Annular reactor testing and Raman surface characterization in the CPO of methane and propylene

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1. Introduction

Thanks to the wide availability and to the easy storage and transportation, the use of liquid fuels in short contact time catalytic partial oxidation (CPO) reformers represents a significant advance in on-board and small-scale power generation technologies. The extensive exploitation of LPG and higher hydrocarbons in CPO reformers is currently hampered by the high temperatures reached on the catalyst surface (>1000 °C) and by the formation of carbon species, which lead the catalyst to deactivation by sintering and coking. Both these issues become increasingly crucial upon increasing the complexity and the C number of the fuel. On one hand, in order to moderate the overheating, solutions based on the optimization of the reactor design have been proposed, which concern the geometry of the catalyst support and the layout of the internal elements of the reactor [1,2]. On the other hand, with respect to the issue of carbon formation, given its kinetic nature, possible solutions necessarily ask for a detailed understanding of the process chemistries involved, both homogenous and heterogeneous, and of their possible interplay. Several works dedicated to CPO and autothermal reforming (ATR) of C₃ and higher alkanes [3–16] report non-negligible selectivity to olefins (mainly ethylene and propylene) and cracking products (methane and ethane) at the exit of the reactor, even when noble metals are employed. Olefins in particular are well known coke-precursors: their presence can be taken as an indicator of the possible occurrence of condensation reactions, which lead to the formation of aromatic compounds and later to the growth of carbonaceous layers on the catalyst surface. As a matter of fact, the experimental results generally suggest that olefins are produced by homogenous pyrolysis routes, which activate in parallel to the mainstream heterogeneous routes giving synthesis gas via reforming.

With respect to Rh-based catalysts applied in CPO, the literature concerning higher alkanes has developed to a much smaller
extent than that dedicated to CH₄. The reason likely lays in that stable operation is commonly experienced in CH₄ oxy-reformers that work under autothermal conditions [17]. Wide agreement is found upon the evidence that CH₄ is not prone to coking on Rh: CH₄ is indeed regarded as difficult to activate on noble metals, thanks to its low tendency to stick on the surface and to its stronger C–H bond energy compared to larger alkanes [18,19]. When observed [20,21], C formation has been reported as a structure-sensitive process, therefore sensitive to the state of the surface in terms of defects and particle size, and also dependent on the network of reaction steps involved, namely upon the breaking of C–H or C–O bonds or the adsorption of phase-intermediates.

In the case of higher alkanes, the group of Schmidt [6,15] reported that Rh-coated alumina foams are able to steadily reform up to C₁₆ paraffins, under autothermal conditions, at short contact times and temperature ranging from 800 to 1100 °C, with no deactivation due to coke formation. Such a remarkable resistance was achieved using very high Rh loading with extremely low particle dispersion (almost a film in some cases). The experiments showed that the selectivity to olefins decreased in favor of synthesis gas when a γ-Al₂O₃ washcoat was applied, i.e. when the metal area active for heterogeneous reforming increased. As well, a lower production of olefins was observed by increase of the foam ppi (from 45 to 800 ppi), that is when the pore size decreased and less empty volume was given to homogeneous chemistry to evolve.

The onset of coke formation at a certain position of the catalytic monolith was shown numerically and experimentally by the group of Deutschmann in the CPO of i-octane over Rh-based catalysts supported over corderite honeycombs [8]. A transition point was individuated between a coke-free region, roughly corresponding to the oxygen consumption zone of the catalyst, and a coke-forming region, associated to the zone where the catalyst experiences gas-phase pyrolysis in parallel to surface steam reforming. The position of this coke transition point was found to be very sensitive to the C/O ratio and to the flow rate: it moves upstream with increasing C/O or decreasing flow rate. Consistently, already at C/O = 1.1 (O₂/C = 0.45), a breakthrough of olefins (propylene and i-butylene) and other cracking products was observed. Along with the role of olefins in the CPO of higher alkanes, our group has recently applied spatially resolved profiles of temperature and composition in the autothermal CPO of C₃H₈ over 2 wt% Rh/α-Al₂O₃ catalysts supported over ceramic honeycombs [22]. The results showed that small amounts of methane, ethane, ethylene and propylene are present at the very inlet of the catalyst, in close correspondence of the hot spot. The formation of these species was attributed to homogenous cracking reactions, followed by consumption via steam reforming on the catalyst surface.

Overall, these results suggest that C₂, and other intermediate olefins may have a significant impact in the oxy-reforming process, especially when non stoichiometric C/O ratios are used. It is indeed expected that the behavior of olefins is more sensitive to C formation, given that the presence of the C=C double bond increases the affinity with the surface. By application of vibrational spectroscopy techniques under ultrahigh vacuum conditions, Somorjai and co-workers [23] analyzed the reactions of thermal decomposition of propylene, propadiene and methylacetylene on Rh(1 1 1) model surfaces, from 80 to 800 K. Friend and co-workers [24,25] extended this analysis by performing theoretical and experimental studies on the partial oxidation of ethylene and propylene. Globally, the results confirm that the C=C double bond is the active functional group of the olefin and that its activation prevails over that of the allylic C–H bond. On Rh clean surfaces, a dehydrogenation pathway leads via CH₃ intermediates to the formation of adsorbed C, which polymerizes to graphic structures upon increasing the temperature. In the presence of chemisorbed oxygen, partial and total oxidation routes compete favorably with dehydrogenation, being this competition dependent on the oxygen surface coverage.

In order to investigate the role of olefins in the CPO mechanism, in this work we analyze the CPO of C₃H₆ (representative C₂+, coke-forming fuel) and CH₄ (assumed as the reference coke-free fuel in CPO) performed on Rh-based catalyst, focusing the attention on the tendency to coke formation. The formation of carbon species as a function of temperature and reaction conditions is followed by combining kinetic investigation performed in an annular micro-reactor, with Raman measurements of the catalyst surface. A companion paper will be presented concerning the kinetic effects observed in the C₃H₆ CPO experiments performed in the annular microreactor. Herein, these effects are briefly recalled in the section of results and discussion.

2. Materials and methods

2.1. Catalyst preparation

A 2 wt% Rh/α-Al₂O₃ catalyst was prepared by dry impregnation of the α-Al₂O₃ support (10 m²/g surface area by BET measurement) with a commercial Rh(NO₃)₃ aqueous solution. The impregnated powders were dried in oven at 110 °C for 3 h. For testing in the annular reactor, the catalyst was deposited in the form of thin layers on sintered alumina tubular supports. A dip coating technique was applied, starting from a slurry of the catalyst powders prepared according to a standard recipe [26]. The coated tubular supports were then flash-dried in oven at 280 °C for 10 min to fix the catalyst layer on the external surface of the support. Well adherent layers were obtained, 20 mm long, between 7 and 12 mg in weight and 15–25 μm thick.

2.2. Annular reactor testing

The CPO experiments were performed in an annular reactor. The reactor was externally heated by a tubular furnace and a MicroGC (3000A by Agilent Technologies) was used to analyze the composition of the inlet and outlet gas streams. Detailed descriptions of the reactor and of the set-up are given elsewhere [27]. Here it is worthy to recall that the annular reactor consists of an inner catalyst-coated ceramic tube (O.D. = 4 mm) coaxially inserted into an outer quartz tube (I.D. = 5 mm), giving rise to an annular duct wherein the gas flows in laminar regime. The laminar regime allows to reach very high gas velocity. In this way, it is possible to test fast and exothermic reactions, like the CPO of light hydrocarbons, far from the thermodynamic limitations, in a wide kinetically informative experimental field. Dilution of the reacting mixture and efficient heat dissipation by radiation allow to reach quasi-isothermal conditions on the catalyst layer. At any time, the temperature profile can be verified by sliding a thermocouple inside the tubular ceramic support, given that thermal equilibrium establishes in the cross section of the reactor.

The CPO experiments were carried out at atmospheric pressure between 200 and 850 °C, increasing the temperature by step-wise increments of 10–50 °C. At each temperature, the conversion of the reactants and the molar fraction of the products were estimated by repeated analyses, showing stable performances within 15–20 min. Prior to the kinetic tests, the catalyst underwent a conditioning procedure that consisted of repeated runs at 8 × 10⁵ NI/(kgcat h) GHSV, feeding a gas mixture with 4% CH₄ (v/v), 22.4% O₂ (O₂/C = 0.56), and N₂ to balance. The conditioning procedure was considered complete when stable performances were achieved in the whole temperature range, typically within three runs. Only in one case, the conditioning procedure was skipped and the catalyst was first exposed directly to the standard C₃H₆ CPO conditions, which
The Raman experiments were carried out with a portable i-Raman BWTEK instrument (TE Cooled 2048 Pixel CCD detector). Laser excitation at 785 nm was used, with 5 cm$^{-1}$ spectral resolution, and 175–3200 cm$^{-1}$ shift range. The Raman instrument was connected to a video microscope sampling system (BAC151A) with integrated camera for tracking the laser beam position and focusing. The measurements were taken in backscattered mode.

In order to investigate the state of the catalyst surface during the reaction and monitor the production of carbon species, the Raman experiments were coupled with the CPO experiments. Indeed, in the annular reactor configuration, the very thin exposed catalyst layers and the transparent quartz glass allowed for a direct spectroscopic investigation of the catalyst surface. Fresh catalyst samples and conditioned catalysts were tested: the data on the fresh catalysts refer to experiments that were performed after several runs under different operating conditions.

In the case of C$_3$H$_6$, Raman measurements were carried out during the first exposure of the fresh catalyst to a standard C$_3$H$_6$ CPO mixture, but also after a set of 40 runs (dedicated to the kinetic investigation). In the case of CH$_4$, Raman measurements were collected during the first exposure of the fresh catalyst to a CH$_4$ CPO conditioning mixture and also after the conditioning procedure had been completed.

The Raman measurements were taken at room temperature, according to the following procedure: (1) after reaching steady state in the annular reactor during the CPO test at a certain temperature, the gas mixture was switched to N$_2$ and the reactor was cooled down to room temperature, under inert N$_2$ flow; (2) the reactor, kept under N$_2$ flow, was extracted from the furnace and fixed to the adjustable table of the microscope; (3) the Raman signal was measured by focusing the beam directly on the catalyst layer through the quartz wall of the reactor, always kept under N$_2$ flow; (4) the gas mixture was switched back to the CPO composition, the reactor was inserted in the furnace and heated up to a new (higher) level of temperature. During each Raman inspection, five positions were scanned along the axis of the catalyst layer, by manually adjusting the movable table of the microscope. The first point was positioned at the very beginning of the layer, within the first millimeter, while the others were collected keeping a 5 mm gap between each other.

2.4. Temperature programmed oxidation tests

Temperature programmed oxidation (TPO) tests were also performed to quantify the amount of carbon accumulated on the catalyst during the CPO of C$_3$H$_6$ at three significant temperatures (300, 425 and 850 °C). The tests were carried out directly in the annular reactor, by heating the catalyst under air flow (GHSV = 10$^4$ Nl/(kg$_{cat}$ h)) from room temperature up to 1000 °C at 2 °C/min, with a final hold of about 2 h. Prior to the TPO tests, the catalyst was exposed for 2 h to standard C$_3$H$_6$ CPO conditions and then cooled down to room temperature under inert N$_2$ flow. For each test, the results are reported as the ratio between the moles of CO$_2$ produced by combustion and the moles of Rh present in the catalyst (2.4 µmol).

3. Results and discussion

3.1. Kinetic dependences: investigation in annular reactor

In order to better appreciate the features observed in the CPO of C$_3$H$_6$, it is worthy to first recall the main characteristics of the CPO process with CH$_4$ and C$_3$H$_8$. CH$_4$ is the reference hydrocarbon in CPO and, by far, the most broadly studied, while C$_3$H$_8$ is herein taken into consideration as it is the saturated homologue of C$_3$H$_6$. Additionally, in our experience, the reactivity patterns of CH$_4$ and C$_3$H$_8$ are widely representative of the CPO of light alkanes. A comparison is proposed in Fig. 1 between the results of CPO tests performed with CH$_4$ (panel a) and C$_3$H$_8$ (panel b). The comparison is realized at equal contact time and C concentration in the reacting gas mixture. The conversion of O$_2$ and fuel, and the molar fractions of H$_2$ and H$_2$O are plotted as a function of the temperature. The total oxidation of CH$_4$ activates around 300 °C and goes to completion at ~460 °C, as indicated by the O$_2$ conversion curve. In the presence of O$_2$, H$_2$O and CO$_2$ are the only products observed. Upon increasing the temperature, a smooth transition between the total oxidation regime and the oxidation plus steam reforming regime is observed: once O$_2$ reaches the complete consumption, steam reforming effectively consumes the fuel and the H$_2$O, with production of syngas and with steady increase of the fuel conversion with temperature and contact time. An almost identical evolution is observed in the case of C$_3$H$_8$: the total oxidation region starts at 300 °C and completes the conversion of O$_2$ at ~400 °C, above which we observe the activation of steam reforming, responsible for the production of syngas and eventually for the complete conversion of the fuel.

The analogy between CH$_4$ and C$_3$H$_8$ CPO is further strengthened by the kinetic dependencies observed. As reported in previous works [27,28], CPO experiments performed at nonstoichiometric O$_2$/C ratios reveal that the rate of total oxidation is independent from the concentration of O$_2$ and first order dependent on the fuel concentration. Zeroth-order equations are therefore proposed with respect to O$_2$ for both CH$_4$ and C$_3$H$_8$. The independence from O$_2$ suggests that the activation of CH$_4$ and C$_3$H$_8$ occurs in the presence of similar surface coverages, namely on a surface saturated by chemisorbed oxygen atoms O$^*$. With reference to the kinetic studies of Ilega and co-workers for methane and ethane on noble metal catalysts [29,30], the activation of CH$_4$ and C$_3$H$_8$ would then occur in the so-called Regime I, that is, by dissociation of the C–H bond on chemisorbed oxygen pairs. Important similarities between CH$_4$ and C$_3$H$_8$ emerge also for the steam reforming: in both cases, experiments at low fuel conversion (<20%) show that the intrinsic rate of the reaction is first-order with respect to the concentration of the fuel and comparable with the rate of total oxidation. As a matter of fact, the steam reforming rate is found independent of the co-reactant concentration (i.e. H$_2$O), thus indicating that the activation of the fuel is again the determining step. Additionally, for both CH$_4$ and C$_3$H$_8$, at higher conversion, it is experimentally found that O$_2$ delays the activation of steam reforming and that the global order of the reaction appears to be lower than 1: coherently, in order to describe these effects, inhibition terms due to O$_2$ and CO adsorption are assumed in lumped rate equations [27,28].

The results of a typical C$_3$H$_6$ CPO test carried out under isothermal conditions in the annular reactor are presented in Fig. 2. The conversion of the reactants and the molar fraction of the products are plotted as a function of temperature. Taking into consideration the characteristics of CH$_4$ and C$_3$H$_8$ CPO, significant differences
Fig. 1. Comparison among CPO experiments with different fuels. $O_2/C = 0.56$ and $GHSV = 2 \times 10^6 \text{NL/(kgcat h)}$. Fuel and $O_2$ conversion are reported. Panels: (a) $\text{CH}_4 = 3\% (v/v)$; (b) $\text{C}_3\text{H}_8 = 1\% (v/v)$. Full symbols are conversion of the fuel (■) and $O_2$ (●). Open symbols are molar fraction of $H_2$ (□) and $H_2O$ (○).

Fig. 2. $\text{C}_3\text{H}_6$ CPO experiment. $\text{C}_3\text{H}_6 = 1\% (v/v)$, $O_2 = 1.68\%$, $N_2$ to balance, $O_2/C = 0.56$, $GHSV = 2 \times 10^6 \text{NL/(kgcat h)}$, $P = 1 \text{ atm}$. Panels: (a) conversion of $O_2$ and $\text{C}_3\text{H}_6$; (b) molar fraction of $H_2$ and $\text{CO}$; (c) molar fraction of $H_2O$ and $\text{CO}_2$; (d) molar fraction of $\text{C}_2\text{H}_6$ and $\text{CH}_4$. Symbols are data. Dashed lines are equilibrium.
emerge. At remarkably low temperature, between 200 and 300 °C, C3H6 reacts with O2 producing exclusively CO2 and H2O. No synthesis gas is formed, in line with the activation of the total oxidation reaction (Eq. (1)). Compared to CH4 and C3H8, the total oxidation of C3H6 is therefore extremely faster: it activates almost 100% to 40%, with further production of CO2 and H2O and very limited formation of syngas, around 400 °C.

\[ \text{C}_3\text{H}_6 + 9/2\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} \]  

(1)

Between 300 and 400 °C, once the conversion of O2 is nearly complete (>90%), the conversion of C3H6 slowly increases from 35% to 40%, with further production of CO2 and H2O and very limited formation of syngas, around 400 °C. At temperatures higher than 400 °C, the conversion of C3H6 steadily increases up to complete consumption, at the expenses of H2O, with steady production of H2 and CO, according to the steam reforming reaction (Eq. (2)). Conversion of CO2 is also observed and attributed to the onset of the reverse water gas shift reaction (Eq. (3)). Differently from the early activation of total oxidation, the steam reforming of C3H6 activates in a temperature range (400–450 °C) comparable with that of CH4 and C3H8 (dashed lines in Fig. 1), but initially progresses with a slow rate, as suggested by the slope of C3H6 conversion curve between 450 and 600 °C.

\[ \text{C}_3\text{H}_6 + 3\text{H}_2\text{O} \rightarrow 3\text{CO} + 6\text{H}_2 \]  

(2)

\[ \text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \]  

(3)

In the whole temperature range, production of trace quantities of CH4 and C2H6 is also observed (Fig. 2d), likely due to the occurrence of surface cracking reactions involving C3H6. The extent of these reactions is extremely limited, nonetheless a catalytic route is possibly active at low temperatures, which could explain the production of CH4 and C2H6 below 450 °C, while a homogenous route could prevail at higher temperatures.

Further details on the individual reaction kinetics observed in C3H6 CPO will be given in the dedicated companion paper. Herein, it is important to note that a remarkable distinction emerges between the ultra-fast total oxidation activity and the steam reforming activity, which results in a discontinuity and in the appearance of a plateau in the conversion of C3H6. Compared to CH4 and C3H8, whose transition between the total oxidation and the steam reforming regimes is smooth, such a discontinuity is a unique feature. In the literature, other authors [31] reported the occurrence of a similar plateau when performing the partial oxidation of propane over Pt and Pt–Ce catalysts, under conditions close to the present ones. The behavior was associated to the difference between the rate of total oxidation and that of steam reforming, which was reported to be delayed on Pt surfaces by the inhibiting effect of water. However, in the present case, the reactivity of C3H6, which is an olefin and has an unsaturated double bond, suggests that different kinetic dependencies may cause the observed behavior, with particular reference to the adsorption characteristics.

In light of this, it is worthy to analyze the main kinetic dependencies of the total oxidation and the steam reforming rate. In the first case, a C3H6 CPO experiment is presented in Fig. 3, performed by increasing the O2 to C ratio while keeping the concentration of C3H6 constant. The increase of O2 concentration shifts the plateau to higher conversion levels, finally leading to its disappearance at O2/C = 1.4. In contrast, in the low temperature and low conversion region (T < 260 °C), an inhibition effect on C3H6 conversion is observed: indeed, at increasing O2 concentration, the conversion of C3H6 decreases. The inhibiting effect of O2 on C3H6 conversion suggests competing adsorption between the two reactants, and, in turn, that the surface is possibly covered by both chemisorbed oxygen and CH4 hydrocarbon intermediates deriving from C3H6 activation. Again, with reference to Ref. [29], we propose that the activation of C3H6 in the presence of O2 in CPO occurs in a kinetic regime similar to what the authors identify as Regime II, i.e. the activation of the hydrocarbon on vacancies coupled with chemisorbed oxygen (O*- pairs).

Along with the high affinity of C3H6 for the Rh surface, steam reforming tests (Fig. 4) show that the reaction activates at temperatures around 500 °C, higher than those observed in the high temperature branch of the CPO experiment, and much higher than those found on the same catalyst under comparable conditions in case of CH4 (~300 °C) and C3H8 (~350 °C) [27,28]. Notably, neither hydrogen nor methane and ethylene are observed before the reaction starts, possibly indicating that cracking is not occurring under steam reforming conditions. Such a delayed activation suggests the occurrence of a self-inhibiting effect of C3H6, which sticks on the catalyst surface, saturates the active sites and prohibits the adsorption of H2O up to the reaching of sufficiently high temperatures.
Overall, the kinetic tests performed in the annular reactor point out that the reactivity of C\textsubscript{3}H\textsubscript{6} is strongly characterized by its high adsorption capability on the Rh surface, which results in a quicker activation of the total oxidation reaction, but blocks the surface in the case of steam reforming. As a consequence of the sticking capability of C\textsubscript{3}H\textsubscript{6}, it is interesting to understand what is the state of the surface during the CPO and whether carbon residues are accumulated, which can potentially lead to the coking of the catalyst. Thanks to its sensitivity to carbon structures, Raman analysis of the surface was individuated as a potentially suitable tool. Carbon accumulation appears to play an important role, given that the catalyst slowly deactivates over the course of repeated standard C\textsubscript{3}H\textsubscript{6} CPO tests.

3.2. Ex situ Raman investigation of the catalyst surface

The state of the catalyst surface was investigated during two reference situations at equal O\textsubscript{2}/C ratio of 0.56, namely the standard C\textsubscript{3}H\textsubscript{6} CPO experiment (1% v/v C\textsubscript{3}H\textsubscript{6} and 2 \times 10\textsuperscript{6} Nl/(kg\textsubscript{cat} h) GHSV) and a C\textsubscript{4}H\textsubscript{4} CPO experiment under the typical conditions adopted in kinetic tests (4% v/v C\textsubscript{4}H\textsubscript{4} and 8 \times 10\textsuperscript{5} Nl/(kg\textsubscript{cat} h) GHSV). As well, the Raman experiments were performed over two different surfaces, the fresh surface, characteristic of the catalyst at its first exposure to the reacting mixture, and the conditioned surface, representative of the surface after reasonable time on stream. The experimental procedure adopted in the measurements is detailed in Section 2.3. In all cases, the same CPO run was repeated after the Raman test, in order to verify the occurrence of possible changes of the catalytic activity. The observed variations were within the experimental uncertainty, suggesting that the procedure had no significant side effects. In the figures that report the Raman spectra (Figs. 5–8), inserts are present that plot the fuel conversion as a function of temperature during (open symbols □) and after (full symbols ■) the Raman measurements. Only in the case of the fresh sample exposed to C\textsubscript{3}H\textsubscript{6} CPO conditions (Fig. 7, insert), the comparison is provided between the conversion obtained during the Raman test and that obtained over the fully conditioned catalyst of Fig. 2. It can be seen that, aside of moderate variations of the activity, all the characteristic features are retained. It is also worthy to note that the Raman spectra reported in the figures were those collected in the middle of the catalyst layer, which represent a reasonable average over the intensity fluctuations. Along the layer, at each temperature, the same peaks were always identified, but with different intensities. These differences are related to the reaction chemistry and are discussed in Section 3.3.

The results of the Raman investigation performed during C\textsubscript{3}H\textsubscript{6} CPO over a fresh surface are reported in Fig. 5. Up to 500 °C, no signal associated to carbon is detected. At 600 °C, when O\textsubscript{2} is totally converted and CH\textsubscript{4} is consumed by steam reforming, weak signals at 1595 cm\textsuperscript{-1} and 1350 cm\textsuperscript{-1} appear, respectively attributed to the formation of graphitic structures (peak G) and amorphous carbon deposits (peak D). Even though the unambiguous attribution of peak D is still debated, for the purpose of this work it can be confidently associated to the presence of amorphous carbon deposits and, more generally, of condensed poly-aromatic moieties embedded in amorphous regions [32] or edge-regions of ordered graphitic structures [33]. At 850 °C, when the reaction reaches the complete conversion, the G and D peaks are accompanied by lines typically...
associated to the formation of carbon nanotubes, i.e. the radial breathing modes of the nanotubes (RBM, 400–180 cm\(^{-1}\) region) and the sharp component of the G peak. The formation of carbon nanotubes (previously reported on Rh foils\[34\]) suggests that more organized structures are present on the surface at high temperatures. Nonetheless, as generally experienced with noble metals, these results confirm that CH\(_4\) has a low sticking tendency and hence also a low tendency to form and accumulate carbonaceous species on the catalyst surface, which maintains relatively clean during the CPO reaction. As a matter of fact, the CPO of CH\(_4\) on Rh-based catalysts is known to proceed with no coking issues also at higher CH\(_4\) concentration and more challenging conditions than the present ones, for instance with CH\(_4\)/air streams within autothermal reformers\[33–37\].

Different features appear in the Raman spectra collected during the CH\(_4\) CPO test over the conditioned catalyst (Fig. 6). At 300 °C, when the conversion of CH\(_4\) and O\(_2\) has not yet started, a sharp G peak, a weak D peak and the RBM signals of the nanotubes\[38\] are already present. The latter low frequency Raman features characteristic of nanotubes are consistent with the diameters of the tubes which can be probed with the 785 nm excitation in a Kataura plot\[38\] and are well distinguished from the low frequency Raman features of other sp\(^2\) carbon species like onions\[39\] or C\(_{60}\) buckyball\[40\]. Some other signals are also distinguished at 2567 cm\(^{-1}\) (2D peak\[41\]), 1850 cm\(^{-1}\) (L peak\[42,43\]) and 1780 cm\(^{-1}\) (M features\[44\]), which can be respectively attributed to the first overtone of the D peak (associated to the formation of extended polycyclic aromatic structures), to linear carbon chains (polyynes) and overlapped contributions from nanotubes and graphite. The appearance of these signals at low temperature is due to the accumulation of the carbon species formed at high temperature during the previous conditioning runs. This accumulation is a direct consequence of the conditioning process, which involves loss of defect sites on the surface and ends up with the establishment of a steady-state limited amount of C-species that does not hinder the activity and the life of the catalyst\[26,45\]. The experimental procedure followed (Section 2) allowed to preserve this C-species also at low temperature: indeed, between each run and the next one, the catalyst is cooled to ambient temperature under inert N\(_2\) atmosphere, so as to keep the state of the surface intact. Upon increasing the temperature to 600 °C, the Raman spectra show that the G and the RBM signals become sharper, while the other peaks weaken or disappear. The final state of the surface is again relatively clean, in line with the results obtained over the fresh catalyst and with the widely recognized stability of CH\(_4\) CPO on Rh. Along with this, it is worthy to note that the signal to noise ratio of the spectra, which in both cases have irregular profiles, can be assumed as an additional piece of evidence of the limited amount of carbon present on the catalyst. Overall, the Raman measurements over the fresh and the conditioned catalysts are consistent with the kinetic dependences discussed in Section 3.1: the surface is almost fully available, so that, once O\(_2\) is consumed, the steam reforming of CH\(_4\) proceeds with high rate and with no temperature gap between the oxidation and the reforming branch (Fig. 1a).

A more elaborate picture emerges from the Raman experiments performed during C\(_3\)H\(_6\) CPO. The results obtained over the fresh catalyst are reported in Fig. 7. No carbon signals are detected up to 200 °C, when O\(_2\) conversion is low (insert). Already at 300 °C, at the beginning of the flat region, weak G and D peaks appear, which grow considerably at 425 °C. Notably, at 300 °C the conversion of O\(_2\) still amounts to 85% only. At 650 °C, when the steam reforming is active, the RBM lines and the sharp G component of the nanotubes are observed. At 850 °C, the G and RBM signals become sharper and the D peak weakens. The 2D, L and M signals are also evident. Clearly, carbon intermediates of complex nature are formed on the catalyst surface during the CPO of C\(_3\)H\(_6\), in line with the pronounced affinity of C\(_3\)H\(_6\) with the Rh surface and with the carbon accumulation tendency of the catalyst.

When the Raman measurements are repeated over a fully conditioned catalyst (Fig. 8), some differences are found. In line with the accumulation effect discussed in the case of CH\(_4\) CPO and related to the experimental procedure, the spectra collected at 200 °C show a pattern essentially analogous to those observed at 850 °C on the fresh surface. Differences are noted in the contributions of peak D and of the RBMs, which are reasonably due to the fact that the catalyst underwent a series of runs at various operating conditions, also with non-stoichiometric C\(_3\)H\(_6)/O\(_2\) mixtures. Most importantly, however, when the temperature is increased to 300 °C, only weak D and G peaks are present, while all the other signals (2D, L, M and RBM) have disappeared. This result is likely due to the cleaning.
effect of O2, which burns off most of the “inherited” carbon deposits and keeps a favorable C balance, avoiding a severe build-up: as a consequence, the spectra are similar to those obtained over the fresh surface at equal temperature (Fig. 7), even though the initial condition is different. The evolution of the Raman spectra from 425°C to 850°C confirms that of the fresh catalyst: a significant growth of D and G peaks is observed, followed by the strengthening of the RBM signals and to the appearance of the 2D, L and M signals at 850°C.

Taken together, these results seem to agree with the kinetic dependences outlined by the experiments in the annular reactor, and also with the results of the TPO tests performed after the C3H6 CPO experiments (Table 1). The strong adsorption of C3H6 leads to the build-up of carbon species: at low temperatures and low O2 partial pressure, carbon species are observed even in the presence of unconverted O2 (Fig. 2a and insert in Fig. 7), as suggested by the spectra at 300°C (Figs. 7 and 8) and by the production of ppm amounts of CH4 and C2H6 between 200 and 300°C (Fig. 2d). Coherently, a low amount of carbon (C/Rh ratio of 13 mol/mol) is found after the CPO experiment at 300°C. At intermediate temperatures, the adsorption of C3H6 followed by formation of relatively stable C species, mainly amorphous, hinders the surface sites and delays the formation of synthesis gas by steam reforming. High temperatures are then required to unblock the surface and allow for the full activation of the steam reforming reaction. In line with this picture, the highest amount of carbon (56 mol/mol) is found after the CPO at 425°C, indicating that the build-up of carbon mostly occurs in the absence of O2 and when C3H6 steam reforming is barely active. Upon increasing the temperature to 850°C, the C/Rh ratio drops to 15 mol/mol: a carbon removal mechanism is therefore active, which is possibly associated with the gasification by H2O and the formation of synthesis gas.

### 3.3. Hypotheses on carbon removal mechanism

Given the key role of the adsorbed intermediates in the reactivity of C3H6, it is interesting to investigate the mechanism that removes the carbon species and unblocks the Rh surface. First, it is important to note that, upon increasing the temperature, an evolution is observed in the carbon structures, which start from amorphous deposits and go to nanotubes, therefore following the direction of increasing order. Such an evolution is better appreciated by a quantitative estimation of the ratio between the intensity of the D and G peaks of each Raman spectra collected during the test. This ratio can indeed be taken as an indicator of the increasing or decreasing disorder of the carbon structures, and, in other words, of the maturity of the C-complexes present on the surface. The ratio between peak D and G calculated during the C3H6 CPO test over the fresh catalyst is reported as a function of temperature in Fig. 9: a constant decrease is observed at increasing temperature. This result suggests that a chemical mechanism is active on the surface, but does not entirely clarify its nature. In fact, it is commonly understood that more disordered carbon structures are also more reactive than ordered ones, thanks to the higher number of edges and active sites: consequently, any C-consuming reaction (combustion, inverse CO disproportionation or gasification) would deplete the amorphous carbon first and cause a decrease of the D/G ratio. As well, the occurrence of a route that reorganizes the amorphous structures into ordered complexes (nanotubes and graphite), unblocking the occupied sites, cannot in principle be excluded. This route would be driven by temperature and could possibly work in parallel to the C-consuming route.

A more detailed picture is given by the analysis of the axial profiles of the D/G ratio collected by scanning the catalyst layer. For each different temperature, the profiles are reported in Fig. 10 as a function of the axial position. At 300 and 425°C the D/G ratio is fairly constant along the layer, while at 650 and 850°C a common evolution is found, wherein the ratio first keeps almost constant (points 1 and 2) and then grows steadily up to the outlet of the layer (points 3–5). These results can be reasonably interpreted on the basis of the axial profiles of gas phase composition encountered during the isothermal CPO tests. Up to 425°C, C-combustion determines the D/G ratio: indeed, almost no synthesis gas is produced (Fig. 2b), CO2 and H2O are the only relevant products (Fig. 2c) and O2 is not completely consumed (at 300°C) or it is totally consumed right by the end of the catalyst (at 425°C, 98% O2 conversion). At 650 and 850°C, the evolution of the D/G ratio is associated with the

### Table 1

Results of TPO tests performed after standard C3H6 CPO experiments at three different temperatures. The C/Rh ratio is estimated as the moles of CO2 produced by combustion divided by the total amount of Rh present in the catalyst (2.4 μmol).

<table>
<thead>
<tr>
<th>CPO T [°C]</th>
<th>CO2 [μmol]</th>
<th>C/Rh ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>31.2</td>
<td>13</td>
</tr>
<tr>
<td>425</td>
<td>135.0</td>
<td>56</td>
</tr>
<tr>
<td>850</td>
<td>36.6</td>
<td>15</td>
</tr>
</tbody>
</table>

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**Fig. 9.** Average D/G intensity ratio as a function of temperature.

**Fig. 10.** D/G intensity ratio as a function of axial position. Raman measurements are taken after C3H6 CPO tests at: 300°C (▲); 425°C (●); 650°C (▲); 850°C (▼).
onset of an oxidation zone, followed by a reforming zone wherein syngas is produced. In the first part of the catalyst, O$_2$ is still present and is being consumed, and C-combustion prevails. In this respect, it is worthy to note that the distance between the scanned points is not exact and regular due to manual positioning of the measuring spot, so that the distances in the graph are not representative of the expected O$_2$ consumption lengths. In the second part of the layer, O$_2$ is completely consumed and H$_2$O and CO are responsible for the removal of C species, anyway less efficiently than O$_2$, as the ratios tell that, in the absence of O$_2$, CO and mostly H$_2$O may have a catalytic role in the oxidation of C species and in the consumption of O$_2$. Consistently, the estimation of the reaction quotients $K_{p}/K_{eq}$ (Fig. 11) shows that, under the investigated conditions, carbon gasification and inverse CO disproportionation are both thermodynamically favored, with the latter reaction being much closer to the equilibrium than the first one. As expected, the reaction quotients also evidence that the C$_3$H$_6$ cracking route (Eq. (4)) and inverse CO disproportionation (Eq. (5)) could be the active routes for C removal. Consequently, the estimation of the reaction quotients $K_{p}/K_{eq}$ (Fig. 11) shows that, under the investigated conditions, carbon gasification and inverse CO disproportionation are both thermodynamically favored, with the latter reaction being much closer to the equilibrium than the first one. As expected, the reaction quotients also evidence that the C$_3$H$_6$ cracking route (Eq. (4)) and inverse CO disproportionation (Eq. (5)) could be the active routes for C removal. (Fig. 11) shows that, under the investigated conditions, carbon gasification and inverse CO disproportionation are both thermodynamically favored, with the latter reaction being much closer to the equilibrium than the first one. As expected, the reaction quotients also evidence that the C$_3$H$_6$ cracking route (Eq. (4)) and inverse CO disproportionation (Eq. (5)) could be the active routes for C removal. 

### References
