Kinetic analysis and Raman surface characterization in the CPO of propane, propylene and n-C₈H₁₈

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Introduction

The Catalytic Partial Oxidation (CPO) of hydrocarbons is a promising solution for the small-scale and on-board production of H_2 or CO/ H_2 mixtures (syngas). The reaction is highly exothermic and extremely fast, and is typically carried out under autothermal conditions, in compact reactors, at millisecond contact time. Fuel flexibility is a major goal for the success of CPO: the reactor should be able to process fuels spanning from NG and LPG (CH₄, C₃H₈ and C₄H₁₀) up to logistic (gasoline and diesel) and biomass-derived fuels. The main drawbacks hampering a wide-range use of hydrocarbons (larger than C₁-C₃) are the high temperatures reached in the reactor (>1000°C) and the formation of C-deposits, which lead to catalyst deactivation even when noble metal are employed. Depending on the nature of the fuel, high temperatures also enhance the activation of gas-phase cracking reactions, which form coke-precursor intermediates, such as C₂H₆, C₃H₆ and C₂H₄. In this work, we analyze the CPO of C₃H₈ (representative of LPG), C₃H₆ (C₂₊ coke-forming fuel) and n-C₈H₁₈ (logistic fuel): focus is given to the reaction kinetics and the coke formation tendency. The formation of C-species as a function of temperature is followed by combining kinetic investigations performed in an annular micro-reactor with Raman measurements of the catalyst surface.

Materials and Methods

2 wt% Rh/ α Al₂O₃ catalysts were prepared by dry impregnation of Rh(NO₃)₃ of the α Al₂O₃ support (10 m²/g BET SA). The CPO experiments were performed in an annular microreactor, at 1 atm, between 300 and 850°C, at high space velocity, under isothermal conditions. A MicroGC (Agilent 3000) was used to analyze the composition of the inlet and outlet gas streams. Ex-situ Raman measurements were carried out with a Raman i-Raman BWTEK instrument (785 nm laser excitation, 5 cm⁻¹ resolution, 175 – 3250 cm⁻¹ spectral range, TE Cooled 2048 Pixel CCD detector). The Raman measurements were taken at room temperature according to the following procedure: after stable conditions were achieved in the annular reactor at a significant temperature, the reaction was quenched under inert N₂ flow to room temperature; the reactor was extracted from the furnace and kept under inert flow; the Raman signal was measured by focusing the beam directly on the catalyst layer through the quartz wall of the reactor.

Results and Discussion

Previous experimental and microkinetic studies on CH₄ and C₃H₈ CPO [1] pointed out strong analogies regarding the nature of the active sites and the rate determining step in the activation of these fuels. Under oxidative conditions ($O_2/C = 0.5$ -1), the C-H bond breaks on O*-O* pairs, i.e. on a Rh surface saturated by adsorbed O* (Regime I, as defined in Ref. [2]). In the absence of O₂, under reforming conditions, the C-H bond breaks on a free Rh site pair *-* (Regime IV). Coherently, Raman characterization suggests that the Rh surface maintains reasonably clean in C₃H₈ CPO and CH₄ CPO: very weak signals of C-structures (amorphous and graphitic) appear only in the spectra collected at $T > 600^{\circ}$ C. As well, the fuel conversion curve measured as a function of T shows a smooth transition between the oxidative and the reforming regime, around 400°C in the case of C_3H_8 (\blacksquare in Fig. 1a and b).

Much different features characterize the kinetics of C_3H_6 CPO (\blacktriangle in Fig. 1a and b). C_3H_6 has a very high oxidation activity (O_2 is completely consumed at ~250°C), followed by a flat plateau in C_3H_6 conversion ($300 - 450^\circ$ C) and by a delayed onset of the reforming activity ($T > 450^\circ$ C). Kinetic analyses [3] indicate that the oxidation rate has an inverse dependence on O_2 and a positive quadratic dependence on C_3H_6 concentration, suggesting that C_3H_6 activation occurs on a surface only partially saturated by O* and that the dissociative adsorption of C_3H_6 on a O-* pair is the determining step (Regime II). In the absence of O_2 , C_3H_6 strongly adsorbs on the surface, forming different C-species, as detected by Raman. These C-species do not partake in the reforming process and lead to surface C-poisoning and to kinetic inhibition. A positive dependence on H_2O is found for the rate of reforming, as a consequence of the beneficial effect of H_2O gasification in contrasting the accumulation of carbon.

The results of n-C₈H₁₈ CPO show an intermediate behavior. Total oxidation is fast, the consumption of O₂ starts at ~250°C and completes at ~325°C (\bullet in Fig. 1a and b). Kinetic tests indicate that the oxidation rate is directly proportional to n-C₈H₁₈ concentration and independent of O₂, fully in line with C₃H₈ and with the activation of n-C₈H₁₈ on O*-O* site pairs (Regime I). Instead, similar to C₃H₆ CPO, a plateau is observed in n-C₈H₁₈ conversion between 300 and 450°C, with a delay of the reforming activity to high T. Inhibition by n-C₈H₁₈ adsorption and C-poisoning are again suggested, and supported by Raman spectra (Fig. 1c): in the presence of O₂, the surface is almost free of C, whereas, once O₂ is consumed, amorphous deposits and graphitic-like platelets form (G, D, 2D lines) with nanotubes (sharp G component, RBM and 2D lines) gradually growing at increasing T.



in n-C₈H₁₈ CPO at increasing T. O₂/C = 0.56, O₂ = 1.7%, GHSV = $2*10^6$ Nl/kg_{cat}/h

Significance

Combined application of Raman characterization and kinetic tests in the annular reactor allows to individuate the nature of site active for the fuel activation (O*-O*, O*-* or *-* pairs) as well as the tendency of the fuel to stick on the catalyst surface and form C-species.

References

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