

INTERACTION OF HOMOGENEOUS AND HETEROGENEOUS CHEMISTRY IN SHORT CONTACT TIME CATALYTIC PARTIAL OXIDATION OF PROPANE PROBED BY SPATIALLY RESOLVED SAMPLING TECHNIQUES

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Ultra-fast catalytic processes for converting hydrocarbons at short contact times are characterized by extremely severe operating conditions, which represent a very unconventional kinetic regime for a catalyst. The application of a novel in situ sampling technique combined with detailed modeling of surface and gas phase chemistry kinetics allowed us to elucidate the complex interplay between the heterogeneous and homogeneous pyrolytic routes that lead to the formation of H_2 and CO in the catalytic partial oxidation (CPO) of C_3H_8 .

1. INTRODUCTION

The interaction between heterogeneous and homogeneous chemistries is a crucial issue for high-temperature catalytic processes. In particular, the assessment of the main routes that control the selectivity to the desired products is essential for the design and safe operation of the reaction units. This is particularly true for the ultra-fast conversion of hydrocarbons in short contact time (SCT) reactors that play a pivotal role in the effort to cope with the worldwide growing demand for more efficient exploitation of energy and material resources. Examples are the catalytically assisted combustion for gas turbines with ultra low emissions, the catalytic partial oxidation (CPO) of hydrocarbons into H_2 or syngas (Choudhary and Choudhary, 2008), the oxidative dehydrogenation (ODH) of light alkanes to olefins (Bodke et al., 1999, Goetsch and Schmidt, 1996). As a common feature, these processes operate in autothermal and compact reactors, with noble metal catalysts (Pd, Rh, Pt). An enormous “energy intensity” is peculiar to the SCT autothermal conversion of hydrocarbons over noble metals. Strongly exothermic and endothermic reactions proceed on the catalyst surface at extremely high rates. As a consequence, sharp gradients of temperature (up to $200^\circ\text{C}/\text{mm}$) and concentration establish within the small reactor volumes. Temperatures ranging from 250 and 1100°C are generally experienced within few mm lengths. Such a level of severity – in terms of power density and extent of temperature and concentration gradients – is typical of flames and gas-phase oxidation processes in general. For a catalytic process, instead, this condition represents a thoroughly unconventional kinetic regime. To grasp at best the intensity and the speed of the involved phenomena, we need to think of SCT conversion of light alkanes as the catalytic analogous of a flame. This analogy can clearly depict the complexity of the process and make apparent the related scientific issues: to what extent a catalytic process “sticks” on the catalyst surface at these very high temperatures, where adsorption of species is thermodynamically unfavored? Can the gas-phase activation of C-H bonds (e.g. the formation and propagation of radicals) cooperate/compete with the catalytic process?

In this respect, it is largely accepted that in the case of CH_4 CPO over Rh the gas-phase paths are negligible at atmospheric pressure and the catalytic route dominates (Horn et al., 2007, Horn et al., 2006b, Schwiedernoch et al., 2003). Conversely, the SCT-ODH of short alkanes over Pt mainly proceeds in the gas-phase, giving rise to the production of olefins and other hydrocarbon species (Lange et al., 2005, Michael et al., 2010). On the basis

of these examples, one could conclude that either catalytic or gas-phase chemistry governs the SCT conversion of hydrocarbons, depending only on the stability of the C-H bond in the gas-phase.

In this work, by using novel techniques for collecting spatially resolved temperature and concentration profiles, we show that the partial oxidation of short chain alkanes over Rh breaks the paradigmatic compartments of heterogeneous processes and gas-phase processes, revealing the real complexity of these “flame-like” processes. Specifically, we examine the reaction of C₃H₈ CPO ($\text{C}_3\text{H}_8 + 3/2 \text{O}_2 \rightarrow 3 \text{CO} + 4 \text{H}_2$) as a case study and we apply novel techniques for collecting spatially resolved gas-phase and solid temperature, as well as concentration profiles within a Rh coated honeycomb monolith to monitor the evolution of a propane/air mixture fed at high flow rate.

2. EXPERIMENTAL

2.1 Catalyst and experimental set-up

The autothermal tests of C₃H₈ CPO were carried out over a 2 wt % Rh/ α -Al₂O₃ catalyst, which was prepared by incipient wetness impregnation of α -Al₂O₃ powders with an aqueous Rh(NO₃)₃ solution and then supported over a 400 cpsi cordierite honeycomb monolith (16 mm long, 23 mm diameter). The catalyst loading was measured by weight difference before and after coating and amounted to 720 mg. The reactor consisted of an externally insulated stainless steel tube with a quartz liner to prevent C formation. The catalytic honeycomb was placed in between two inert heat shields (a FeCrAlloy foam and a 400 cpsi honeycomb) kept at 1.5 cm from the inlet and the outlet section of the catalyst.

For the spatially resolved temperature measurements, the reactor was equipped with a K-type thermocouple (0.25 mm diameter) and with a narrow-band infrared pyrometer (Impac Infrared, IGA 5-LO) connected to an optical fiber (Polymicro, FVP300, 1.5 m long). The IR detector of the pyrometer was an Indium-Gallium-Arsenic photodiode, sensitive to radiation in the wavelength range 1.45 – 1.8 μm and calibrated between 350 and 1100°C. The optical fiber (300 μm core diameter, 330 μm OD, 45° cut tip) was housed inside a transparent quartz capillary (530 μm ID, 670 μm OD) sealed at one end, which acted as an inert sleeve for the fiber and was moved by a linear translation stage. It is important to note that the signal of the pyrometer is affected by artifacts at the boundary of the monolith such as the measurement of high temperatures before the catalytic monolith and the sudden drop of temperature close to the exit monolith section (Donazzi et al., 2010), probably due to the fact that the optical fiber tip tends to collect some light also from zones in front of it. These phenomena do not influence significantly the temperature measurement within the monolith channel.

For the spatially resolved gas-phase composition measurements, the sampling system consisted of a quartz capillary (200 μm ID, 340 μm OD) inserted into the central channel of the honeycomb. The capillary was cut at one end and connected to the linear actuator at the other end. The gases were sampled at specific axial positions and pumped to a micro gas chromatograph (3000 A, Agilent Technologies) through the capillary. C and H mass balances closed within a $\pm 5\%$ error while water was calculated by closing oxygen mass balance to 1.

2.2 Reactor model

A 1D, dynamic, fixed bed, single-channel, mathematical model of the adiabatic reactor was used to support the interpretation of the experimental results (Maestri et al., 2005). It consisted of mass, enthalpy and momentum balances equations for the gas phase and the solid phase, which included axial convection and diffusion, solid conduction and gas-solid transport terms (Table 1).

The model accounted for the formation of syngas on Rh through an indirect consecutive scheme, consisting of deep oxidation and steam reforming of propane and methane, water gas shift and its reverse, H₂ and CO post-combustion and methanation. The rate equations were developed on the basis of an independent kinetic study, which was performed in an isothermal microreactor. The propane scheme was also extended to account for the catalytic conversion of hydrocarbon intermediates generated in the gas-phase, such as C₂H₆, C₂H₄ and C₃H₆. Gas phase reactions for C₁ – C₃ species were taken into account according to the detailed kinetic scheme by Ranzi and co-workers (Ranzi et al., 1994)

Table 1: Model equations and boundary conditions

Gas phase	
Mass balance	$\frac{\partial \omega_i}{\partial t} = -\frac{G}{\rho_g \cdot \varepsilon} \cdot \frac{\partial \omega_i}{\partial z} - \frac{a_v}{\varepsilon} \cdot k_{mat,i} \cdot (\omega_i - \omega_{i,wall}) + \frac{Diff_i}{\varepsilon} \cdot \frac{\partial^2 \omega_i}{\partial z^2} + \left(\sum_{j=1}^{NR} \nu_{i,j} \cdot r_j^{hom} \right) \cdot MW_i$
Enthalpy balance	$\frac{\partial T_g}{\partial t} = -\frac{G}{\rho_g \cdot \varepsilon} \cdot \frac{\partial T_g}{\partial z} - \frac{a_v \cdot h \cdot (T_g - T_s)}{\varepsilon \cdot \rho_g \cdot \hat{C}_{p,g}} + \left(\sum_{j=1}^{NR} (-\Delta H_j^R) \cdot r_j^{hom} \right)$
Momentum balance	$\left(-\frac{1}{\rho_s} + \frac{G^2}{\rho_s^2 \cdot p} \right) \cdot \frac{dp}{dz} - \frac{G^2}{\rho_s^2 \cdot T_s} \cdot \frac{dT_s}{dz} = \frac{1}{2} \cdot \frac{G^2}{\rho_s^2} \cdot a_v \cdot f$
Solid phase	
Mass balance	$0 = a_v \cdot \rho_g \cdot k_{mat,i} \cdot (\omega_i - \omega_{i,wall}) + \left(\sum_{j=1}^{NR} \nu_{i,j} \cdot r_j^{eff} \right) \cdot MW_i \cdot \rho_s \cdot \xi$
Enthalpy balance	$\frac{\partial T_s}{\partial t} = \frac{a_v \cdot h \cdot (T_g - T_s)}{\rho_s \cdot \hat{C}_{p,s} \cdot (1-\varepsilon)} + \frac{1}{\rho_s \cdot \hat{C}_{p,s}} \cdot \frac{\partial}{\partial z} \left(k_{ax}^{eff} \frac{\partial T_s}{\partial z} \right) + \left(\sum_{j=1}^{NR} (-\Delta H_j^R) \cdot r_j^{eff} \right) \cdot \frac{\xi}{\hat{C}_{p,s} \cdot (1-\varepsilon)}$
Boundary conditions	
Reactor Inlet ($z_1=0$)	
$\omega_{i,z=z_1} = \omega_{i,feed}$	Reactor Outlet ($z_2=L_{rect}$)
$T_{g,z=z_1} = T_{room} \quad p_{z=z_1} = p_{feed}$	$-k_{ax}^{eff} \cdot \frac{\partial T_s}{\partial z} \Big _{z_2} = -\sigma \cdot \varepsilon_s \cdot \left(T_g^4 - T_s^4 \Big _{z_2} \right)$
$-k_{ax}^{eff} \cdot \frac{\partial T_s}{\partial z} \Big _{z_1} = \sigma \cdot \varepsilon_s \cdot \left(T_g^4 - T_s^4 \Big _{z_1} \right)$	
Initial conditions	
$\omega_i(z,0) = 0 \quad T_g(z,0) = T_{room} \quad T_s(z,0) = 400^\circ C$	

Heat and mass transfer terms were calculated according to specific correlations for laminar flow in square ducts (Shah and London, 1978). Heat conduction in the solid phase was described with an effective axial thermal conductivity, accounting for a corrective contribution of radiation by means of Lee and Aris correlation (Lee and Aris, 1977).

The numerical analysis was fully predictive, with no parameter adjustment and the only input data of the calculations were the thickness of catalytic phase, the Rh-dispersion and the geometric parameters of honeycomb support (void fraction, channel opening, wall thickness).

3. RESULTS AND DISCUSSION

The C₃H₈ CPO experiments were performed under relevant operating conditions by feeding non-diluted C₃H₈/air mixtures (O/C = 1.12, C₃H₈ = 11 v/v %) at 5 Nl min⁻¹ flow rate and atmospheric pressure. The temperature and

the composition of the reacting system were monitored from the inlet reactor section where the mixture was fed, to the outlet section of the catalytic unit where the syngas stream was delivered.

The results are reported in Figure 1 in terms of spatially resolved profiles of temperature and molar fraction of reactants and products. In the first 5 mm of the honeycomb, a sharp drop of O_2 and C_3H_8 concentration was observed, accompanied by the formation of total oxidation products (CO_2 and H_2O) and partial oxidation products (H_2 and CO). Correspondingly, a hot spot formed on the catalyst surface ($980^\circ C$, measured by the pyrometer) and a steep rise was observed in the gas temperature (up to $945^\circ C$, measured by the thermocouple). In line with the occurrence of the endothermic steam reforming reaction, the evolution of H_2O showed a maximum. As well, the temperatures of the solid surface and of the gas phase decreased toward the exit of the honeycomb.

Qualitatively this is what our and other research groups have observed, also in the case of a CH_4 -CPO experiment on Rh, and can be fully explained by the syngas catalysis of Rh (Horn et al., 2007, Donazzi et al., 2010, Donazzi et al., 2008, Horn et al., 2006a). Thus, integral measurements (i.e. measurements of temperature and composition collected exclusively at the reactor outlet) would have suggested the unique existence a heterogeneous process. A purely catalytic process was, for instance, inferred by Deutschmann and coworkers (Hartmann et al., 2010), analyzing integral data of iso-octane partial oxidation over Rh at $O/C > 1$. However, in this work, the spatially resolved measurements revealed for the first time that several other species, such as C_2H_4 , C_3H_6 and C_2H_6 were formed at the very reactor inlet and were then completely consumed before the ending section of the catalyst, passing through maxima.

We also observed a complex evolution of CH_4 that, similarly to C_2 and C_3 species, was initially formed and then consumed within the first half of the reactor, but tended to be formed again in the ending portion of the reactor. On one hand, since hydrocarbon species like olefins cannot be explained by the syngas formation paths on Rh, this experimental finding provided evidence of gas-phase chemistry. On the other hand, the gas-phase chemistry alone could not explain the outlet selective formation of syngas. Hence, a possible scenario could be that the gas-phase generated intermediates stuck back on the surface and eventually converted to syngas.

Figure 1 also reports model calculations for axial profiles of temperature and concentration (solid lines). All the general trends of temperature evolution, reactants conversion and product distribution were captured by the model. This is a very satisfactory result, considering that the simulations were fully predictive and no parameter was adjusted to match the data.

The model analysis revealed that gas-phase activation of C_3H_8 was responsible for the production of all the hydrocarbon species observed at the reactor inlet: cracking and dehydrogenation reactions can explain the formation of CH_4 , C_2H_4 and C_3H_6 . According to the model, the consumption of O_2 was almost entirely due to surface oxidation reactions (mass transfer controlled), while homogenous oxidative pyrolysis had a negligible role. Formed in the gas phase, the hydrocarbon species were then mainly consumed on the catalytic surface via steam reforming with formation of syngas. The consecutive reactions of these species are in fact much slower in the gas phase than on Rh.

Concerning the complex evolution of CH_4 , the model simulations showed that this could be very well explained by a series of contributions consisting of: (1) gas-phase formation via propane cracking, (2) catalytic consumption via steam reforming, (3) catalytic formation via methanation, which was kinetically favored by the increasing partial pressures of H_2 and CO and thermodynamically favored by the decreasing temperatures.

By neglecting the heterogeneous conversion of gas-phase generated hydrocarbon intermediates, we verified that the evolution of temperature and product distribution would not be correctly described (dashed lines in Figure 1). The overall production of H_2 and CO would be greatly underestimated, while the outlet composition would be rich of olefins and other hydrocarbons. Also, predicted outlet temperatures would be much higher than observed.

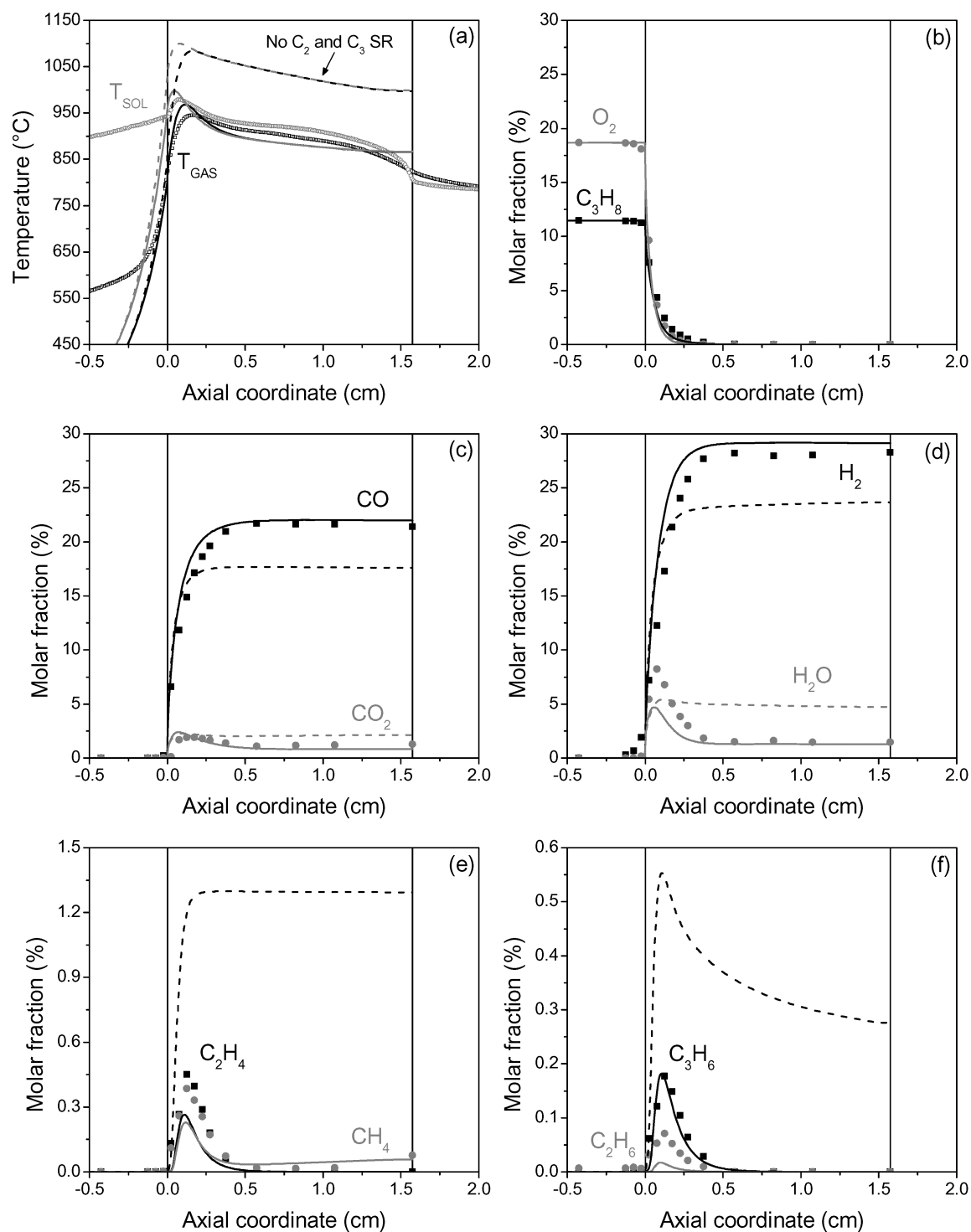


Fig. 1: Axial profiles of temperature and concentration in a C_3H_8 CPO experiment. Operating conditions: C_3H_8 /Air feed, 11 v/v % C_3H_8 , O/C = 1.12, Flow rate = 10 $Nl\ min^{-1}$, $P = 1\ atm$. Experimental results (symbols) and model predictions (solid lines) are reported. Dashed lines are calculations obtained by neglecting steam reforming reactions of C_2H_4 , C_3H_6 and C_2H_6 in the heterogeneous kinetic scheme.

Thus, in spite of the very high reactivity to syngas of Rh, this experiment showed for the first time that the conversion of propane to syngas includes also a “by-pass” route in the gas-phase, that involves the conversion of propane to smaller and reactive hydrocarbons species and their consecutive heterogeneous conversion to syngas. This is a clear indication of a concerted heterogeneous-homogenous process. Under the operating conditions of interest for the small scale production of H₂ herein studied, this interaction turns out to be a synergy: gas-phase reactions enrich the main fuel with additional reactive species that make even faster and more efficient the catalytic conversion to syngas. Nevertheless, undesired consequences can be also envisaged, such as loss of selectivity, soot formation and catalyst deactivation in case the by-pass line breaks and gas-phase intermediates do not complete their catalytic conversion to syngas (at higher temperatures, for instance). All these aspects have a crucial impact and must be taken into account for the design and safe operation of distributed hydrogen units. The new mechanistic picture that we draw from this case can be easily generalized and fully explain all the previous results in the literature. Specifically, the “by-pass” route is significant only when the thermal activation of C-H bonds is sufficiently fast, which rules out methane activation at atmospheric pressure and explains why methane CPO is mainly a heterogeneous process. Also, the “by-pass” may exist only if the reforming capability of the catalyst is sufficiently high to quench the gas-phase chain process; this rules out Pt, which has much lower reforming activity than Rh, and explains why the ODH of short alkanes on Pt is mainly a homogeneous process.

4. CONCLUSIONS

In this paper, we have investigated the interplay between surface chemistry and gas phase cracking chemistry in the catalytic partial oxidation of propane at short contact times. The experimental results and the modeling analysis showed that the conversion of propane to syngas passed through a by-pass route in the gas phase with the formation of smaller and reactive hydrocarbon intermediates and a consecutive heterogeneous conversion of such species to H₂ and CO. The understanding of this concerted mechanism was possible by the application of the in situ sampling technique, coupled with the detailed modeling of gas-phase and surface kinetics. This powerful combination of methodologies has revealed the “complex harmony” with which surface and gas-phase reactions cooperate in high temperature short contact time partial oxidation of hydrocarbons.

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