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New insight into the role of gas phase reactions in the partial oxidation of butane

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Abstract

The partial oxidation of *n*-butane at high alkane to oxygen ratio was studied in the presence of a Pt–Rh gauze and in an empty tubular reactor under identical conditions.

Temperature-programmed reaction (TPR) experiments with the metal gauze showed dramatic changes in the product distribution in the range 25–500 °C. Total oxidation of butane at low temperature is followed by selective conversion to olefins and oxygenates around 400 °C; a further increase in the oven temperature enhances selectively olefins formation.

In situ infrared and visible imaging of the reacting gauze revealed remarkable ignition/extinction phenomena of the surface reactions. Fast ignition on the metal catalyst was observed around 200 °C; upon further raising the oven temperature, suppression of these reactions occurred at a temperature level corresponding to the transition to high selectivity conditions. These results indicate a shift from heterogeneous to homogeneous reaction mechanism, the latter being responsible for high selectivity to partial oxidation products (84% olefins + oxygenates). With the empty reactor, conversion and selectivity were similar to those obtained in the presence of the catalyst.

The study shows that the gauze plays no significant role in butane partial oxidation, as reactions take place in the void upstream of the catalyst, presumably via an alkylperoxy intermediate.

Keywords: Partial oxidation; Butane; Gas phase reactions; Pt–Rh gauze; Surface imaging

1. Introduction

A strong research effort was devoted in the past two decades to the development of efficient processes for the partial oxidation of hydrocarbons. To this purpose, a large variety of catalysts have been studied, mainly in form of mixed oxides or oxospecies supported on porous carriers. The preferred components in these formulations are vanadium for alkane oxidative transformation and molybdenum for olefin partial oxidation [1].

The role of homogeneous reactions in these conversion processes has been outlined in several studies. Burch and Crabb [2] found that in propane ODH, heterogeneous systems are not more efficient than gas phase reactions, the latter giving higher olefin selectivity. They concluded that the best route to an efficient process seems to be a combination of homogeneous and heterogeneous reactions. Xu and Lunsford [3] found that addition of a catalyst can slightly enhance propane conversion, compared to a homogeneous system; however, selectivities at a given conversion are similar in catalytic and non-catalytic experiments. In a study of propane conversion over supported vanadyl phosphate, surface ignition of the

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reaction mixture was shown to enhance the olefins yield via a gas phase mechanism [4].

Attempts to improve efficiency in the partial oxidation of alkanes were also made through special reactor design, in which gas phase reactions are supposed to play a key role. By using a Pt-coated foam monolith at contact time of the order of 1 ms, high olefin selectivity was obtained from propane and other alkanes [5]. Effective conversion to olefins was also achieved with catalytic systems consisting of a single layer of woven metal gauze (Pt or Pt–Rh) over which alkanes and oxygen were passed at very short contact time [6,7]. Whereas with C_1–C_3 paraffins only synthesis gas and olefins could be produced with this type of reactor, butane was converted to oxygenated products with appreciable selectivity [6,8]. The authors of these studies outlined the importance of homogeneous reactions in this conversion; the metal surface, though, was considered to play an important role in generating the heat necessary to initiate the reactions, and possibly in forming active intermediates which promoted partial oxidation in the colder downstream zone of the reactor.

The present investigation is aimed at obtaining a better insight into the mechanism of *n*-butane partial oxidation in the presence of a metal gauze. Temperature-programmed and steady state experiments were carried out in a specially designed microreactor, equipped with infrared and visible imaging systems. Special attention was devoted to the determination of temperature profiles on the catalyst surface and inside the reactor, and to the analysis of transient phenomena taking place in this highly reactive system.

2. Experimental

2.1. Apparatus and materials

The oxidation of *n*-butane was studied in a specially designed 8 mm i.d. tubular reactor, which guaranteed at least 80% transmittance to infrared radiation in the 2–5 μm range. The microreactor system was equipped with an Agema Thermovision 900 apparatus, capable of providing high-resolution thermal maps of the reacting surface by means of real-time image analysis and processing. Visible images of the gauze where obtained by a Kappa DX 30 digital colour system.

The lower half of the vertical reactor was filled with quartz granules (diameter 0.2–0.8 mm). At the extremes of this bed, two quartz wool plugs (2 mm) were placed. The upper part of the reactor was empty. A metal gauze was located on top of the quartz wool, in the middle of the reactor. The gauze (Alfa Aesar) was woven from a Pt:Rh 90:10% wire with diameter 0.0762 mm, resulting in a 80 mesh sieve with about 60% open area. The gauze was placed in such a way as to form an angle of about 45° with the horizontal plane, in order to obtain an optimal exposure to the imaging devices.

The reactor was heated by a forced ventilation oven, in which air was passed through an electrical resistance connected to a temperature controller-programmer. Axial temperature profiles inside the vertical reactor were determined by movable thermocouples placed in two quartz thermowells, one located in the upper part and ending 1 mm above the gauze, the second in the lower half of the reactor, ending 2 mm below the gauze.

2.2. Methods

A butane-rich mixture ($C_4H_{10}/O_2/N_2 = 50/20/30$) was fed downward to the reactor at atmospheric pressure by mass flow controllers (Brooks). Feed flow rate was between 100 and 500 ml_N/min, corresponding to superficial velocities between 33 and 165 mm/s.

Reaction products were analysed on line by a 5890 HP gas chromatograph equipped with two capillary columns (AT-1 from Alltech, Poraplot from Chromosorb) connected to a FID and a TCD detector, respectively. In both steady-state and temperature-programmed experiments, O_2, CO and CO_2 were monitored by a continuous gas analyser (Rosemount NGA 2000) equipped with a paramagnetic and two NDIR detectors. Selectivity to oxidation products was determined on a carbon atom base.

Butane oxidation was studied by temperature-programmed reaction (TPR) between 25 and 500 °C, with heating or cooling rate of 3 °C/min. Steady state measurements in the same temperature range were also carried out.

3. Results

When the fresh gauze was exposed to the $C_4H_{10}/O_2/N_2$ mixture flowing at 100 ml/min between

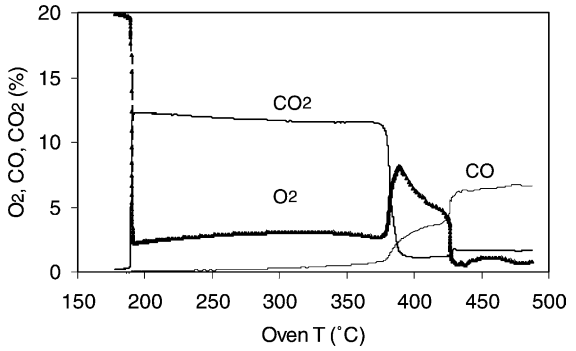

Fig. 1. Outlet concentrations determined during temperature-programmed reaction over a Pt–Rh gauze. Feed composition: $C_4H_{10}/O_2/N_2 = 50/20/30$; flow rate 100 ml_N/min.

ambient temperature and 400 °C, it was completely inactive. Only after about 30 h on stream at 300 °C, was oxidation revealed by formation of CO_2. Subsequently, the catalyst showed no significant evidence of deactivation for the duration of experiments (about 80 h). At the end of catalytic runs, though, the material exhibited strong evidence of physical change: the wire appeared altered and worn-out; in addition, small fragments detached from the gauze when it was removed from the reactor.

As to the nature of this lost material, it has to be noticed that no evidence of carbon formation either on the reactor wall or in the quartz packing was apparent at the end of the runs. The carbonaceous material deposited on the aged gauze was evaluated from the CO_2 produced during temperature-programmed oxidation in air flow in the range 25–500 °C. The amount of carbon removed corresponded to 1.1% of the gauze's mass (48 mg). After this treatment, the gauze still showed tendency to release debris upon handling. It can thus be supposed that the material coming off the gauze was predominantly inorganic. A marked structural degradation of Pt and Pt–Rh gauzes during oxidative alkane conversion was reported in previous studies [6,7,9].

The reactivity of butane in the presence of the Pt–Rh gauze was studied by temperature-programmed reaction experiments, in which some key species (CO, CO_2, O_2) were continuously analysed at the reactor outlet (Fig. 1). At 180 °C, a sharp decrease in the O_2 concentration, in parallel to a jump in CO_2 formation, reveals the ignition of the oxidation reaction. At this stage, CO concentration is negligible. Around 380 °C, a second remarkable transition is observed; CO_2 drops quickly, while CO rises. Oxygen increases also initially, and then gradually declines. A further transition takes place around 430 °C, as revealed by a drop in O_2 and a simultaneous increase in carbon oxides.

Upon raising the flow rate from 100 to 300 ml/min, the concentration profiles during TPR experiments are qualitatively the same, the major difference being a 20–30 °C increase in the temperature of the transitions.

Analysis of the reaction products by gas chromatography at different temperatures under steady conditions, revealed in greater detail the nature of the changes in the reaction system (Fig. 2). Above 180 °C, butane is essentially converted to carbon oxides, and no significant change in the product distribution is observed up to 350 °C. After the second transition, olefins and oxygenates are formed in large amount, whereas CO_x selectivity drops from 90 to 10%; butane conversion rises markedly. Above 450 °C, olefins show a further increase at the expense of oxygenates.

In order to get a deeper insight into the nature of these transitions in the reaction system, visible and infrared imaging of the gauze were utilised. The thermal maps of the gauze during the low temperature transition, reveal a fast ignition of exothermic reactions on the surface (Fig. 3). A thermal front is generated on the upper edge of the gauze and propagates to the whole surface in 1.6 s. In the same time, the metal temperature jumps to over 500 °C. At steady state, with a flow rate of 300 or 500 ml/min, the surface temperature after ignition largely exceeds the level above which the material starts to glow, as shown by the visible image of the gauze (Fig. 4). However, when the oven temperature is further increased above the temperature of the second transition (around 400 °C), visible radiation disappears, revealing a sudden drop in surface temperature (Fig. 5).

The plot of surface and gas temperature, measured by thermography and by a thermocouple, respectively, allows a better evaluation of these effects (Fig. 6). With a flow rate of 300 ml/min, the gauze temperature jumps from 220 to 570 °C upon ignition, and in the same time the gas temperature, measured just downstream of the gauze, also rises markedly. The two plots show a parallel increasing trend until the second transition occurs; at this point, the gauze temperature drops by about 150 °C, and thereafter remains constant. As the

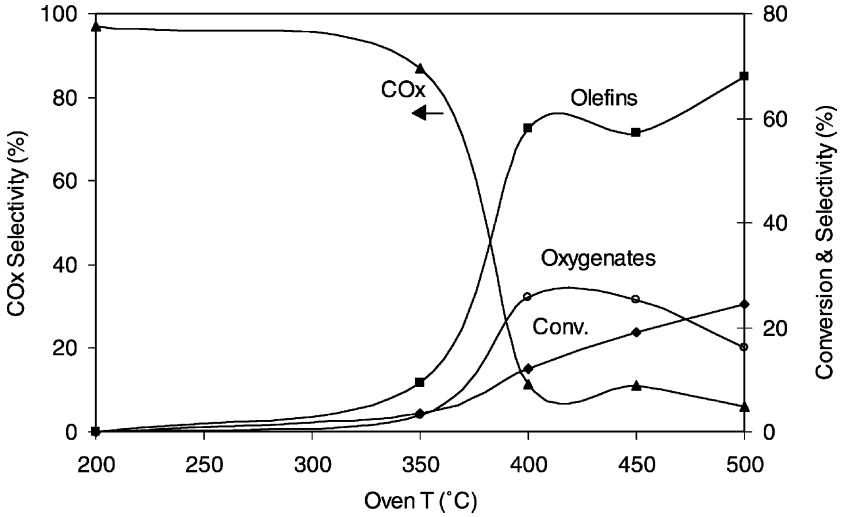

Fig. 2. Conversion and selectivities obtained at steady state with the metal gauze. Feed composition: $C_4H_{10}/O_2/N_2 = 50/20/30$; flow rate 300 ml_N/min.

gas temperature, after a drop, continues to rise, the two curves eventually coincide towards the end of the run (500 °C).

To obtain a more accurate description of the thermal effects generated inside the reactor, axial temperature profiles were determined. With a flow rate of 100 ml/min, thermal effects are localised in a narrow zone around the gauze after the first transition (Fig. 7, curve a). After the second transition, the temperature profile dramatically changes, and shows a broad band positioned near the reactor inlet, where exothermic reactions take place. In the central part of the reactor, instead, no thermal effect is observed. In these conditions, the gauze does not seem to play any role. When the flow rate is raised to 300 ml/min, the reaction front again stabilises close to the inlet, but some oxidation reactions take place also on the gauze, as revealed by a moderate heating of the metal surface.

In order to evaluate the contribution from homogeneous reactions to the overall mechanism, TPR runs were carried out in the absence of the gauze, under the same conditions of previous experiments (Fig. 8). At low temperature no reaction takes place; however, around 380 °C a fast transition is observed, with a sudden drop in O_2 and a rise in CO, and a second transition is observed at 420 °C. These results suggest that at high temperature, the behaviour of the reaction system is similar with and without the gauze.

A confirmation is provided by the axial temperature profile recorded at 400 °C (Fig. 9). The temperature distribution closely resembles the one obtained in the presence of the gauze; in fact, a maximum is observed near the reactor inlet, indicating a reaction front quite similar to the one observed with the gauze.

Product distributions measured at steady state in the two different configurations, are reported in Table 1. Butane conversion is 21% in the presence of the gauze, compared to 20% obtained in the empty reactor. In both cases, the overall selectivity to partial oxidation

Table 1
Comparison of *n*-butane conversion in the presence and absence of the catalyst

	Empty reactor	Pt–Rh gauze
Oven T (°C)	400	400
Flow rate (ml/min)	100	100
C_4 Conv. (%)	20.0	21.0
O_2 Conv. (%)	97.5	96.5
Selectivity (% C)		
C_4 olefins	37.5	41.8
C_2–C_3 olefins	13.8	13
C_4 oxygenates	13.2	13.1
C_1–C_3 oxygenates	16.8	16.2
CO	12.7	10.4
CO_2	2.5	3.2

Feed: $C_4H_{10}/O_2/N_2 = 50/20/30$.

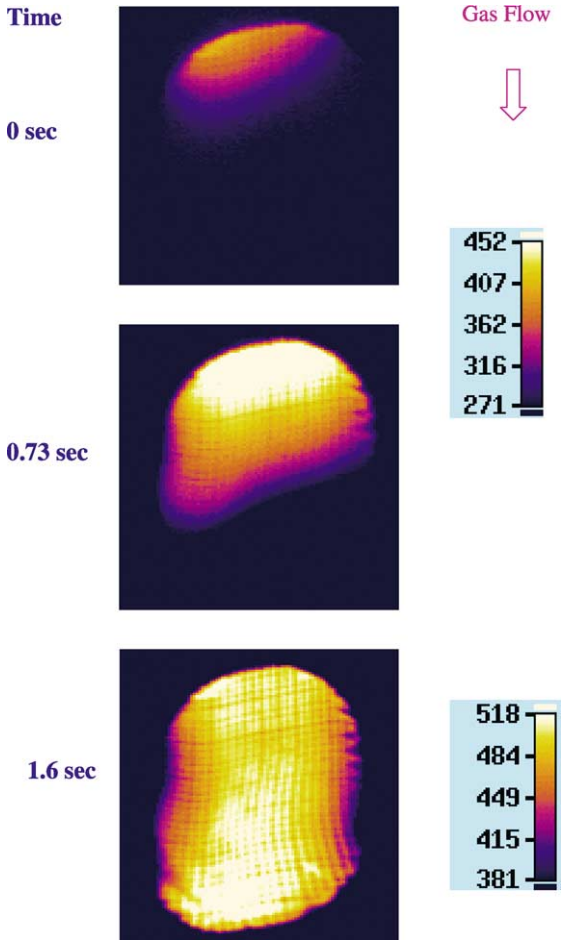

Fig. 3. Thermal infrared images of the Pt–Rh gauze during ignition. Feed composition: $C_4H_{10}/O_2/N_2$ = 50/20/30; flow rate 300 ml_N/min.

products is above 80%. The similarity in the product distributions obtained in the two different conditions is striking. The only noticeable differences concern olefins and the CO_2/CO ratio, which are higher with the gauze, whereas oxygenates are slightly lower.

4. Discussion

Experiments of temperature-programmed reaction showed that the alkane-rich $C_4H_{10}/O_2/N_2$ mixture exhibits multiple reaction pathways in the presence of the Pt–Rh gauze. Below 380 °C, butane is converted

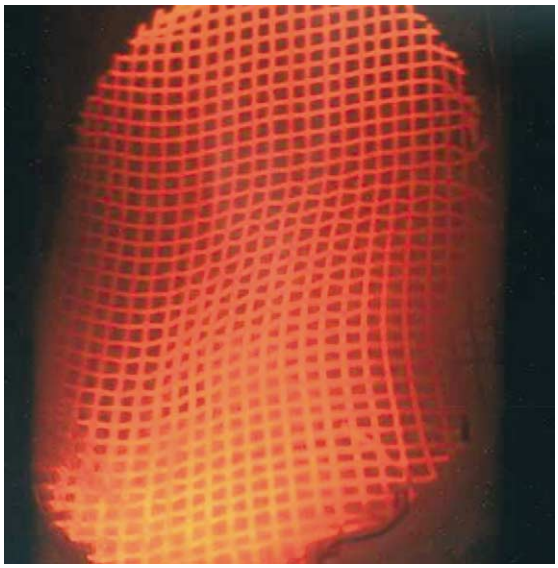

Fig. 4. Visible image of the gauze after ignition of the surface reactions. Flow rate 300 ml_N/min, oven temperature 400 °C.

on the metal surface yielding mainly CO_2. Between 380 and 420 °C, depending on the flow rate, a dramatic change in the reaction system occurs; surface reactions are substantially suppressed, and a different

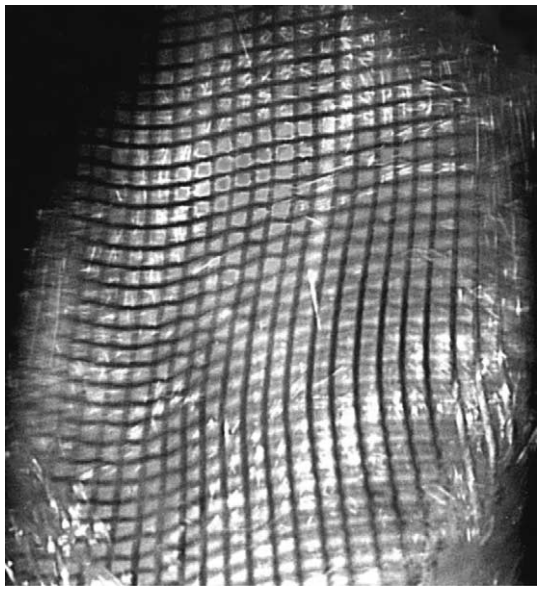

Fig. 5. Visible image of the gauze after transition to high selectivity conditions. Flow rate 300 ml_N/min, oven temperature 500 °C.

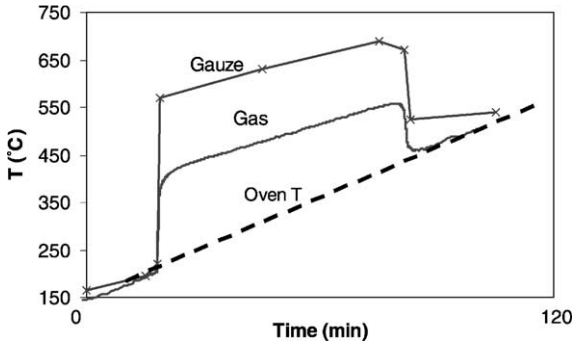

Fig. 6. Temperature of the gas phase and of the metal surface during a TPR run. Flow rate 300 ml_N/min.

mechanism brings to formation of significant amounts of olefins and oxygenates.

The nature of the observed transitions represents a key point in this investigation. The sudden rate increase at low temperature, is associated with ignition on the Pt–Rh surface. In fact, temperature measurements show that the exothermic effects are restricted to the gauze, and in situ imaging reveals the details of the propagation of a thermal wave on the metal surface. In addition, the high selectivity to CO_2 is typical of alkane oxidation on noble metals.

The second transition is the most intriguing and unexpected result of this study. It involves a substantial suppression of a catalytic reaction upon simply raising the oven temperature above a certain level, without any evidence of deactivation; in fact, the inverse transition from low to high rate of surface reactions, could be obtained by lowering the oven temperature.

Infrared imaging and temperature measurements show a marked temperature drop on the catalyst surface during the transition, and reveal the formation of a reaction front upstream of the gauze, where up to 20% of butane and 97% of oxygen are consumed. The mixture which impacts onto the gauze is thus deprived of most of the reactants, which causes the surface reactions to collapse.

The relocation of the reaction front from the metal surface to the initial zone of the reactor, involves a shift from a predominantly heterogeneous reaction mechanism to an homogeneous one. In fact, as the reaction front is stabilised a few centimetres upstream of the gauze, any contribution by the metal gauze is hardly conceivable: all the chemistry takes place within the first quarter of the reactor.

As to the mechanism causing this front migration, the homogeneous ignition of the feed mixture could appear a likely explanation. In fact, although the feed

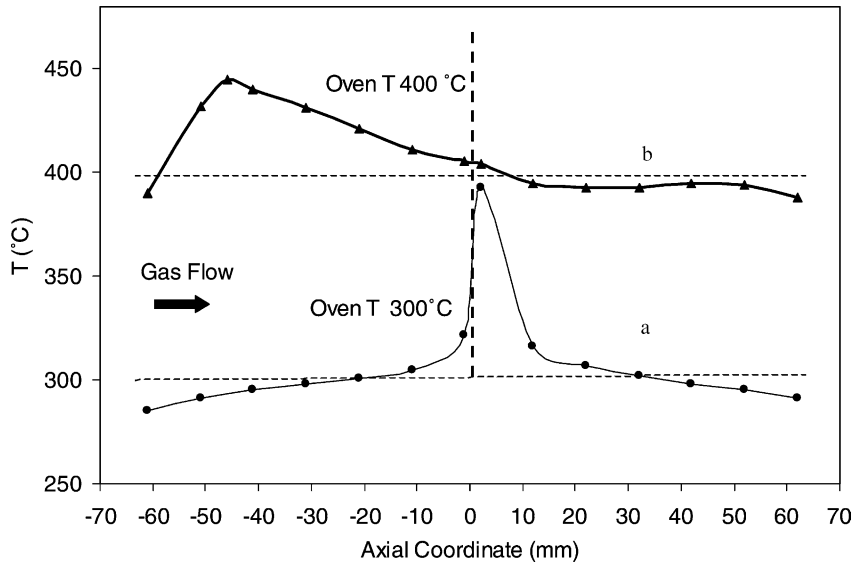

Fig. 7. Internal temperature profiles after ignition of surface reactions (curve a) and after transition to high selectivity (curve b). The vertical line marks the position of the gauze. Feed composition: $C_4H_{10}/O_2/N_2 = 50/20/30$; flow rate 100 ml_N/min.

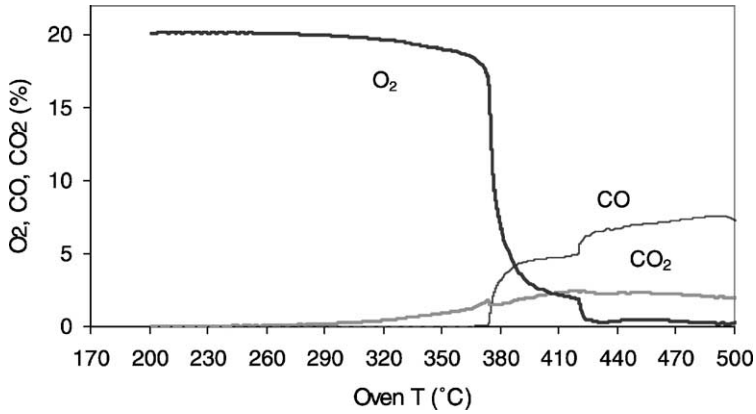

Fig. 8. Outlet concentrations measured during temperature-programmed reaction with the empty reactor. Feed composition: $C_4H_{10}/O_2/N_2 = 50/20/30$; flow rate 100 ml_N/min.

mixture has a composition outside the flammability region (Fig. 10) determined on the basis of literature data valid at ambient temperature [10], heating by the oven and by exothermic reactions on the gauze could widen this region to such an extent as to make the mixture flammable.

However, some aspects of this transition are to be considered. The rate of the upstream migration of the reaction front, evaluated by temperature measurements, is very low (of the order of 1 mm/s); this means that the absolute flame speed would be only slightly higher than the superficial velocity of the feed mixture, about 10 cm/s. This value represents an extremely low flame speed, which could be justified only by the close proximity of the reaction mixture to the flammability limits [11]. Other experimental evidence, though, is against the hypothesis of a flame formation. The gas temperature expected in this case would be much higher than that recorded after the transition (below 450 °C). A further important aspect is represented by the product distribution: oxygenated compounds such as aldehydes and alcohols, which are obtained in significant amounts, are not stable at the temperature characteristic of the flame.

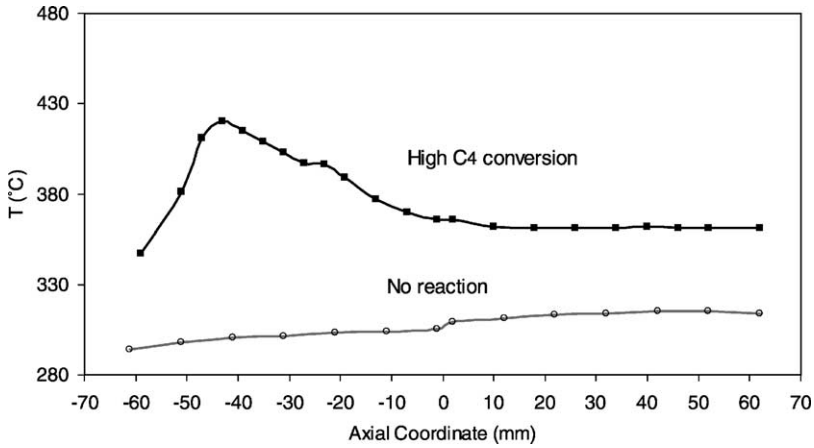

Fig. 9. Internal temperature profiles with the empty reactor at zero conversion and after transition to high conversion. Zero coordinate corresponds to the middle of the reactor. Feed composition: $C_4H_{10}/O_2/N_2 = 50/20/30$; flow rate 100 ml_N/min.

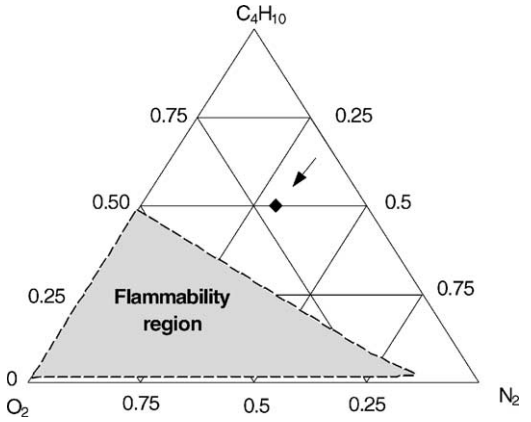

Fig. 10. Flammability region of butane at ambient temperature, derived from literature data. Arrow shows the mixture utilised in this study.

The likely mechanism leading to the product distribution reported in Table 1, is the one described for the oxidation of butane and higher hydrocarbons at low temperature, in the range 330–470 °C [12,13]. It involves initiation of the reaction in the gas phase by hydrogen abstraction from butane and formation of an alkyl radical; this is followed by addition of oxygen to form the peroxy radical $C_4H_9O_2\cdot$; subsequent steps involve internal hydrogen abstraction and various elimination and decomposition reactions, which form olefins and C_1–C_4 oxygenates. This reaction pathway has been proposed in previous studies on butane oxidation with Pt–Rh gauzes [6,8]. A mechanism involving peroxidic free radicals is also known to control the oxidation of butane and higher alkanes, in the region of cool flames, near the borderline of the explosion region [11].

Formation of significant amounts of cyclic C_4 oxygenates (butenoxide, dimethyl oxirane) in our catalytic tests, is in line with such mechanism. In addition, the results of experiments with the empty reactor (without the gauze) prove that the reactions leading to high selectivity in olefins and oxygenates are purely homogeneous.

Initiation of the homogeneous reactions by the surface of the packing material could represent a variant in the proposed mechanism. However, one has to consider that the inlet section of the reactor is empty, and only the lower half contains the quartz packing. The metal gauze is placed on top of this packing, approximately in the middle of the reactor, in catalytic experiments. Should the gas phase reactions be initiated by the packing material, one would expect a large difference in the onset temperatures between the two series of measurements—with and without the gauze—as the Pt–Rh surface is likely to be far more active than pure quartz. Instead, a comparison of Figs. 1 and 8 shows that the second transition occurs at about the same temperature in the two cases.

The transition observed above 430 °C, leading to an increase in olefin selectivity and a drop in oxygenates, represents a further change in the reaction pathway, typical of the homogeneous oxidation of alkanes; in fact, a high temperature mechanism has been proposed [12], which involves non-peroxidic radicals and forms mainly olefins.

5. Conclusions

The study sheds new light onto the mechanism of partial oxidation of butane in the presence of a metal gauze. Temperature-programmed experiments show that heterogeneous and homogeneous reactions can be resolved both in time and space. At low temperature (180–380 °C), deep oxidation occurs on the metal surface. At higher temperature, surface reactions are substantially suppressed as a consequence of gas phase oxidation occurring in the void upstream of the gauze, where oxygenates and olefins are formed via a peroxidic intermediate. Above 400 °C, a further transition reveals the onset of a different homogeneous mechanism involving alkyl radicals.

In previous studies on the catalytic conversion of butane to oxygenates [6,8], the metal gauze was considered instrumental in providing intense local heating and possibly active intermediates, which would lead to formation of partial oxidation products in the downstream reactor zone. Our results show that high, steady yields of olefins and oxygenates can be obtained from butane also in the absence of a catalyst. In fact, when a sufficient void is available, a reaction front tends to stabilise in the initial section of the reactor, where butane is homogeneously converted to partial oxidation products; this front can be generated and maintained independent of the presence of a metal catalyst.

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