Journal of Catalysis **184,** 455–468 (1999)
Article ID jcat.1999.2446, available online at http://www.idealibrary.com on IDEAL®

# An Investigation on the Role of a Pt/$Al_2O_3$ Catalyst in the Oxidative Dehydrogenation of Propane in Annular Reactor

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

**Oxidative dehydrogenation of propane was studied over a commercial Pt/$\gamma$-$Al_2O_3$ catalyst using an annular reactor, wherein high space velocities (referred to the catalyst load) and controlled temperature conditions can be realized. The reaction was studied in a wide temperature range. Tests in the presence of the catalyst showed that up to 500°C, only products of combustion were produced; above this temperature olefins were also formed in large amounts. Comparison with additional experiments which were carried out in the absence of the catalyst showed that: (1) the oxidation of propane at low to medium temperatures was purely catalytic; the reaction rate was so fast that in the present annular reactor the catalytic combustion underwent interphase mass transfer control already at 200°C oven *T*; (2) above 500°C gas-phase oxidative pyrolysis of propane was active and could explain the formation of olefins observed in the catalytic tests. Tests of sensitivity of the product yields upon variation of the catalyst load were performed; while the yields of $CO_2$, CO, $H_2O$, and $H_2$ increased with increasing amount of catalyst, the yields of propylene, ethylene, and methane decreased progressively. No positive evidence of heterogeneous formation of olefins was thus provided by the various experiments. The data were coherent with a homogeneous formation of propylene and ethylene.** © 1999 Academic Press

*Key Words:* **propane oxidative dehydrogenation; annular reactor; Pt/$\gamma$-$Al_2O_3$.**

## INTRODUCTION

The oxidative dehydrogenation (ODH) of light alkanes for the production of short-chain olefins is one of the novel routes currently proposed for the exploitation of natural gas as raw material for highly priced and clean chemicals (1). Baerns and Buyevskava (2) have reviewed the best results reported in the oxidative dehydrogenation of ethane and propane; they showed that, although a number of catalytic systems have been proved to be active in the synthesis of olefins including V–Mg–O systems, phosphates, and molybdates of various transition metals, the development of stable catalysts with economically sustainable performances (that is olefin yields >20%) is still challenging.

Very high yields to olefins were reported by Schmidt and coworkers in the oxidative dehydrogenation of ethane (3), propane (4), *n*- and iso-butane (4, 5), as well as $C_5$ and $C_6$ alkanes (6) over Pt-coated $\alpha$-$Al_2O_3$ foam monoliths operating adiabatically at very short contact times (few milliseconds). In the cases of ethane and propane, they obtained almost complete conversion of the alkanes and selectivities to olefins over 60%. In spite of the extremely high reactor temperatures (750–1100°C) associated with the autothermal conditions, the influence of gas-phase reactions in the formation of ethylene and propylene was ruled out and purely heterogeneous mechanisms and kinetic models (3, 4, 7) were proposed.

However, pieces of evidence have been provided in the literature supporting the existence of a significant contribution from the gas-phase pyrolysis reactions to the synthesis of olefins at high reaction temperatures. Burch and Crabb (8) demonstrated that previous data on the oxidative dehydrogenation of ethane over a MgO-based catalyst at temperatures >550°C were strongly affected by noncatalytic reactions, as ethylene yields higher than 30% could be obtained in the empty reactor under the same operating conditions as those used for the catalytic tests. Holmen and coworkers (9) have recently shown that the formation of ethylene via oxidative dehydrogenation of ethane in the presence of Pt and Pt/Rh gauze catalysts at microseconds contact times and temperatures of 700–900°C occurred in the gas-phase; the gauze catalyst was shown to be effective in the heat supply to the reacting gas stream. Faravelli *et al.* (10) have compared the results of experiments in the partial oxidation of *n*-pentane, *n*-hexane, and cyclo-hexane realized in Pt-coated foam monoliths at high temperature and 5-ms contact times (6) with the predictions of a detailed homogeneous reaction scheme (11). They found that most of the data could be well explained by the gas-phase oxidative pyrolysis; though, at hydrocarbon/oxygen feed ratios greater than 0.9 (corresponding to adiabatic temperatures lower than 850–900°C) the experimental product

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distribution was characterized by higher amounts of $CO_2$ than predicted by the homogeneous kinetic model, and these were attributed to the catalytic phase.

Concerning the catalyst, most of the data reported in the literature on partial oxidation of light paraffins refer to low surface area Pt-coated $\alpha$-$Al_2O_3$ foam monoliths. Huff and Schmidt (4) found that Pt was the best catalyst for olefin production among other noble metals; they found for instance that Rh mainly produced $CO/H_2$ mixtures, while Pd rapidly deactivated due to coking. Bodke *et al.* (12) have analyzed the effect of the nature and morphology of the monolith support in various selective oxidations; mullite was found to be the best ceramic support for olefin production in the partial oxidation of ethane. Flick and Huff (13) compared the performance of a Pt/$\alpha$-$Al_2O_3$ monolith with that of much higher surface area Pt/$\gamma$-$Al_2O_3$ pellets and found that the Pt/$\gamma$-$Al_2O_3$ catalyst was active (though slightly less selective than the firmer system) in the oxidative dehydrogenation of ethane with 50% C-selectivity to ethylene and 85% conversion of ethane under adiabatic operation at few-millisecond contact times.

In this work, a study of the oxidative dehydrogenation of propane in the presence of a commercial Pt/$\gamma$-$Al_2O_3$ catalyst is addressed. The experimental investigation was carried out by using a novel structured reactor with annular configuration (14), wherein the catalyst is deposited in the form of a thin and short layer onto a tubular ceramic support which is coaxially inserted in a quartz tube. Elsewhere (15) the authors have shown the advantages of this reactor configuration for the study of high-temperature and high-space velocity catalytic processes, in comparison with standard packed bed reactors. As pressure drops are absent and few milligrams of catalyst can be deposited, very high flow rates and extremely short contact times with respect to the catalytic phase ($10^{-6}$–$10^{-3}$ s) can be easily realized. Also, the peculiar geometry of the system favors the dispersion of heat produced onto the catalyst surface by radiation; as a result, almost isothermal conditions arise along the catalyst layer even in the presence of a highly exothermic reaction. The catalyst temperature, then, can be measured from inside the catalytic coating by exploiting the catalyst tubular support as a thermocouple-well.

The versatile character of the annular reactor was exploited in the present work with the purpose of studying the performance of the Pt/$\gamma$-$Al_2O_3$ catalyst on a wide operating field, especially with regard to temperature. Most of the data on the partial oxidation of paraffins over Pt-coated monoliths reported by previous papers refer to adiabatic tests, with reaction temperatures usually higher than 700–800°C (3–5, 9, 10, 12). New pieces of evidence were herein searched about the performance of the Pt/$\gamma$-$Al_2O_3$ catalyst and the mechanism of formation of olefins from propane on a wider $T$ range, by spanning from low to high reaction temperatures (200–750°C). Based on the indications from the literature (4), small amounts of catalyst were used in order to realize millisecond contact times with respect to the catalytic phase. However, as the void volume of the annular channel is much greater than the volume of the catalyst layer, then a complete characterization of the contributions from the void reactor was pursued by performing a number of blank experiments at varying temperatures, flow rates, and feed compositions and the results were compared with those of the catalytic tests. Finally, an effort to better focus the performances of the single catalytic phase was made by analyzing the sensitivity of the yields of the single reaction products to the addition of increasing amounts of catalyst under operating conditions which minimized the extent of gas-phase reactions.

## EXPERIMENTAL

*Catalyst.* The catalyst used in this work was a commercial 5% by weight Pt/$\gamma$-$Al_2O_3$ catalyst (Engelhard ESCAT 24); the catalyst was crushed and sieved with a 325-mesh sieve. The fine powders were gradually wetted with deionized water until a fluid slurry was obtained; 2 $cm^3$ of $H_2O$ was necessary for 1 g of catalyst. This was dropped unto tubular ceramic supports kept under rotation and then dried in air. Catalyst layers (located onto the central portion of the ceramic tube) from few millimeters to several centimeters long could be prepared with this technique; in this work, layers ranging from 1 to 5 cm were used. The layer thickness (measured through an optical microscope) usually ranged between 50 and 100 $\mu$m. More details on the catalyst deposition were given elsewhere (16).

*Testing unit.* Propane was fed from a 5-kg bottle containing the hydrocarbon in the liquid phase. High-purity air, $N_2$, and $O_2$ were fed from high-pressure cylinders. All the gases were fed separately through stainless steel lines equipped with check valves, filters, and Brooks mass-flow controllers. Upstream from the reactor, a relief valve was located in correspondence with the cross-type fitting wherein propane and air (or propane, nitrogen, and oxygen) were mixed.

The reactor consisted of a 60-cm-long quartz tube (Fig. 1) wherein the catalyst-coated ceramic tube was inserted. The mullite tubes had a diameter of 4.75 mm. A 7-mm-i.d. quartz tube and a 9-mm-i.d. quartz tube were used in the catalytic and homogeneous experiments, respectively. Special Cajon fittings were used to keep the inner (ceramic) and outer (quartz) tubes in coaxial position and to connect the resulting annular chamber to the inlet and outlet lines. The reactor was heated by a three-zone CARBOLITE oven. The reactor could be bypassed for periodic sampling and analysis of the feed stream.

*Safety.* The experiments were always carried out with fuel-rich feed mixtures, outside of the flammability limits,

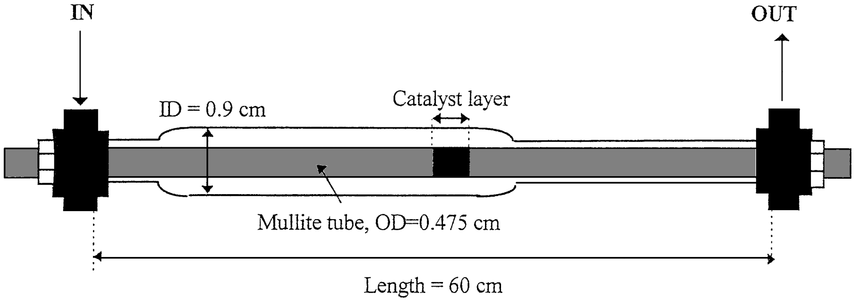

**FIG. 1.** Section of the annular reactor. The mullite tube is also used as a thermocouple well.

which is with propane : oxygen ratios $\geq 1$. In order to avoid risks of explosions during the procedures of start-up and shut-down of the rig, care was taken to feed or remove the single components in the proper sequence: at the start-up, first propane was fed in a purging flow of nitrogen, and then air (or oxygen) was fed too; finally the excess nitrogen was removed. The opposite sequence (flush of nitrogen, removal of air or oxygen, removal of propane) was run at the end of the experiments. However, for the sake of safety, the rig was built under a hood equipped with a CO sensor.

*Analyses.* Analyses were performed with two gas cromatographs operating in parallel. In a Varian 2000 GC with He as carrier gas, a molecular sieve column and a PoparapakQ column both connected to a TCD were used to quantify CO, $CO_2$, methane, ethane, ethylene, water, propylene, propane, and heavier species; $N_2$ was used as internal standard and relative response factors were estimated on the basis of calibrated mixtures. A Carlo Erba GC equipped with a molecular sieve column using Ar as carrier gas and connected to a TCD was used to analyze the amount of hydrogen in the product mixture. Carbon, hydrogen, and oxygen balances were always checked by comparing the number of moles consumed in the form of reactants and the number of moles present in the reaction products; for the data herein presented, balances were closed within 10% error.

## ODH OF PROPANE IN ANNULAR REACTOR

Preliminary experiments of propane oxidative dehydrogenation over the Pt/$\gamma$-$Al_2O_3$ catalyst were performed with the annular reactor under reference operating conditions. A high space velocity with respect to the catalyst load was realized, in line with literature indications (4): for a 1.3 cm-long catalyst layer (about 7 mg of catalyst), a total flow rate of 130 $cm^3$(STP)/min was adopted, which corresponded to a gas hourly space velocity (GHSV) of 1,100,000 L(NTP)/kg cat/h. Also, the reference feed of propane in air with a $C_3H_8 : O_2 : N_2 = 1 : 1 : 4$ mole ratio was used.

*Activity tests.* Experiments were performed at varying oven temperatures. Figure 2 reports the results. At the heating temperature of 200°C, conversion of the reactants was first observed in the form of a light-off: conversion of propane and oxygen instantly grew from zero to about 17 and 85%, respectively. The products observed were only $CO_2$ and water; stoichiometry of the reaction and composition of the product mixture were in line with the existence of the sole complete oxidation of propane. The reactant conversions and the product mixture compositions kept almost constant for further increase of the heating temperature up to 450–500°C. The comparison with void-reactor tests which were carried out under the same operating conditions (these are presented in detail in a following section) showed that in the same temperature range thermal activation of the reactants did not occur; the oxidation of propane in the presence of the Pt/$\gamma$-$Al_2O_3$ had thus a purely catalytic nature. Based on previous studies (15), the flat trend of oxygen and propane conversion vs $T$ was associated to the onset of gas–solid diffusion resistances (these often affect the behavior of structured reactors (17)). The catalytic reaction was thus extremely fast. It has been verified that the extent of oxygen conversion (the limiting reactant in the case of deep oxidation) which was measured at these lower temperatures corresponded to a dimensionless interphase mass transfer coefficient (average Sherwood number) of about 2.8; this is in very close agreement with the correlation developed elsewhere for mass transfer in the present annular reactor based on CO oxidation experiments (15).

At higher oven temperature, a dramatic increase of propane conversion was observed; at about 700°C the conversions of both reactants were almost complete. As a consequence, the overall stoichiometry of the process changed from a 1/5 (characteristic of combustion to $CO_2$ and water) into a 1/1 propane/oxygen mole ratio. In correspondence with the increase of propane consumption, the product distribution changed remarkably. As shown in Fig. 2b, which reports the percentage C-mole selectivity of the reaction products, starting from 500–550°C the selectivity of propylene (absent at lower $T$ values) increased up to a maximum value of 28–30% in correspondence with the heating temperature of 625°C; for further increase of $T$, propylene selectivity decreased and equaled 13% at 700°C at complete propane conversion. Also the formation of ethylene was

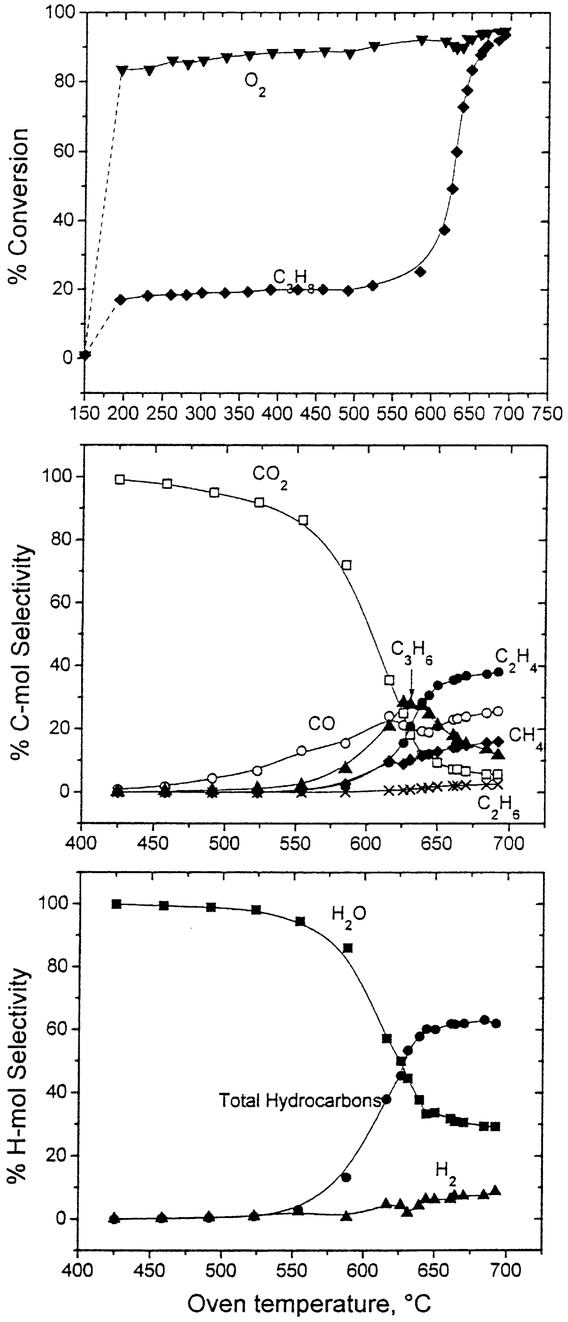

**FIG. 2.** Oxidative dehydrogenation of propane over $Pt/Al_2O_3$ catalyst in an annular reactor. GHSV = $1.1 \times 10^6$ L(STP)/kg cat/h Feed mole composition: $C_3H_8/O_2/N_2 = 1/1/4$.

observed starting from about 550°C oven *T*; it increased progressively and amounted to 40% at the highest temperatures tested. Within the whole range investigated, the formation of ethylene was accompanied by a practically equimolar production of methane. Ethane was also observed in small quantities. A total C-selectivity to olefins of 55–60% was thus observed at propane conversions higher than 60%.

$CO_2$ selectivity (100% at the lowest temperatures) dramatically decreased beyond 500°C and amounted to less than 5% at 700°C. The selectivity of CO, instead, increased with increasing temperature up to about 25% in correspondence with complete conversion of the reactants.

The product mixture included also water and hydrogen; Fig. 2c reports the distribution of the H-containing products. The production of water greatly decreased at oven temperatures higher than 500–550°C (in analogy with $CO_2$), in correspondence with the formation of hydrocarbons (propylene, ethylene, ethane, and methane) and $H_2$.

*Temperature profiles.* The data of Figs. 1 and 2 have been formally associated to the furnace temperature (the controlled variable). The temperature of the tubular catalytic layer was measured indirectly from inside the mullite tube; however, a posteriori calculations (discussed elsewhere (15)) have shown that the measurement effected by the thermocouple which slides internally to the mullite tube represents a good approximation of the surface catalytic layer temperature. In fact, it has been verified that, assuming the measurement of the thermocouple as the real surface temperature, the sum of the calculated contributions to heat dispersion which are provided by conduction along the mullite tube, flow convection, and radiation can account for over 90% of the theoretical reaction enthalpy. Besides, it was found that, due to the very thin wall of the tube (<0.9 mm), dispersion of heat by conduction along the ceramic tube upstream and downstream from the catalyst layer is negligible. It is thus unlikely that great *T* gradients establish between the inner (thermocouple side) and the outer (catalyst side) surfaces of the mullite tube.

Figure 3a reports an example of the measures of temperature effected during each experiments by sliding the thermocouple inside the coated mullite tube (reactor axial temperature profile) and the thermocouple laid on the oven internal wall (oven axial temperature profile). *T* measures were taken at each centimeter upstream and downstream from the catalyst layer, but at each millimeter in correspondence with the catalyst bed. Typically, while along most of the reactor length the two longitudinal profiles were comparable, in correspondence with the catalyst layer the mullite tube showed an overheated zone with respect to the oven, with a bell-shaped *T* trend.

A concise representation of the temperature profiles observed during the activity tests is given in Fig. 3b; it reports the difference between internal reactor temperature and oven temperature along the whole length at varying set points of the oven *T*. The catalyst layer was located between the axial coordinates 40 and 41.3 cm. It is shown that, at low reaction temperatures which corresponded to the production of $CO_2$ and water, the catalytic layer established at temperatures over 100°C higher than the oven. At increasing heating temperatures, in correspondence with the formation of olefins, the hot spot located on the catalyst

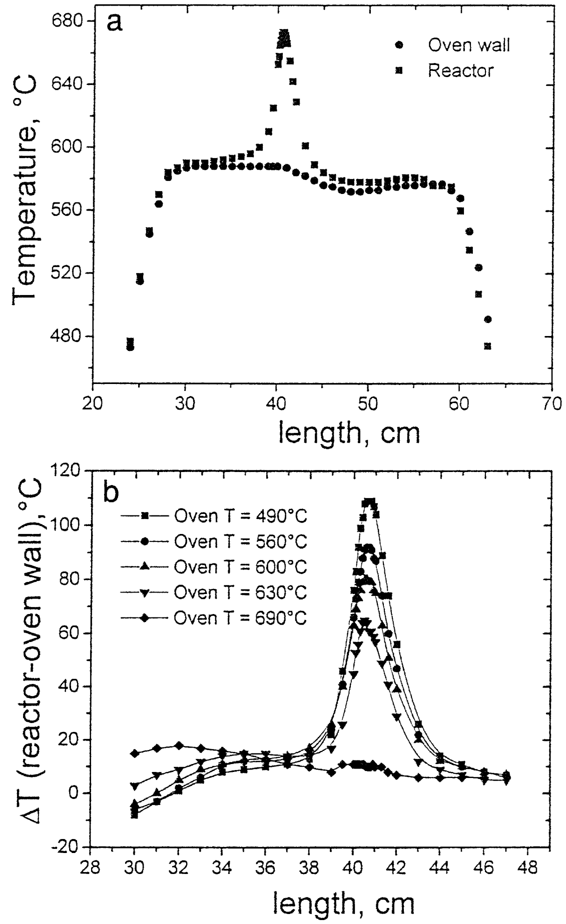

**FIG. 3.** (a) Axial temperature of the reactor (measured by the thermocouple sliding inside the mullite tube) and longitudinal temperature profile of the oven wall. The length coordinate increases along the direction of gas flow. The catalyst layer is located between 40 and 41.3 cm. (b) Differences between reactor and oven temperature profiles during the experiments of Fig. 2.

decreased progressively. At the highest temperature tested, the temperature of the catalyst layer was practically the same as the oven wall, 690°C.

This behavior could be attributed to different factors, among which are: (i) the decrease of the reaction enthalpy which is associated with the shift from a propane combustion process ($\Delta H^\circ = -2043$ kJ/mol) prevailing at low $T$ to a process wherein olefins are formed (e.g., $\Delta H^\circ = -118$ kJ/mol for the oxidative dehydrogenation of propane to propylene); (ii) a more and more effective dispersion of heat from the catalyst to the oven via radiation (approximately $\propto T^4_{\text{catalyst}} - T^4_{\text{oven}}$). However, the same behavior could be attributed to the onset of gas-phase reactions, presumably upstream from the catalyst, which were responsible for a decrease of the reactant concentration over the catalyst surface; indeed, Fig. 3b shows that a heated zone upstream from the catalyst appeared at the higher reaction temperatures. The $T$ profile at 690°C furnace temperature seemed to suggest that the reaction took place prior to reaching the catalyst surface with no significant exothermic reaction on the catalyst surface.

*Effect of the preheating temperature.* In order to verify the possible existence of gas-phase reactions far from the catalyst surface, experiments were performed wherein the temperature of the central portion of the oven (heating the annular reactor in correspondence with the catalyst layer) was kept constant at 670°C, while the temperatures of the inlet and outlet portions of the oven (heating the gas stream upstream and downstream from the catalyst layer) were gradually decreased. As shown in Fig. 4, at decreasing inlet and outlet temperature, propane conversion gradually decreased; indeed gas-phase reactions were likely to be involved in the consumption of the alkane in the heated ends of the reactor upstream and downstream from the catalytic portion. Oxygen conversion decreased to a much lesser extent. The product mixture enriched in oxygenated species; the distribution changed in fact in favor of a higher C-selectivity of $CO_2$ and a higher H-selectivity of $H_2O$. Also, the temperature profiles along the reactor significantly changed while lowering the reactor preheat; as shown in Fig. 5, the enhancement of the deep oxidation products was accompanied by an increase of the hot spot in correspondence with the catalyst layer and the disappearance of the heated zone upstream from the catalyst.

These results have supported the hypothesis of the copresence of catalytic and gas-phase reactions. The role of the latter ones was better investigated through a focused campaign of blank experiments.

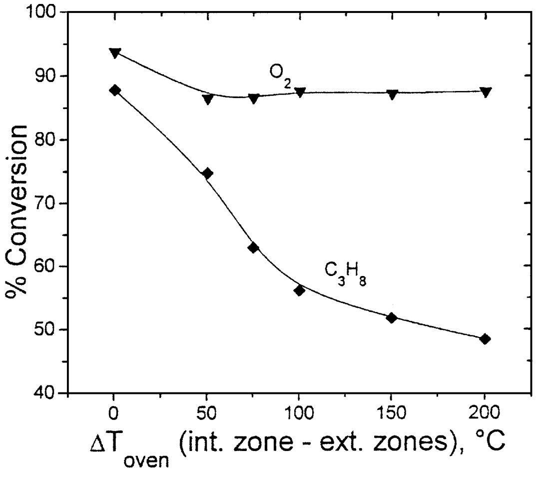

**FIG. 4.** Effect of lowering the temperatures of inlet and outlet oven zones, while keeping constant at 670°C the temperature of the central oven zone, on propane and oxygen conversions. Flow rate and feed composition as in Fig. 2.

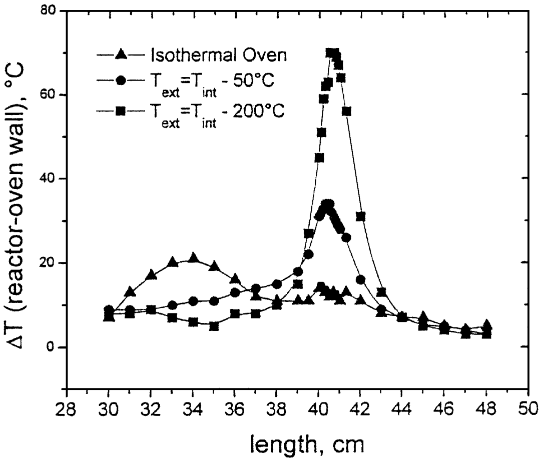

**FIG. 5.** Effect of lowering the temperatures of inlet and outlet oven zones on the catalyst *T* profiles.

## TESTS IN THE ABSENCE OF CATALYST

Gas-phase experiments were performed under the same operating conditions as those of Fig. 1 in order to evaluate the contribution of the empty reactor (e.g., wall-assisted ignition of the reactant mixture, homogeneous thermal pyrolysis) to the results obtained in the presence of catalyst. A bare mullite tube was used in the experiments, with a total isothermal void volume of 7.3 cm$^3$. Likewise, the previous catalytic experiments, the ceramic tube was used as a thermocouple-well and the axial temperature profile was measured during each experiment. This was compared with the corresponding longitudinal temperature profile of the oven wall; differences between the two profiles were always negligible. Even if the thermocouple sliding inside the mullite tube was not directly in contact with the gas-phase, it has been calculated that at the linear velocities used in the present experiments (0.1–1 m/s, with 0.1 m/s for most of the experiments) the gaseous stream reached the same temperature of the inner mullite tube within an extremely short length (few millimeters to few centimeters). Absence of radial temperature gradients could be thus reasonably assumed, so that mullite tube temperature ( = furnace *T*) was taken as fully representative of the gas-phase temperature.

*Effect of temperature.* The same reference flow rate and feed composition were used as those previously adopted in the presence of catalyst (130 cm$^3$(STP)/min of an air/propane mixture with mole composition $C_3H_8 : O_2 : N_2 = 1 : 1 : 4$). The residence time in the heated annular chamber corresponded to 3.6 s at ambient temperature and about 1 s at the highest temperature investigated.

Figure 6 shows the results obtained at increasing temperature. At about 600°C, few units of percentage of conversion for both propane and oxygen were first observed (Fig. 6a). The conversion of the reactants then increased strongly with increasing *T*; at 715°C propane conversion was as high as 90%, and oxygen conversion equaled 85%. Figures 6b and 6c report the C-mole and H-mole selectivity of the reaction products as functions of temperature. In the whole range investigated, very high selectivities to olefins were observed. At the lowest temperature, in correspondence with small conversions of the reactants, propylene

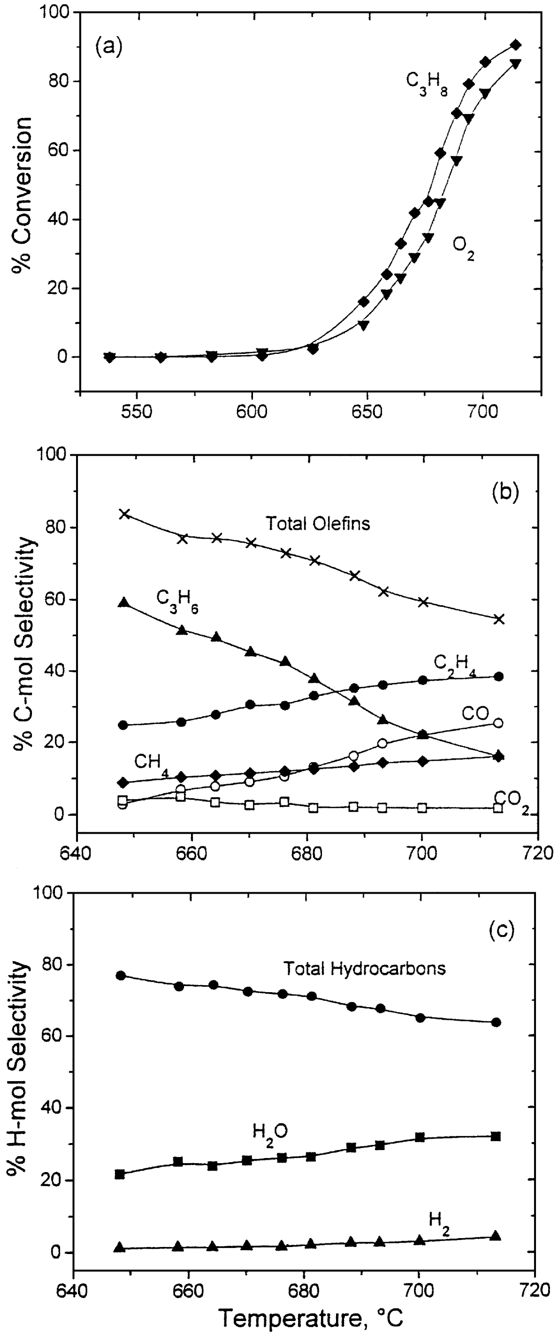

**FIG. 6.** Homogeneous oxidative dehydrogenation of propane. Effect of temperature on the conversion of reactants (a) and distribution of the C-containing (b) and H-containing (c) products. Flow rate = 130 cm$^3$(STP)/min. Feed composition: $C_3H_8/O_2/N_2 = 1/1/4$.

was the most abundant product with a C-mole selectivity of 60%; it decreased progressively with increasing $T$ and lowered to 17% at 715°C. The selectivity to ethylene instead increased from 25% at 650°C to 40% at almost complete conversion of propane. The total selectivity to olefins was thus higher than 55% in the whole range of propane conversions. Production of CO also increased with increasing temperature. $CO_2$ was instead formed in very low amounts with selectivities ranging between 2 and 5%. Production of $H_2$ was significantly lower than that of $H_2O$.

These trends are in line with the well established theory of hydrocarbons oxidative pyrolysis (18, 19). According to the radical kinetic scheme proposed by Ranzi and coworkers (18), propylene and ethylene are produced via $\beta$-abstraction of a H• or a $CH_3$• group from propylic radicals, respectively, while $CO_x$s are terminal products of the process. Selectivity to olefins is thus expected to be favored at short contact times. Also, as observed experimentally, at increasing reaction temperatures propylene is expected to decompose in favor of shorter and more stable species, with consequent increase of ethylene yield.

A quantitative comparison of the present results with the predictions of the cited detailed kinetic scheme (18) which has been developed for the case of isothermal plug flow reactor. The comparison showed that in a PFR the same extent of reactant decomposition as well as the same product distributions as those observed experimentally would be obtained at shorter residence times (by a factor of 2) than that realized in the annular reactor. However, it must be considered that contact times herein reported are average values. In reality, the viscous flow regime which characterizes the annular reactor (Reynolds numbers <50–100) results more properly in a broad distribution of residence times; this is known to cause an apparent "retardation" of the gas-phase reaction rates with respect to the case of flat radial velocity and concentration profiles.

*Effect of residence time.* It was studied by varying the flow rate in the range 27–470 $cm^3$(STP)/min, while keeping constant the reactor temperature at 686°C and the feed composition at $C_3H_8 : O_2 : N_2 = 1 : 1 : 4$ mole ratio. Contact time ($\tau$) ranged between 0.175 and 3 s.

Figure 7a shows that propane and oxygen conversion increased rapidly with increasing contact time from 0.175 to 1.3 s; for further increase of $\tau$, conversion of propane kept almost constant at 80–85%, while oxygen conversion slowly increased. It is likely that, once most oxygen was consumed, conversion of the residual propane did not proceed further as the reactor temperature was not high enough to activate the thermal pyrolysis of the hydrocarbon. This has been verified with specific tests, reported below. Also, the product distribution showed the same asymptotic trend as propane conversion. As reported in Fig. 7b, propylene was the major product at short contact times and its selectivity decreased to nearly 20% at increasing $\tau$, in line with the behavior of an intermediate species of the reaction network. Ethylene selectivity increased moderately from 30 to 35% at increasing contact time. Accordingly, also methane selectivity increased only slightly. CO selectivity, as expected on the basis of the behavior of a terminal product, increased significantly with increasing contact time; it was lower than 5% at short $\tau$ and equal to 25% at $\tau = 3$ s. Also in these

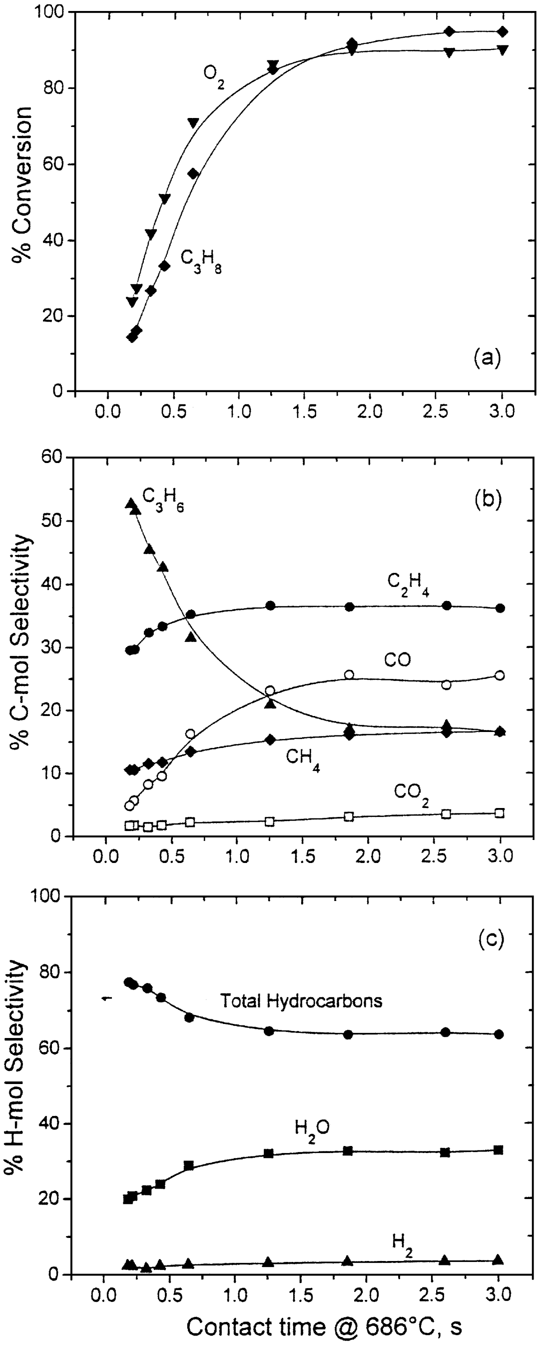

FIG. 7. Homogeneous oxidative dehydrogenation of propane. Effect of contact time on the conversion of reactants (a) and distribution of the C-containing (b) and H-containing (c) products. $T = 686$°C. Feed composition: $C_3H_8/O_2/N_2 = 1/1/4$.

experiments, the total selectivity to olefins was always higher than 55% even at high levels of reactants conversions. As the experiments performed at varying reaction temperature, formation of $H_2$ was observed at a much lower extent than $H_2O$.

*Effect of dilution.* Additional experiments were performed wherein the flow rate of propane and oxygen were kept constant, while the total flow rate was increased by increasing the single flow of nitrogen. The results are reported in Fig. 8 (open symbols) and compared, at equal total flow rate, with those obtained at constant feed composition (solid symbols). The enrichment of nitrogen resulted in a decrease of oxygen and propane conversions. The product distribution did not vary significantly from that already observed at increasing total flow rate and, for brevity, is not reported.

The present experiments suggested that the contribution of the gas-phase reactions could be drastically reduced by simply adding a high flow rate of diluent to the feed stream; this was applied in those experiments reported in the following which focused on the effect of the catalyst phase.

*Pyrolysis experiments.* Tests were also performed in the absence of oxygen, by feeding 22 $cm^3$(STP)/min propane in 109 $cm^3$(STP)/min nitrogen. Figure 9 reports the measures of propane conversion at increasing temperature; these are also compared with the results of the experiments in the presence of an equimolar amount of oxygen. Thermally activated pyrolysis occurred at much higher temperatures than oxygen-activated pyrolysis; in the absence of $O_2$, propane conversion kept within 30% by increasing the reactor temperature up to 740°C. The main reactions of cracking and dehydrogenation of propane were present and resulted in the formation of equal amounts of ethylene and methane on one side and of propylene and hydrogen on the other side. As reported in Fig. 9b, the total selectivity to olefins was extremely high, about 80% at the highest temperature tested.

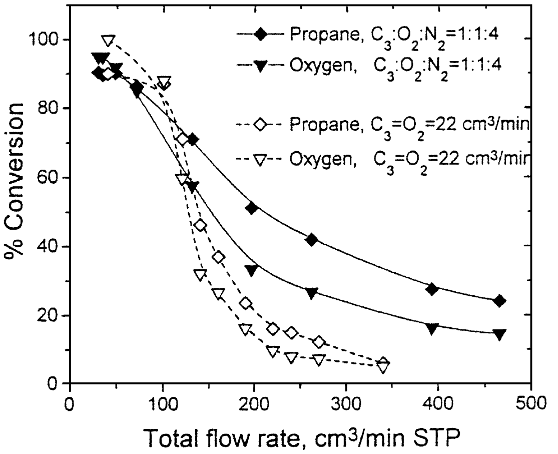

**FIG. 8.** Homogeneous oxidative dehydrogenation of propane. Effect of dilution (open symbols: propane and oxygen flow = 22 $cm^3$(STP)/min, nitrogen at balance) vs effect of flow rate at constant feed composition (solid symbols, $C_3H_8/O_2/N_2 = 1/1/4$) at $T = 686°C$.

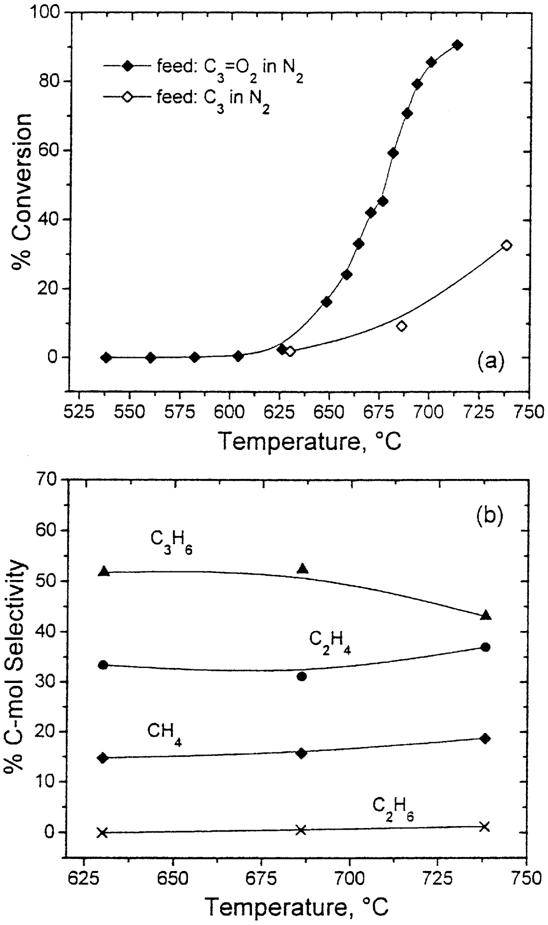

**FIG. 9.** Pyrolysis: (a) propane conversion in the absence of oxygen (open symbols, propane flow = 22 $cm^3$(STP)/min in $N_2$) vs oxidative dehydrogenation (solid symbols, from Fig. 2). Total flow rate = 1130 $cm^3$(STP)/min. (b) Distribution of the C-containing products.

## EXPERIMENTS UNDER DILUTED CONDITIONS: EFFECT OF CATALYST ADDITION

High flow rate and high diluent content were chosen as proper operating conditions for better enlightening the role of catalyst, being that they associated to an expected small contribution from the gas-phase reactions, based on the trend shown in Fig. 8. Three cases were examined: absence of catalyst, 1.5-cm-long layer of catalyst (about 10 mg), and 5-cm-long layer of catalyst (about 50 mg). Comparing the outlet molar flow of the single reaction products in the three cases was expected to identify which species yields were indeed favored at increasing catalyst load. The comparison was effected under the following feed compositions: $C_3H_8 : O_2 = 1 : 1$, $C_3H_8 : O_2 = 1 : 0.25$, $C_3H_8 : O_2 = 1 : 0$.

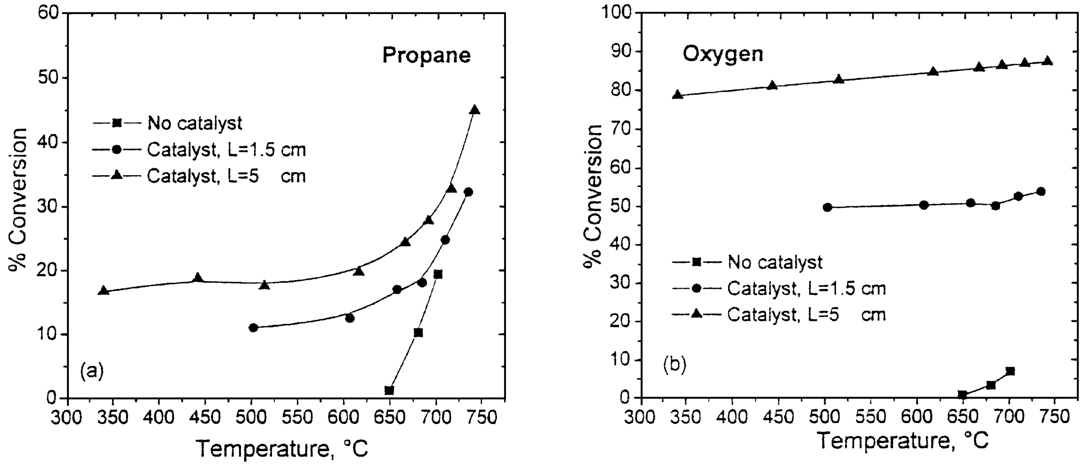

**FIG. 10.** Propane (a) and oxygen (b) conversion at increasing $T$ in the cases of: empty reactor, catalyst layer = 1.5 cm long, and catalyst layer = 5 cm long. Operating conditions: $C_3H_8 = O_2 = 22$ $cm^3$(STP)/min in $N_2$. Total flow rate = 578 $cm^3$(STP)/min.

*Activity tests with $C_3H_8/O_2$ feed ratio = 1/1.* Equal flow rates of propane and oxygen (22 $cm^3$(STP)/min) were fed to the reactor diluted in nitrogen for a total feed stream of 578 $cm^3$(STP)/min.

Figure 10 shows the conversions of the reactants at increasing oven temperatures for the three cases under study: absence of catalyst, short catalyst layer, and longer catalyst layer. In the absence of any catalyst, conversion of propane

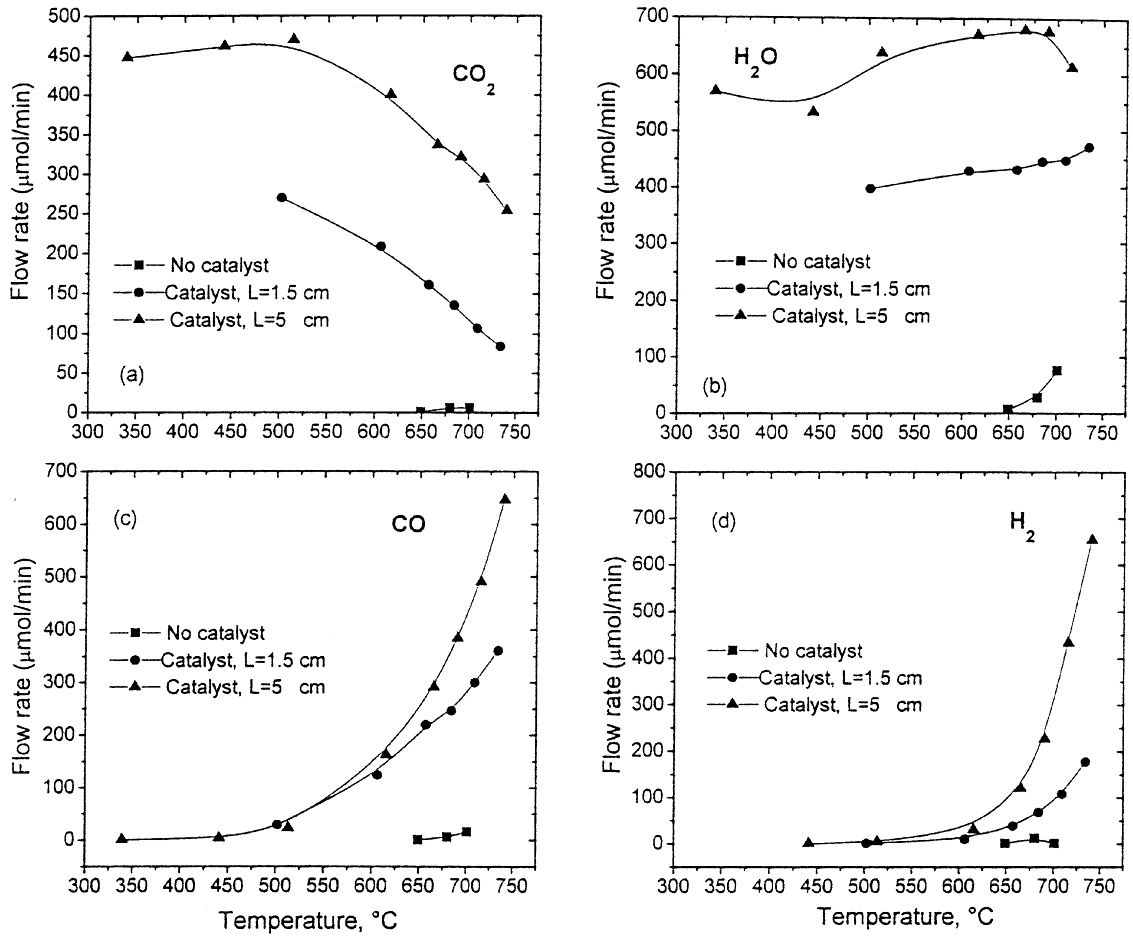

**FIG. 11.** Production of $CO_2$ (a), $H_2O$ (b), CO (c), and $H_2$ (d) under conditions as in Fig. 10.

and oxygen started around 650°C; the consumption of both reactants kept below 15–20% up to 700°C.

Under the same feed flow rate and composition, but in the presence of a 1.5-cm-long layer of catalyst, conversion of propane was significant at lower temperatures and showed the same characteristic *T* dependence already observed in previous experiments (see Fig. 2a): it kept almost constant up to 600–650°C and increased sharply at higher temperatures. The same trend with a higher level of conversion was observed by further increasing the catalyst load with the 5-cm-long layer. Also the conversion of oxygen, moderately increasing with increasing temperature, strongly increased with increasing amount of catalyst.

Let's now examine the behavior of the single reaction products. Figure 11 shows the measured outlet molar flow of the products of deep and partial oxidation routes: $CO_2$, $H_2O$, CO, and $H_2$. In the absence of catalyst, very little $CO_2$ was produced by the single gas-phase process; however, this increased remarkably in the cases of smaller and larger amounts of catalyst. The production of $CO_2$ was almost constant with varying temperature up to 500°C; in this same range propane and oxygen conversions were also constant. A decrease was observed, instead, at higher temperatures, in correspondence with the increase of the reactant conversion. Similar trends were found for $H_2O$: while a negligible amount was produced in the gas phase, water production greatly increased with increasing catalyst load. CO and $H_2$ were also present in very small amounts in the gas-phase product mixture; in the presence of increasingly long layers of catalyst, their production was markedly enhanced, though confined to the range of temperature >500°C. The formation of these species could be attributed to the onset of partial oxidation or steam (dry) reforming routes. The same reactions have already been reported for the production of synthesis gas via catalytic partial oxidation of methane over noble metal-based catalysts (20, 21).

The twofold evidence of (i) the negligible contribution from the gas-phase reaction and (ii) the increasing yield with increasing catalyst amount clearly indicated that CO, $CO_2$, $H_2$, and $H_2O$ were produced on the catalyst surface. Pt is in fact known to be an excellent combustion catalyst.

Conversely, as shown in Fig. 12, the production of propylene decreased with increasing amount of catalyst with respect to the case of an empty reactor, which provided the highest yields. The same trend was observed also in the cases of methane and ethylene; the addition of increasing loads of catalyst resulted in a progressive decrease of their productivity. No positive proof of a contribution of the catalytic phase to the formation of olefins can be deduced by the data. The authors are aware that many explanations of the data could be given still involving catalytic routes followed by thermal decomposition routes; however, these results can be reasonably and very simply explained assuming that gas-phase reactions only were responsible for the formation of propylene and ethylene, while the catalyst phase did not contribute to their formation. Besides, as the presence of the catalyst resulted in a decrease of the olefins yield with respect to the case of void reactor, it could be further thought that the catalyst activity in oxidations effected a partial consumption of propylene, ethylene, and methane. It

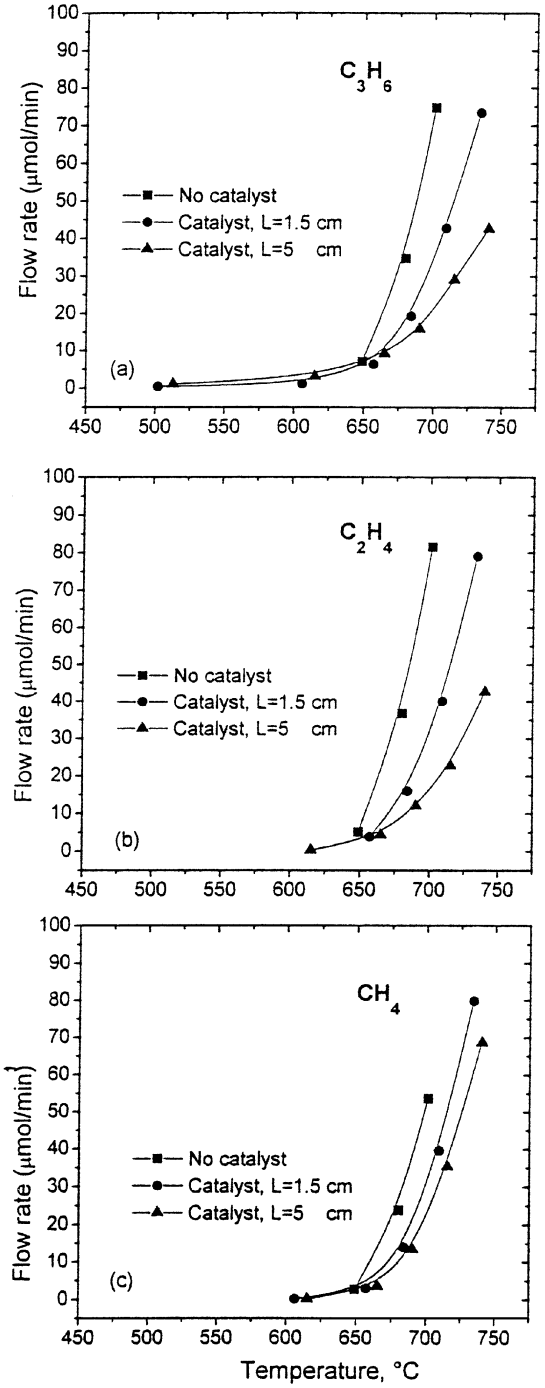

FIG. 12. Production of propylene (a), ethylene (b), and methane (c) under conditions as in Fig. 10.

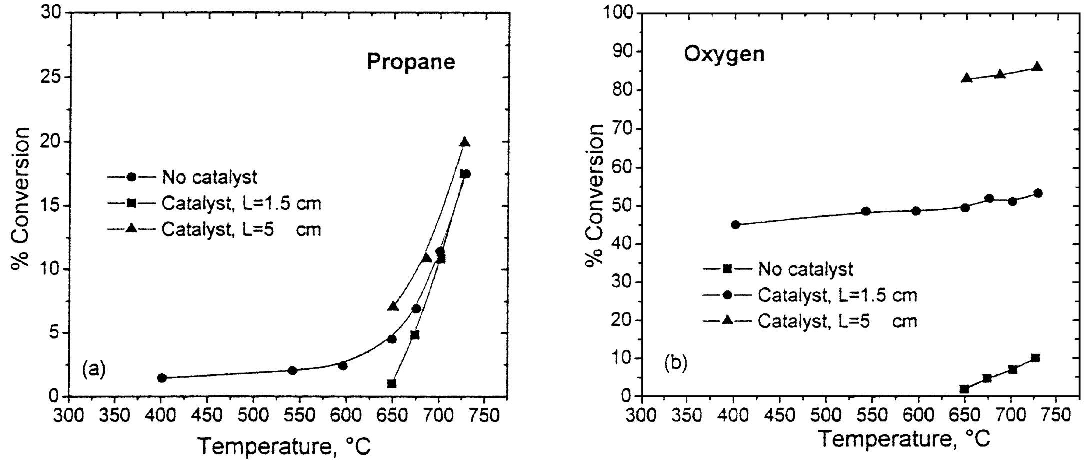

FIG. 13. Propane (a) and oxygen (b) conversion at increasing *T* in the cases of empty reactor, catalyst layer = 1.5 cm long, and catalyst layer = 5 cm long. Operating conditions: $C_3H_8$ = 22 $cm^3$(STP)/min, $O_2$ = 5.5 $cm^3$(STP)/min in $N_2$. Total flow rate = 578 $cm^3$(STP)/min.

was observed that the presence of catalyst, however, slightly anticipated the formation of olefins at a lower temperature (600°C oven *T* in the case of catalyst vs 650°C oven *T* for the blank experiments); this could be explained by the local heating exerted by the catalyst surface on the surrounding gas-phase with consequent local activation of the gas-phase reactions at a lower oven temperature.

*Activity tests with $C_3H_8/O_2$ feed ratio = 1/0.25.* Additional data were obtained at a lower oxygen concentration,

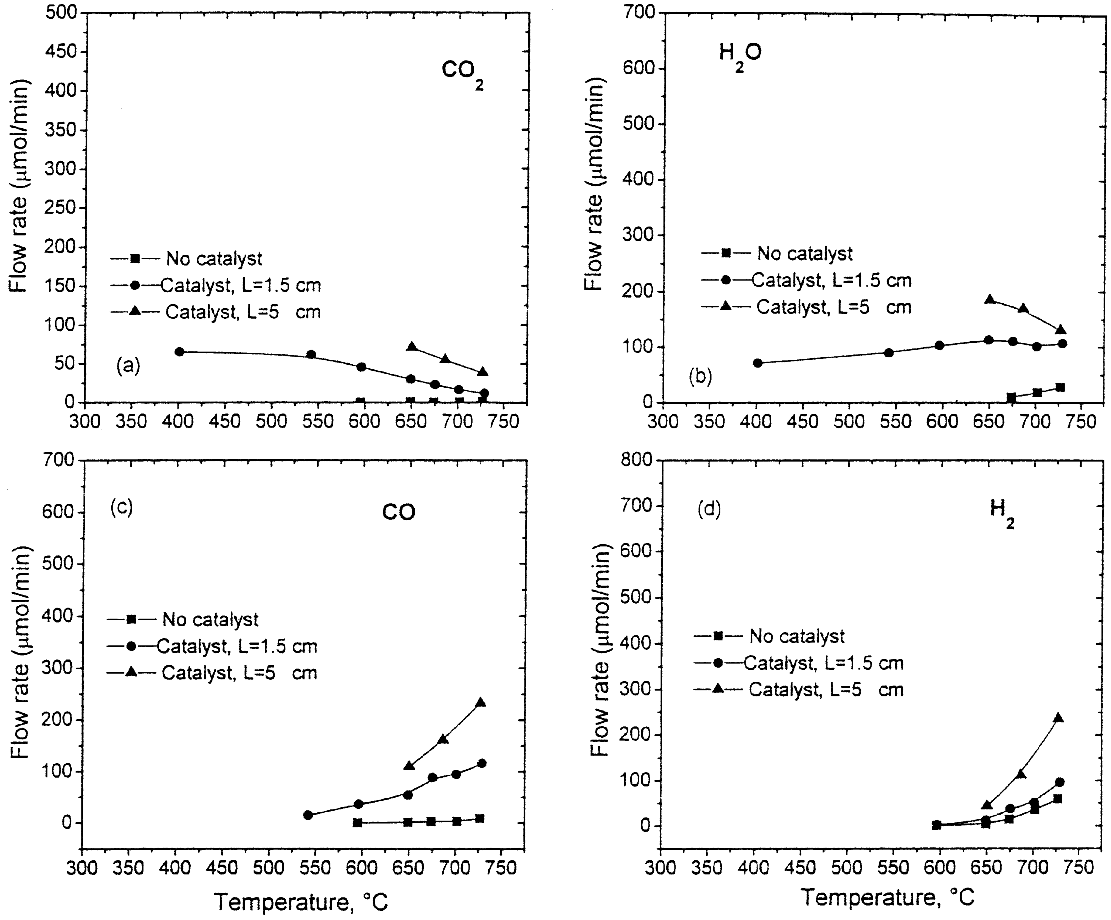

FIG. 14. Production of $CO_2$ (a), $H_2O$ (b), CO (c), and $H_2$ (d) under conditions as in Fig. 13.

by feeding 22 $cm^3$(STP)/min of propane and 5.5 $cm^3$(STP)/min of oxygen in nitrogen, while keeping a total flow rate of 578 Ncc/min. As shown in Fig. 13, the extent of oxygen conversion was very similar to that observed at higher $O_2$ concentration. Propane conversion, instead, was lower and less sensitive with respect to the increase of catalyst load (Fig. 13a).

The production of $CO_2$, $H_2O$, CO, and $H_2$ was significantly depressed by the decrease of oxygen feed content both in the experiments with the empty reactor ($CO_2$ was practically absent and CO was present in traces) and in the presence of catalyst layers. Still, the yields of these species grew with increasing catalyst load, which confirmed their heterogeneous genesis.

The outlet molar flow of propylene, ethylene, and methane in the purely homogeneous experiments moderately decreased with lower oxygen concentration. Again, the addition of increasing amounts of Pt-catalyst caused a reduction in the productivity of these species. Such reduction, however, occurred to a lesser extent than in the previous case of equimolar flow of reactants. This might be interpreted as further evidence that the catalyst surface did not contribute to the formation of olefins, but only to the formation of nonselective oxidation products. The lower partial pressure of oxygen could have been responsible for lowering the catalyst reaction rate in decomposing part of the reactants and products (lower production of $CO_2$) and thus producing a minor interference with the gas-phase formation of olefins.

*Activity tests without $O_2$.* Finally, experiments were performed in the absence of oxygen, by feeding 22 $cm^3$(STP)/min of propane in nitrogen (total flow rate = 578 $cm^3$(STP)/min). The conversion of propane measured at increasing temperature was exactly the same in the three cases of empty reactor and smaller and larger loads of catalyst. Four main reaction products were observed: propylene, hydrogen, ethylene, and methane. Their measured flow rates are reported in Fig. 16. The gas-phase production of these species was thoroughly unaffected by the presence of the Pt-catalyst. There is no proof thus of a contribution of the catalyst phase to the activation of propane. An explanation of the data could be that in the absence of oxygen the thermal dehydrogenation of propane to propylene and hydrogen and the thermal cracking to ethylene and methane were the unique routes responsible for the observed product distribution.

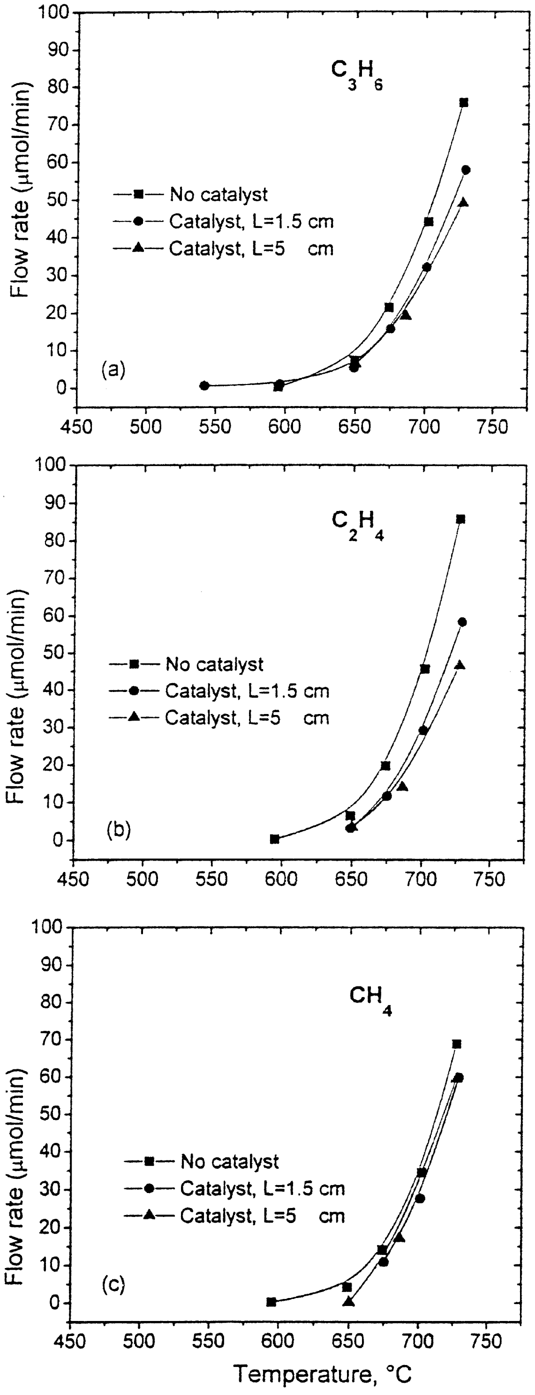

**FIG. 15.** Production of propylene (a), ethylene (b), and methane (c) under conditions as in Fig. 13.

It must be noted that while Pt-based catalysts are industrially used for endothermic dehydrogenation reactions, in the present application the catalyst was apparently ineffective in dehydrogenating propane to propylene. It must be considered, however, that the high ratios between gaseous flow rate and catalyst amount herein adopted ($10^6$–$10^7$ LSTP/kg cat/h) are by far larger than those characteristic of the industrial chemical processes wherein the same catalyst is used ($10^2$–$10^4$ LSTP/kg cat/h).

## CONCLUSIONS

In this work, a structured reactor with annular configuration has been applied to the study of the oxidative

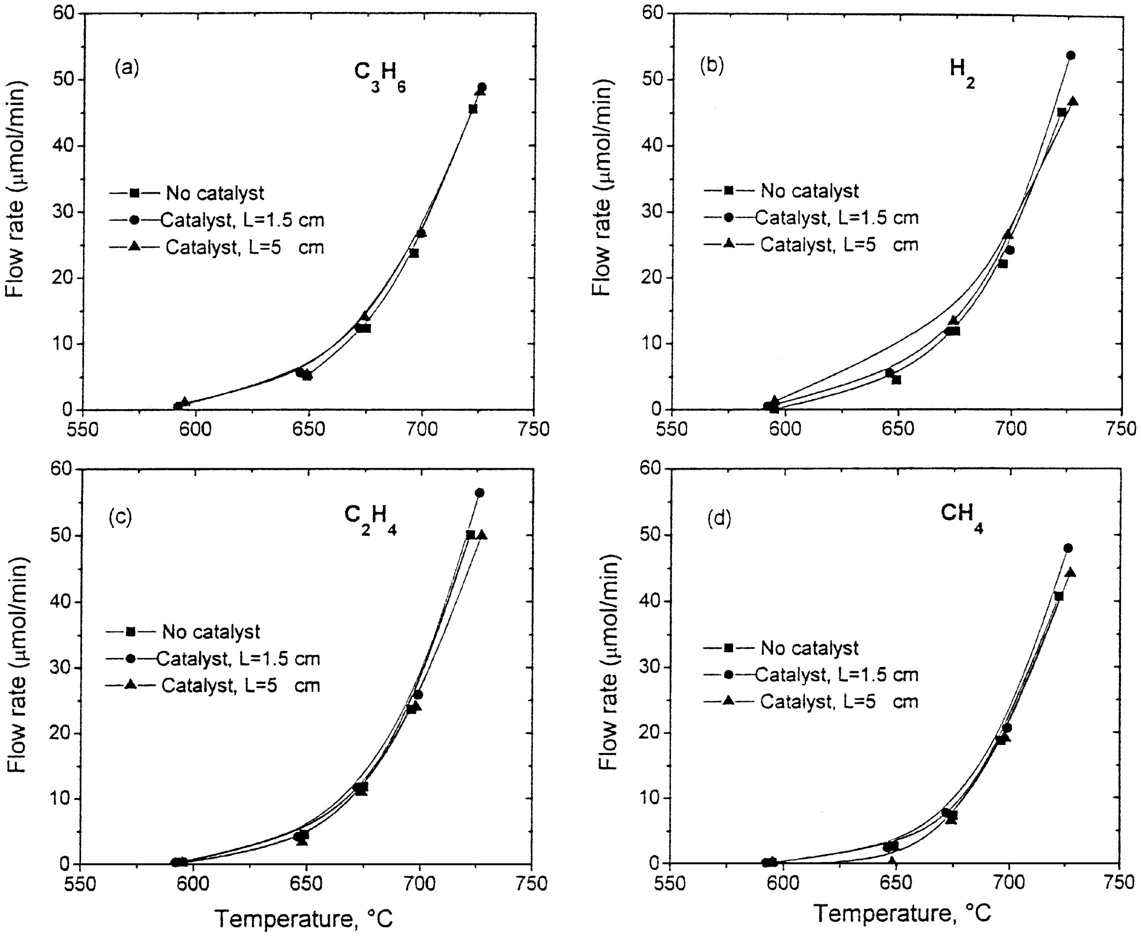

FIG. 16. Production of propylene (a), hydrogen (b), ethylene (c), and methane (d) at increasing *T* in the cases of empty reactor, catalyst layer = 1.5 cm long, and catalyst layer = 5 cm long. Operating conditions: $C_3H_8$ = 22 $cm^3$(STP)/min in $N_2$. Total flow rate = 578 $cm^3$(STP)/min.

dehydrogenation of propane over a commercial Pt/$\gamma$-$Al_2O_3$ catalyst. The catalyst was used in very small amounts in order to realize high space velocities (referred to the catalyst volume) in the shape of a thin layer onto a tubular ceramic support and was longitudinally contacted by the gas stream flowing in a laminar regime. The reactor temperature was varied within a wide range in order to investigate the catalyst performance also below the high temperature values associated with the more studied adiabatic operation.

In the range of low to medium temperatures (200–500°C furnace *T*) only products of combustion were present in the product mixture. Comparison with the results of blank experiments indicated that no contribution to propane activation was present in the void reactor within the same *T* range. The combustion was thus thoroughly attributed to the catalytic phase; also, the *T* profiles indicated that the exothermic process was located on the catalyst layer. The reaction rate over the Pt surface was so fast that, in the present structured reactor, the process underwent interphase diffusion control already at 200°C; this was evidenced by almost flat temperature dependencies of propane and oxygen conversions up to 500–550°C.

Olefins were formed in large amounts in the presence of the Pt/$\gamma$-$Al_2O_3$ catalyst above 550°C; however, a wide series of homogeneous-phase experiments showed that in the same *T* range gas-phase oxidative pyrolysis was active and could produce the same amount of olefins as that observed in the catalytic tests. The gas-phase process was shown to be extremely selective in the formation of olefins, with C-selectivities of propylene + ethylene > 55% even at high conversions of propane. $CO_x$s are terminal products of the oxidative pyrolysis; accordingly, short contact times were found to be extremely favorable for enhancing the olefins selectivity.

Additional pieces of evidence were sought by choosing specific operating conditions which minimized the role of homogeneous reactions (high flow rate, high degree of dilution) and in these conditions the sensitivity of the product distribution upon variation of the catalyst load was investigated. By increasing the catalyst layer length, the yields of the combustion products increased. Conversely, no increase of olefin yields was observed; instead, the "background" though small production of propylene and ethylene due to the void reactor progressively decreased upon addition of catalyst.

While a purely catalytic reaction mechanism has been presented in the literature for interpreting the results obtained in the partial oxidation of high alkanes in Pt/$\alpha$-$Al_2O_3$ foam monoliths under autothermal operation, the present results do not provide any positive proof of heterogeneous formation of olefins. Strong pieces of evidence were instead obtained that: (1) the Pt/$\gamma$-$Al_2O_3$ catalyst was extremely active in the nonselective oxidation of propane at all the temperatures investigated and that this was the only active route at low temperatures; (2) gas-phase reactions were active and extremely selective in the formation of olefins at high temperatures.

A number of mechanisms could explain the data, but the results herein presented are consistent with a homogeneous formation of olefins.

## ACKNOWLEDGMENTS

Financial support by ENI is acknowledged. The authors thank Prof. Mario Dente and Prof. Eliseo Ranzi, Politecnico di Milano, for sharing their expertise in the oxidation and pyrolysis of hydrocarbons.

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