.5
CO_2 C selectivity (%)	10	8	8	9	8.5
C_2H_4 C selectivity (%)	30	40	39	38	37
C_3H_6 C selectivity (%)	1	10	15	17.5	23
CO_2 C selectivity (%)	47	28	24	23.5	18
Olefins C selectivity (%)	31	50	54	55.5	60

Note. Catalyst bed length, 2 mm. Oxygen flow rate, 164 cm^3(STP)/min; total flow rate, 491 cm^3(STP)/min.

TABLE 5

Optimization of Total Olefin Yield

Temperature (°C)	868	900	930	910	957
Propane conversion (%)	57	72	82	90	99
Oxygen conversion (%)	96	100	100	100	100
CO C selectivity (%)	9.5	12.5	17.5	17.1	20
CO_2 C selectivity (%)	8.5	7.8	3.9	3.0	2
C_2H_4 C selectivity (%)	37	38	38.7	40.5	42
C_3H_6 C selectivity (%)	23	20	17.5	13.6	5
Olefins yield (%)	34	42	46	49	47

Note. Catalyst bed length, 2 mm. Oxygen flow rate, 164 cm^3(STP)/min; total flow rate, 491 cm^3(STP)/min; propane/oxygen feed ratio, 2.3. Yield of species *i* is defined as: (C selectivity of species *i*) × (propane conversion).

Again, the increase in C_3H_8/O_2 feed ratio from 1 to 2.3 was accompanied by a decrease in the maximum temperature (though still higher than those reported in Fig. 7) and of propane conversion (from 99 to 57%). Also in this case, then, a remarkable increase in olefins productivity was observed; the total C selectivity of ethylene and propylene progressively increased and reached 60%. At the highest propane/oxygen feed ratio, total selectivity to CO_x was instead very low, equal to 18% in correspondence with the highest selectivity to olefins.

Optimization of Olefin Yield

Once the feed composition that guaranteed the best selectivity of olefins was identified, an effort was made to increase the yields of the desired products by enhancing the propane conversion. This was obtained by increasing the oven temperature in the pre-heat zone and in the central portion around the catalytic zone; by compensating the reactor heat-losses, temperature inside the catalytic region slightly increased from 870 to nearly 960°C. The results are reported in Table 5. This 90°C *T* increase was sufficient to enhance propane conversion from 57% up to complete conversion. Selectivity to ethylene moderately increased from 37 to 42%. Propylene selectivity decreased especially at the highest temperatures; however, the total selectivity to olefins was always very high. The yields to olefins, thus, progressively increased and at the catalyst temperature of 910°C the best yield to ethylene and propylene was reached and corresponded to 49% with a propane conversion of 90% and total conversion of oxygen.

CONCLUSIONS

Oxidative dehydrogenation of propane in autothermal conditions has been theoretically and experimentally investigated. The experiments were performed in the presence of a Pt/Al_2O_3 catalyst deposited onto a high void fraction metallic support, at contact times in the range of fractions to a few milliseconds. The catalyst (active in the highly exothermic oxidation of propane to CO_x) acted as ignitor of the gas-phase radical process. Reduction of contact time and propane/oxygen feed ratios >2 were favorable conditions for producing selectively olefins. The best total yield to ethylene and propylene, which was realized in the present experimental campaign, amounted to nearly 50% with 90% conversion of propane and 100% conversion of oxygen.

The theoretical investigation about the expected behavior of propane/oxygen mixtures in the sole gas phase provided very useful elements for better rationalizing the results of the lab-scale reactor. It has been shown that oxidative pyrolysis of propane can be run adiabatically also in the absence of a catalyst, that is in a purely homogeneous process, provided a proper design of pre-heat temperature and oxygen content of the feed stream. However, the data herein presented seemed to suggest by comparison with the model simulations of a homogeneous adiabatic reactor that the addition of the Pt catalyst allowed a reduction of contact times, which was especially appreciable at the highest propane/oxygen feed ratios investigated. The authors are aware that this effect could in principle be attributed to a catalytic promotion of olefin production. However, the similitude between the observed product distributions with those characteristic of a homogeneous reactor and the strong evidence that $Pt/\gamma\text{-}Al_2O_3$ is an excellent catalyst for propane combustion (1) suggest that in the adiabatic tests the catalytic phase simply provided an acceleration of the light-off. It seemed also that under steady-state conditions (once the gas-phase reactions were ignited) the role of the catalyst phase was rather small; the yields to olefins realized in the presence of the Pt catalyst were in fact comparable with the maximum value obtainable in a purely homogeneous process.

ACKNOWLEDGMENTS

This work was financially supported by ENI and SNAMPROGETTI. The authors are grateful to Professor Mario Dente-Politecnico di Milano for his precious suggestions; they also thank Ing. Laura Piovesan, SNAMPROGETTI, for participating in the discussion of the research.

REFERENCES

1. Beretta, A., Piovesan, L., and Forzatti, P., *J. Catal.* **184**, 455 (1999).
2. Huff, M., and Schmidt, L. D., *J. Catal.* **149**, 127 (1994).
3. Dente, M., and Ranzi, E., *in* "Pyrolysis: Theory and Industrial Practice" (L. F. Albright *et al.*, Eds.), Chap. 7, Academic Press, New York, 1983.
4. Ranzi, E., Faravelli, T., Gaffuri, P., Pennati, G. C., and Sogaro, A., *Combust. Sci. Tech.* **100**, 299 (1994).
5. Ranzi, E., Faravelli, T., Gaffuri, P., Garavaglia, E., and Goldaniga, A., *Ind. Eng. Chem. Res.* **36**, 3336 (1997).
6. Albright, L. F., Crines, B. L., and Corcoran, W. H., "Pyrolysis: Theory and Industrial Practice." Academic Press, New York, 1983.
7. Huff, M., and Schmidt, L. D., *J. Phys. Chem.* **97**, 11815 (1993).