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

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ABSTRACT

In this work, the catalytic partial oxidation (CPO) of C_3H_6 over a 2 wt% Rh/α-Al_2O_3 catalyst is analyzed with attention to the tendency to form coke. Kinetic tests in an annular microreactor are combined with the ex situ Raman investigation of the catalyst surface. A comparison is made with CH_4, assumed as the reference "non-coking" fuel on Rh.

The remarkable affinity of C_3H_6 for the metal surface characterizes the kinetic behavior. Competition between adsorption of C_3H_6 and adsorption of O_2 is observed at 200–250 °C, at which temperatures total oxidation only occurs; at higher temperatures, the adsorption of C_3H_6 seems to saturate the surface, hindering the steam reforming to synthesis gas. The ex situ Raman characterization after the C_3H_6 CPO tests shows that the surface is relatively "clean" at the lowest temperature, where gaseous O_2 is still available, but C-structures accumulate at increasing temperature on the surface: also, from 300 to 850 °C, an evolution is observed in the direction of more ordered and extended structures, passing from amorphous carbon deposits, through graphitic-like forms and finally nanotubes. The Raman spectra collected along the axis of the catalyst layer also show a distribution of the carbon structures, which can be well associated to the axial evolution of the gaseous species in the CPO reaction. Comparatively, the Raman experiments performed with CH_4 reveal a much cleaner surface, in line with the lower sticking capability and the lower coking tendency, although the various forms of C-aggregates are still visible. Both in the case of propylene and in the case of CH_4, the formation of C-nanotubes does not prevent at the highest reaction temperatures the stable and efficient conversion of the fuel to synthesis gas via steam reforming.

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 C_3 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

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extent than that dedicated to CH_4. The reason likely lays in that stable operation is commonly experienced in CH_4 oxy-reformers that work under autothermal conditions [17]. Wide agreement is found upon the evidence that CH_4 is not prone to coking on Rh: CH_4 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 gas-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 C_{16} 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-Al_2O_3 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 homogenous 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 cordierite 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 (O_2/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 C_3H_8 over 2 wt% Rh/α-Al_2O_3 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 C_{2+} 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 CH_x intermediates to the formation of adsorbed C, which polymerizes to graphitic 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 C_3H_6 (representative C_{2+} coke-forming fuel) and CH_4 (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 C_3H_6 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-Al_2O_3 catalyst was prepared by dry impregnation of the α-Al_2O_3 support (10 m^2/g surface area by BET measurement) with a commercial $Rh(NO_3)_3$ 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 8×10^5 Nl/(kg_{cat} h) GHSV, feeding a gas mixture with 4% CH_4 (v/v), 2.24% O_2 (O_2/C = 0.56), and N_2 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 C_3H_6 CPO conditions, which