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Fuel rich catalytic combustion: Principles and technological developments in short contact time (SCT) catalytic processes

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Abstract

This work describes fundamental and technological aspects of short contact time catalytic chemistry devoted to the oxidation of hydrocarbons into synthesis gas. These aspects have been chosen with the aim of following the pathway linking the fundamental discoveries with the technological development. To this purpose the discussion will touch molecular chemistry, heat and mass transfer, reactor and industrial design issues.

Keywords: Short contact time (SCT); Hydrocarbon; Synthesis gas

1. Introduction

The short contact time (SCT) hydrocarbon oxidation processes are produced colliding for few milliseconds, gaseous premixed reactant flows with extremely hot catalytic surfaces. These conditions determine a fast and selective chemistry confined inside a thin (<1 μm) solid–gas inter-phase zone surrounding the catalyst particles. Here the molecules spend 10^{-6} s at temperatures that can be varied between 700 and 1300 °C. For this reasons the SCT conditions favour the formation of primary reaction products inhibiting their degradation and the occurrence of chain reactions.

The principles of the SCT catalytic processes can be applied for developing:

(a) catalytic burners,
(b) synthesis gas/hydrogen production systems utilising gaseous and liquid hydrocarbon sources also containing sulphur and a romatic compounds,
(c) olefin production.

↓ Fuel richness

The first traces in open literature concerning fuel-rich SCT catalytic hydrocarbon oxidation appeared in years 1989–1990 when BP researchers issued two patents concerning to a “Process for the production of mono-olefins, etc.” [1]. Subsequently in years 1992–1993 scientists of the Governative Research Centre of Pune [2] and of the Minnesota University [3], independently published two literature articles on an SCT catalytic partial oxidation (CPO) process for converting the NG into synthesis gas. Contemporaneously the research activities spread into industrial environments [4,5] and nowadays more that 200 patents and 350 scientific articles have been published.

The understanding of the technological and economical potential of this chemistry has also prompted the realisation of some pilot and demonstrative scale activities. Among these we mention those of: (i) Shell that realised an air blown small scale plant for producing H_2 to be delivered at fuel cell vehicles, (ii) ConocoPhillips that more recently operated in Ponka City (OK) two oxygen blown COPOX^{TM} pilot scale reactors for producing the synthesis gas required for a 400 BBLD Fischer-Tropsch plant and (ii) the Eni group (Snamprogetti S.p.A.) that realised and operated in 2001 together with Haldor Topsoe A/S Air Blown SCT-CPO reformer in Houston (TX) and more recently, in September 2005, started-up another multi-purpose SCT-CPO pilot scale plant in Milazzo (EniTecnologie) for producing H_2 and/or synthesis gas from gaseous and liquid hydrocarbons also including S (0.5–35 wt.%) and aromatic compounds (60–80 wt.%) such as light cycle oils (LCO) and the de-asphalted oils (DAO). In conclusion it is mentioned that EniTecnologie is also defining the technology handbook of a small air blown SCT-CPO based H_2 generator. The characteristics of this

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system will be demonstrated within the framework of a EU project named ZeroRegio [6]. This project is targeted to realise and operate multi-fuel stations located in the city of Mantova and Frankfurt, for refuelling internal combustion engine (ICE) and fuel cell (FC) vehicles.

This work describes some of the main milestones we encountered in along the pathway followed for understanding how some of the fundamental principles of SCT phenomena could be turned into technological hints useful for refinery utilisations, gas to liquid (GTL) transformations and in conclusion for contributing to the generation of the H_2 fuel for a ‘‘futurable’’ mobility system.

2. Chemical reactivity aspects

The chemical reactivity of SCT-CPO phenomena has been examined at the molecular level with several experimental and theoretical approaches. The performed work provided a number of valuable findings whose review description is not attempted in the following. Instead in initiating the description of the pathway linking fundamental research and technological development we mention some early results produced by:

(1) isolating elementary reactivity steps and measuring their energetic characteristics,
(2) monitoring the reaction dynamics,
(3) catching spectroscopic signals of surface molecular species originated inside packed catalytic beds under real reaction conditions.

The great part of activities devoted to the examination, with a micro-kinetic perspective, of the energy variations accompanying main elementary steps involved in CH_4 and O_2 dissociation, surface atom recombination and product molecules desorption [7–17] considered controlled environments and ordered surfaces. In these situations the reactions were occurring at the surfaces of single crystal catalysts of Ni, Pd, Pt, Rh metals. Here it is relevant to summarise some conclusions of these studies indicating that:

- O_2 dissociation is faster and much more exothermic than CH_4 dissociation,
- formation and desorption of surface CO groups is thermally activated while the same formation and desorption of surface CO_2 species is not thermally activated,
- the surface temperature of Rh, Ru, Pt and Ni crystals can be adjusted above 1000 K for determining a high selectivity towards partial oxidation reactions.

To sustain these points Table 1 includes, as an example, the energy characteristics estimated for the micro-reactivity steps produced colliding CH_4 and O_2 molecules with the Ni(1 1 1) surface [8].

Other molecular dynamic studies have also examined the energy variations involved in the catalytic oxidation reactions. These studies did not consider the chemical event as composed by micro-steps and instead examined the variation of the microscopic forces persisting between the reactant species throughout their interactions. Among these studies we found particularly relevant those utilising supersonic molecular beams [19–22] colliding with metal foils under high vacuum conditions (Fig. 1). Here the product molecules desorbed in nearly collision free environments and released their excess energy by emitting IR radiations. The IR emissions where collected with high resolution spectrometers producing roto-vibrational spectra containing information on the population of vibrational and rotational excited states and allowing to estimate vibrational (T_v), rotational (T_r) and transitional (T_t) temperatures [18].

Table 2 includes comparisons between surface temperatures (T_s) values and the T_v and T_r temperatures of desorbed CO and CO_2 molecules measured during surface oxidation of butane [21,22]. These temperature comparisons and other results [23] indicated that:

1. CO product molecules, differently from the CO_2 molecules, were not thermally accomodated with the surfaces and desorbed in excited vibrational states.
2. CO and CO_2 molecules originated through the intermediate formation of C–O species with the two atoms linked to the surfaces thus inhibiting the rotational modes and determining low rotational temperatures.
3. At $T_s < 1000$ K the C–O surface species were stabilised allowing further reactive encounters with oxygen atoms that originated CO_2.
4. At $T_s > 1200$ K the C–O surface species desorbed before colliding with other oxygen atoms originating gaseous CO molecules.

The existence of common surface intermediates that could originate both total and partial oxidation products, was also

Table 1
Energy variations during CH_4 and O_2 reactions at Ni(1 1 1) crystal surfaces—$CH_{4,s} \mapsto C_s + 4H_s$: −18.7 kcal/mol; $O_2 \mapsto 2O_S$: −106.3 kcal/mol

	Combination energy (kcal/mol)	Activation energy (kcal/mol)	Desorption energy (kcal/mol)
$H_s + H_s \mapsto H_{2,s} \mapsto H_2$	25.2	29.7	0.7
$C_s + O_s \mapsto CO_S \mapsto CO_g$	−13.8	30.4	50.5
$CO_g + O_s \mapsto CO_{2,s} \mapsto CO_{2,g}$	−20.1	0.00	0.00
$H_s + O_s \mapsto OH_s$	2.8	0.00	–
$H_s + OH_s \mapsto H_2O_s \mapsto H_2O_g$	18.7	0.00	0.00

Taken from Ref. [7].

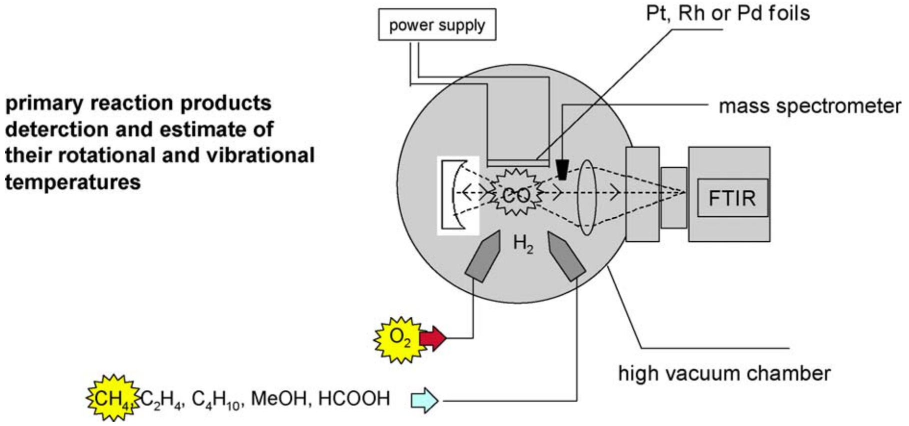

Fig. 1. Scheme of the experimental apparatus utilising supersonic molecular beams of reagents (flux of molecules around (1–10) × 10^{18} cm^{-2} s^{-1}) and originating nascent molecules that were desorbed in a nearly collision free environment in which the vibrational and/or rotational excited states distribution depended on reaction dynamics and were analysed with high resolution spectrometers (Yale University Department of Chemisty Engineering, Tsukuba University, Department of Physical Chemistry).

detected with another ''in situ'' perspective: observing with spectroscopic means the catalytic environment under high pressure high temperature conditions. With this purpose an extensive research program was developed studying the surface chemistry of small ($n < 20$) Rh, Ru, Ir clusters at the surfaces of polycrystalline Al_2O_3, MgO and CeO_2. The program included the definition of synthetic procedure that could lead to the formation of highly reproducible materials whose reactivity was studied with a network of 14 multi-step spectroscopic experiments each repeated at least three times for ensuring reproducibility (see Fig. 2). These experiments were designed in order to provide information that could be compared and cross linked and were performed at 0.12 MPa by flowing the gaseous reactants through powdered samples inside reaction chambers equipped with diffuse reflectance Fourier transform IR (DRIFT), laser Raman, extended X-ray fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) and mass spectrometry. In this way we investigated: (i) the CO and CO_2 methanation reactions (experiments 1–8), (ii) the CO_2 reforming and water gas shift reactions (experiments 9–10) and (iii) the partial and total oxidation of CH4 (experiments 11–14). Many of the results have been included in literature documents [24–30] others remain unpublished. In summary the spectroscopic information taken during the occurrence of the stoichiometric and catalytic surface reactions pointed out some characteristics of five noble metal containing surface species namely: (a) bare metallic clusters, (b) clusters containing highly reactive oxygen atoms, (c) clusters containing carbidic species, (d) carbonyl clusters and (e) hydridocarbonyl clusters.

Table 2

	T_s (K)	T_v (K)	T_r (K)
CO	1500	2300	380
CO_2	1500	1600	600

Surface temperature (T_s) values and for comparison the vibrational (T_v) and rotational (T_r) temperatures of desorbed CO and CO_2 molecules measured during surface oxidation of butane [20,21].

Focusing to the aspects more relevant to the SCT-CPO chemistry we report that small Rh clusters containing highly reactive oxygen species could be obtained at moderate temperatures (373–573 K) under flowing oxygen. These oxidic species reacted, at the same temperatures, with CH_4 producing hydridocarbonyl clusters. These lasts, in He flow, could be decomposed by increasing the temperature above 700 K originating H_2 and CO with selectivity close to 100%. Instead when the same hydridocarbonyl clusters were exposed to flowing O_2 the gaseous products consisted mainly in CO_2 and H_2O. Utilising these reactivity characteristics and alternating oxidative treatments and interactions with CH_4, it was possible to link stoichiometric reactions producing a catalytic loop that consumed CH_4 and O_2 in separate steps producing only CO and H_2 or alternatively only CO_2 and H_2O (see Fig. 3).

In conclusion to this chapter the information obtained with these three micro-kinetic, molecular dynamics and ''in situ'' observations indicated that:

(i) the formation of partial oxidation products is thermally activated and favoured versus the non-thermally activated total oxidation reaction at high ($T_s > 1200$ K) surface crystal temperatures,
(ii) the CO and the CO_2 molecules can be selectively generated at different temperature ranges by reacting molecular beams of small hydrocarbons (CH_4, C_4H_{10}) and O_2 with noble metal foils and their formation occurs through the reactions of a common surface intermediate,
(iii) the same hydrido-carbonyl species of Rh, Ru, Ir formed at the surfaces of polycrystalline oxides originated total or partial oxidation products depending on gaseous composition and temperature conditions.

These findings justified the pursuing of a technology in which the partial oxidation of the hydrocarbons could be directly attempted at the catalysts surfaces under conditions that could potentially allow advantages in economics and plant

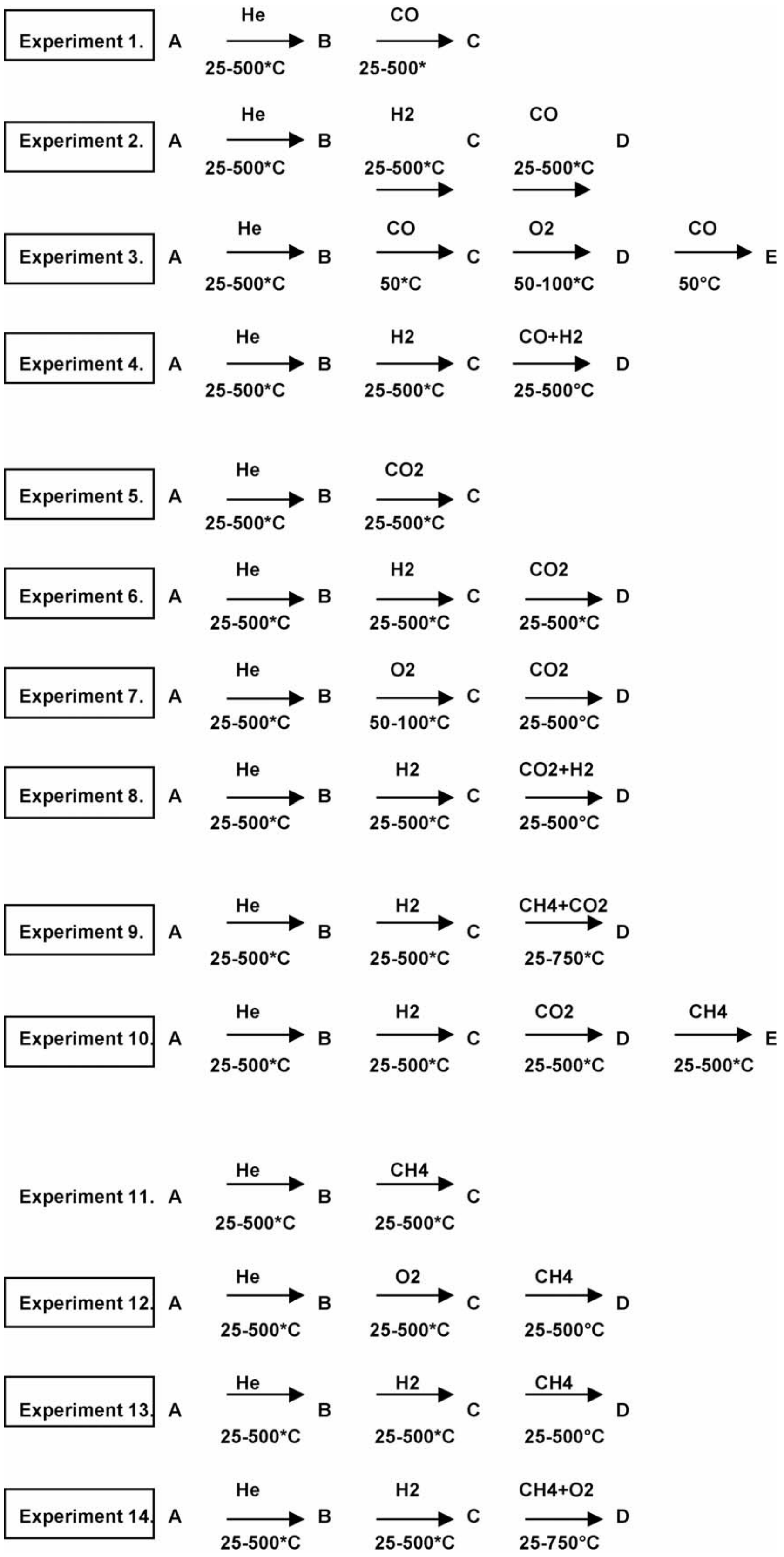

Fig. 2. Scheme of the experimental sequences utilised to investigate at the molecular level the reactivity of Rh, Ru, Ir surface clusters.

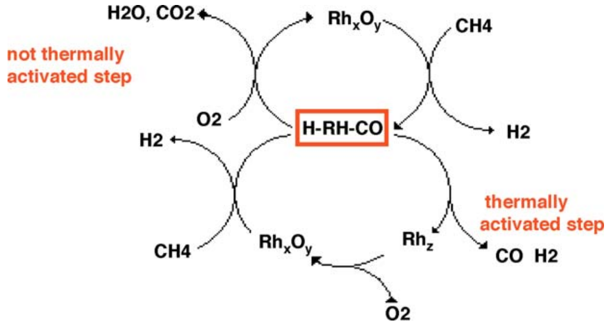

Fig. 3. Comparisons between signals produced during the catalytic reaction conditions and during stoichiometric cycles of reactions have revealed the formation of hydrido-like carbonyl clusters. These were able to originate total oxidation products if exposed to O_2 while could be decomposed into CO and H_2 when heated under inert flowing environment. A sequence of stoichiometric steps could be linked to obtain the partial oxidation of CH_4 at temperatures lower than 773 K with a selectivity close to 100%.

operability features as it will be discussed in the conclusive paragraph.

3. Heat and mass transfer versus chemical reactivity

To the purpose of this work some experimental observations on the thermo-chemical properties of the SCT catalytic environments generated within laboratory scale plug-flow reactors will be summarised as follows [31]:

(a) the temperature of the solid phase raises steeply at the beginning of the bed and is stabilised at relatively constant values in the axial and radial directions,
(b) large temperature differences are originated in some zones between the gas and the solid phases,
(c) the great part of the surface temperature result higher than the adiabatic temperatures,
(d) the gas temperatures are always lower than the adiabatic temperatures and gradually increase from the entrance to the exit of the bed.

Fig. 4A and B illustrate some of these characteristics showing the surface and gas temperature profiles measured inside two SCT-CPO catalytic reactors of different shape but utilising the same amount (1.5 g) of spherical (o.d. 1.5 mm) catalyst particles.

Several numerical 1D, 2D and 3D models, also including detailed micro-kinetics descriptions, have provided a quantitative description of these experimental aspects. However aiming at describing the SCT-CPO characteristics that can be turned into technological opportunities we comment on some simple thermodynamic aspects by considering the system composed by the Eqs. (1)–(7). Among these, the exothermic oxidation reactions (1) and (2) would have highest probability to occur at the beginning of a catalytic bed of a “plug-flow” reactor fed with a relatively cool CH_4 and O_2 mixture. Instead the WGS (3) and the endothermic steam (SR) and CO_2 (CR) reforming reactions (4) and (5) would have the highest probability of occurring in following zones since these reactions require reactants produced with total oxidation reactions.

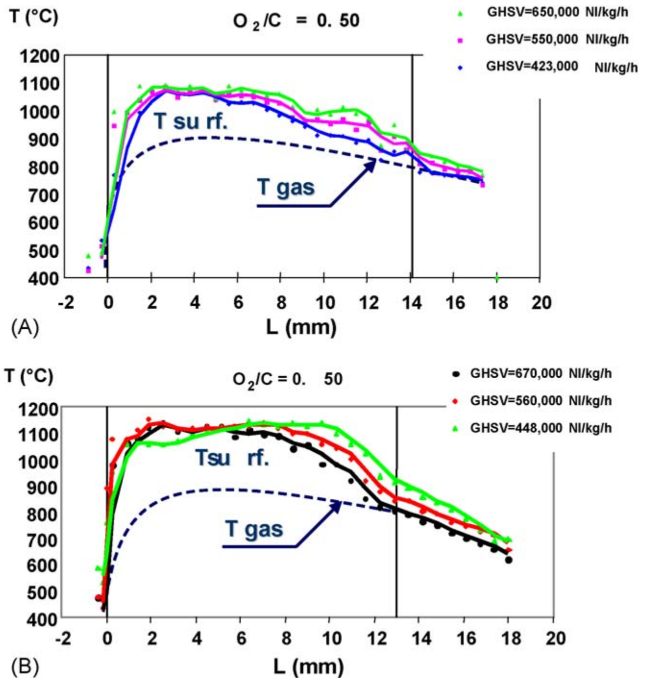

Fig. 4. Surface and gas temperature profiles measured with hermocouple and IR thermography means inside: (A) a conical shape and (B) a cylindrical shaped laboratory scale reactor.

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H^\circ = -191.8\,\text{kcal/mol} \tag{1}$$

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2, \quad \Delta H^\circ = -8.5\,\text{kcal/mol} \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H^\circ = -9.8\,\text{kcal/mol} \tag{3}$$

$$H_2O + CH_4 \rightarrow CO + H_2, \quad \Delta H^\circ = +49.3\,\text{kcal/mol} \tag{4}$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2, \quad \Delta H^\circ = +59.1\,\text{kcal/mol} \tag{5}$$

$$CO + (1/2)O_2 \rightarrow CO_2, \quad \Delta H^\circ = -57.3\,\text{kcal/mol} \tag{6}$$

$$H_2 + (1/2)O_2 \rightarrow H_2O, \quad \Delta H^\circ = -68.3\,\text{kcal/mol} \tag{7}$$

The slightly exothermic and direct partial oxidation reaction (2) would instead be favoured at high temperature values provided that the oxygen would not be entirely consumed by total oxidations.

In conclusion, it is observed that reactions (6) and (7) would be thermodynamically favoured at high CO and H_2 and O_2 partial pressures and at temperatures lower than 1000 K.

Indeed also the molecular kinetic studies discussed in the previous paragraph indicated that total combustion (1) would be the most competitive reaction at “low temperatures” ($T < 1000$ K) and high oxygen partial pressure while reaction (2) would prevail at higher T values.

Experiments utilising bench-scale showed that at high contact times (≅1 s) the strongly exothermic reaction (1) and the strongly endothermic steam and CO_2 reforming reactions (4) and (5) were heavily involved in the synthesis gas production. However this reaction sequence originated very large axial temperature gradients and propagated the reactions into the gaseous phase originating, particularly at high-pressure conditions, a rather unselective radical chemistry leading to soot formation.

Instead, under SCT (≅0.01 s) condition, reactions remained confined into the thin solid–gas interphase zone also under high-pressure (5–30 atm) and we believe this was the result of the reduction of the contribution of the total oxidation (1), (6) and (7) and steam/CO_2 reforming (4) and (5) and the increase of the contribution of direct partial oxidation (2). This achievement was then consolidated with an appropriate optimisation of reactor and catalyst design solutions also utilising quantitative numerical reaction/reactor models [33,34]. These models, in agreement with experimental observations, described the occurrence of local temperature differences between the relatively hot solid surfaces and the relatively cool gas phase. The temperature difference is a consequence of the confinement of the reactions at the catalyst surfaces and of the occurrence of heat and mass transfer limitation.

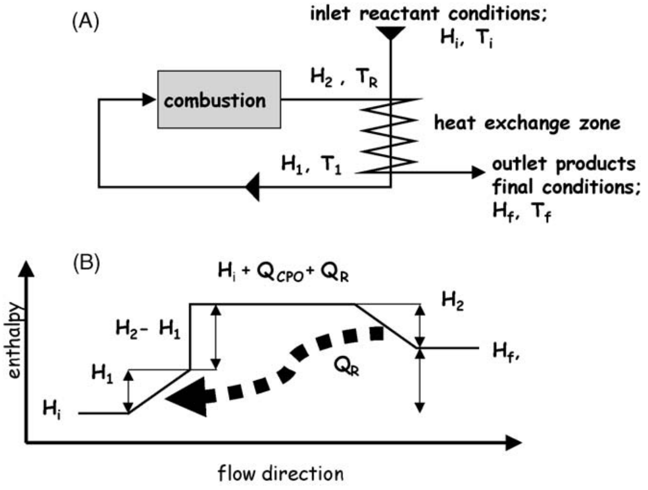

Fig. 6. (A) Scheme of a one-phase combustor with external heat recuperation from the products and pre-heating of the feedstock; (B) enthalpy vs. distance diagram for the same combustor; the diagram holds also in case of internal heat recuperation phenomena occurring through a ceramic bed.

Another point useful for addressing the technological development was taken by observing with IR thermography the characteristics of the propagation of the reactions throughout the catalytic bed after igniting few single catalyst particles (see Fig. 5). In these conditions the chemical heat generated at the surfaces of the few catalyst particles and emitted by radiation, was absorbed and scattered along the catalytic bed through ‘‘a particle by particle’’ mechanism. This coupling between enthalpy variation and chemical reaction propagation suggested some analogies with the effects achievable in a gaseous system in which some heat is recuperated from the reaction products through a gas–gas heat exchanger (see Figs. 6 and 7). These phenomena have been described in literature since 1971 as ‘‘enthalpy recirculation’’ phenomena [32].

We propose that the enthalpy and temperature distribution effects have some responsibility in promoting the preheating of the incoming reactants determining the reactions ignition at enthalpy and temperature levels promoting direct partial

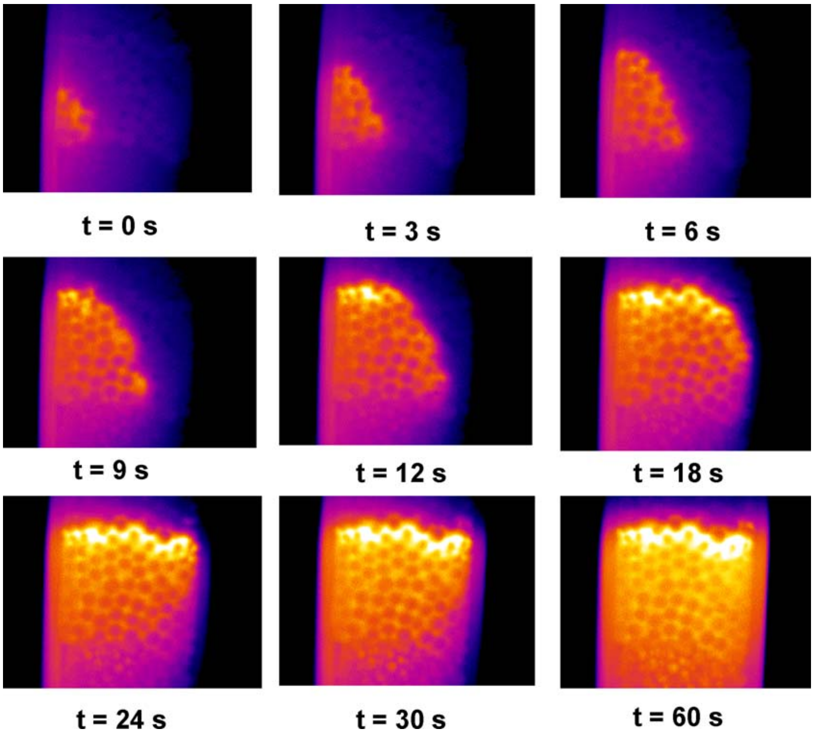
t = 0 s
t = 3 s
t = 6 s
t = 9 s
t = 12 s
t = 18 s
t = 24 s
t = 30 s
t = 60 s

Fig. 5. IR thermography images of the reaction-heat propagation mechanism during the reaction ignition in a tubular reactor.

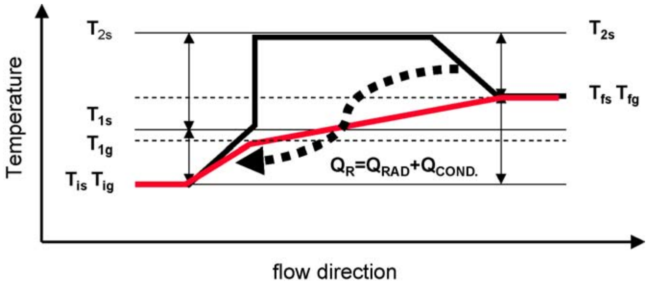

Fig. 7. Qualitative scheme of the temperature vs. distance diagrams for the solid and gaseous phases produced during CPO under stationary flow conditions in an adiabatic reactor (solid phase, black line; gas phase, red/gray line). T_{iG}, T_{iS}, inlet temperatures of the gas and solid; T_{1G}, T_{1S}, ignition temperatures affected by the heat recuperation term (Q_R); T_{2G}, T_{2S}, reaction temperatures; T_{fG}, T_{fS}, final exit temperatures.

oxidation reactions. In order to explain this point it is briefly noted that, in absence of heat recuperation the final adiabatic temperature in a homogeneous phase partial oxidation process, would be given by Eqs. (7)–(8)

$$Q_{CPO} = \int_{T_i}^{T_f} C_p \, dT \tag{8}$$

$$T_f = \frac{Q_{CPO}}{c_p} + T_i \tag{9}$$

where Q_{CPO} is the molar heat release produced by the chemical reactions, C_p is the molar heat capacity of the products at constant pressure and T_i and T_f are the initial and final temperature values.

Instead Eqs. (7) and (8) modify in Eqs. (9) and (10) when a heat recuperation/recirculation mechanism is established and some enthalpy is transferred from the product into the reactants. In these equations the reaction temperature T_R is higher than the final temperature T_f and Q_R represents the heat recuperation term.

$$Q_{CPO} + Q_R = \int_{T_i}^{T_f} C_p \, dt + \int_{T_f}^{T_R} C_p \, dt \tag{10}$$

$$T_R = \frac{Q_{CPO} + Q_R}{c_p} + T_i \geq T_f \tag{11}$$

Fig. 7 represents schematically the experimentally observed effects that are produced inside a catalytic bed of a SCT reactor. Here the reaction heat is partially distributed from the hotter towards the cooler zones located at the very beginning of the catalytic bed obtaining the effect of preheating the reactants and igniting the reactions at higher enthalpy and temperature values. This effect coupled with the occurrence of local surface temperatures higher than the final adiabatic temperatures determines product compositions that correspond to non-equilibrium compositions.

Not surprisingly, it has been found that the differences between experimental and equilibrium compositions have been reduced by increasing the overall residence time.

This finding can be utilised for designing a SCT-CPO technology with reduced pre-heating requirements allowing the occurrence of the great part of the reactions in local environments having surface temperatures higher than the thermodynamic equilibrium temperatures and hence in conditions allowing the reduction of the oxygen consumption as it will be discussed in the final section of this work.

Indeed, as already mentioned, this qualitatively represented picture has also been included in numerical models [33,34] that have simulated the experimental features. These models have been developed considering a diffusion-reaction system in which transport phenomena and chemical kinetics are interrelated in a transfer controlled operating regime where local T differences are originated between the catalyst surfaces and the gaseous phase. In this regime the oxygen transport from the bulk gas phase to the catalyst surface has been considered as the rate-limiting step. Mono- and poly-dimensional models have been much more extensively developed in various academic environments describing the reaction/reactors characteristics utilising detailed surface kinetics [35–37]. In our work, the numerical simulations have been utilised for deepening the analysis of the relation between the reactor performance and transport phenomena, emphasizing the role of thermal conduction and radiation within a fixed bed and for designing reactors for maximising the productivity and at the same time, for reducing the O_2 consumption that represent a relevant cost in the synthesis gas production.

4. SCT-CPO technological applications

H_2 and synthesis gas have been widely used in the last 70 years in chemical and refinery industries. Their usage is growing and some new technological needs are emerging related to:

1. providing with H_2 the refineries for enhancing their residue conversion capacity and contemporaneously for obtaining ‘‘clean burning’’ gasoline and diesel fuels with very low S amounts and with a reduced aromatic and olefin content;
2. reducing the capital costs of the via-syngas gas to liquid (GTL) processes converting NG into high quality energy vectors (gasoils, naphta, methanol and dimethylether);
3. accomplishing the H_2 or the synthesis gas production for fuel cell technologies.

4.1. H_2 for the refineries via SCT-CPO

The H_2 consumption in refineries is continuously raising for enhancing the residue conversion capacity and for producing ‘‘clean burning’’ fuels. The worldwide on-purpose H_2 capacity has increased 70% between 1995 and 2003. The 96% of this on-purpose H_2 is produced with steam reforming [4] (SR) (76% from NG, 20% from light naphtha) while partial oxidation (PO) of residues (petroleum coke, deasphalter pitch, residual oil) produces the remaining 4%. SR produces the H_2 from desulphurated and light hydrocarbons through highly endothermic catalytic reactions. Its costs, particularly for medium and large capacity capacities ($F > 50{,}000\ \mathrm{N\,m^3/h}$), are dominated by the feed costs. PO is instead based on very exothermic oxidation reactions produced inside a combustion chamber. PO has a unique flexibility with respect to the possibility of utilising various feedstock ranging from NG to petroleum coke. However requires a high capital expenditure. This, together with the relatively low energy efficiency, make its economics advantageous versus SR when a low cost feedstock (coke, pitch) is utilised in large scale applications ($F_{\mathrm{H_2}} \gg 150{,}000\,\mathrm{N\,m^3/h}$) [38].

Other intermediate feedstock, such as light cycle oils (LCO), or some de-asphalted oils (DAO) cannot be utilised by SR and would not be economic for PO.

This situation determines the opportunity of developing a technology having a high flexibility with respect to feedstock composition and production capacity; with energy efficiency values comparable with those SR and capital costs much lower than those of PO.

The SCT-CPO characteristics allow in principle the utilisation of ‘‘heavy’’ feedstock containing relevant amount of S since it is expected that the high surface temperature could avoid the formation and the stabilisation of metal sulphide that would poison the catalysts. Moreover the high temperature surface chemistry is expected to be rather unselective towards soot formation reactions.

Accordingly the bench-scale level testing of the SCT-CPO of NG containing H_2S, of refinery off-gases, of LCO, and DAO feedstock, was investigated and the results indicated that the catalysts were not poisoned provided that their surface temperature could be kept above 900 °C. These experiments have been successfully performed at space velocities comprised between 50,000 and 250,000 h^{-1} with feedstock containing relevant amounts of S and aromatics (0.5–3.5 wt.% of S and 60–80 wt.% of aromatics). Technical and economic analysis sustained the appealing of SCT-CPO process able to deal with these feedstock. For this reason we have initiated a scale up effort utilising a pilot plant unit realised in Milazzo (Sicily) designed as a multi-purpose facility for experimenting the technical feasibility of the SCT-CPO method utilising various hydrocarbons and oxidant mixtures. Currently the main technical issues to be addressed concern the definition and the scale up of a mixer and an inlet zone preventing the ignition of gaseous reactions before of the catalytic bed.

4.2. Synthesis gas for GTL

The synthesis gas preparation is responsible for a significant amount (in literature these values range between 40 and 70%) of the total production cost of the GTL initiatives. Currently the most preferred synthesis gas production technology is the autothermal reforming (ATR). This is a well-established technology whose main limitation is in the necessity of mixing some steam with the NG feedstock for operating in soot-free conditions. The steam addition raises the H_2/CO ratios in the synthesis gas above the desired 2 (v/v) ratios [39] that would permit the maximum carbon efficiency in GTL, combining high conversion per pass in the F–T reactor with good selectivity towards the desired liquid products. Currently the steam versus carbon ratio (S/C) limit in the ATR feedstock cannot be lowered below 0.6 (v/v). This value determines the amount of CO_2 rich synthesis gas exiting from the F–T reactor (see Fig. 8) that has to be recycled to the ATR for reducing through the occurrence of reaction (5), the H_2/CO close to 2. However the larger the amount of the CO_2 rich gas recycled, the larger are the dimensions of the synthesis gas section per ton of product and the related investment costs. A representative process configuration (see Fig. 9) shows that the utilization of ATR implies: (a) an initial hydrodesulfurisation step, (b) the mixing and heating of the desulphurised NG with Steam (reaching a S/C = 0.6 (v/v)), (c) the pre-reforming of the NG for converting the C_2 + hydrocarbons, (d) the mixing of the pre-reformed NG with some of the CO_2 rich synthesis gas produced at the exit of the F–T reactor, and finally (e) the ATR step and the synthesis gas cooling step.

By studying the SCT-CPO it appeared that the S/C limit could be reduced below the 0.6 value since the reactions were not occurring in the gaseous phase and the selectivity could be catalytically addressed. Indeed this possibility was confirmed by an extensive (more than 20,000 h at S/C between 0 and 0.5 (v/v)) bench-scale testing.

The synthesis gas generation section based on the SCT-CPO technology would then appear as in Fig. 10. Here it is shown that the pre-reforming section could be avoided and that, since the S/C can be reduced to 0.2 v/v, the recycle of the CO_2 rich stream coming from the F–T recycle loop can be greatly reduced. Moreover the small recycle from the FT reactor and the low feedstock pre-heating (around 250 °C) required for avoiding flame ignition would greatly reduce (reduction around 35%) the ‘‘duty’’ and consequently the capital cost expenditures for the

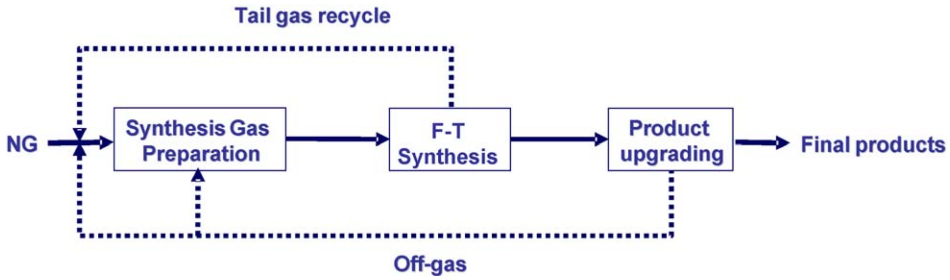

Fig. 8. Simplified GTL scheme including the three main block processes and showing main recycle options to the synthesis gas preparation.

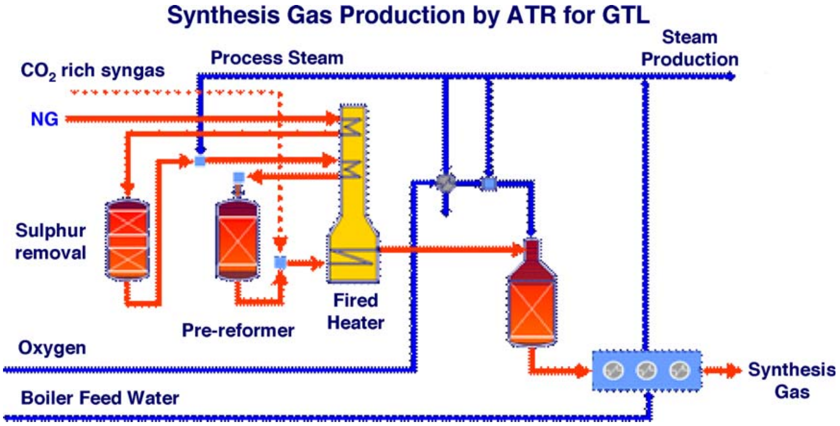

Fig. 9. Simplified process scheme utilising ATR technology for producing synthesis gas for the low-temperature *F–T* synthesis.

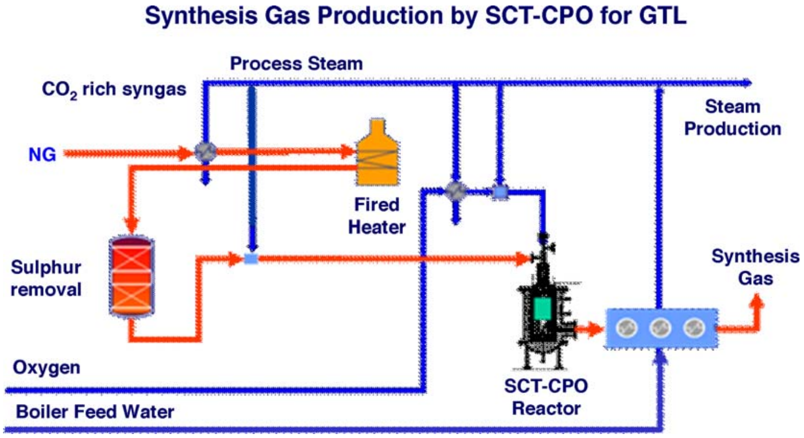

Fig. 10. Simplified process scheme utilising SCT-CPO technology for producing synthesis gas for the low-temperature *F–T* synthesis.

synthesis gas generation. Contemporaneously the avoidance of the recycling of the CO_2 rich synthesis gas would determine a relevant increase of the entire GTL single line capacity [38]. Oxygen consumption would be raised by the reduction of the preheating temperature but would be lowered by the reduction of the CO_2 rich synthesis recycle. These two tendencies would compensate at an extent that would vary with the different process scheme and FT technology solutions. However it is expected that the possibility of reducing the S/C value would add new opportunities for investigating solutions for the reduction of the capital costs expenditures. However it is clear that before proposing this method for large-scale initiatives its reliability needs to be consolidated in pilot and demonstrative scales and this is a still ongoing process.

4.3. *Air blown SCT-CPO for stationary FC or for producing the H_2 inside filling stations*

Many fuel cell systems do exist and their characteristics are widely reviewed and described in the literature. The ultimate fuels that FC consumes at the anode side are H_2 or synthesis gas. Even if a great effort has been devoted to develop on board reformers virtually all the fuel cells powered vehicles (520 worldwide at the end of 2004) utilise H_2 that is stored onboard and that can be produced in large centralised facilities or in small and easy to handle reformers localised at the distribution sites. The most desirable characteristics of these small reformers can be listed as follows: (a) compactness and simplicity, (b) safety and easy operability, (c) low manufacturing cost, (d) multi-fuel capability.

These characteristics would be allowable to an air blown SCT-CPO based technology that has been successfully tested either ant bench-scale and pilot scale levels. The results have justified the design and the realisation of a prototype demonstrative unit that will be located within a multi-fuel station under realisation inside the urban area of the Italian city of Mantova. In this station the gasoline, diesel, NG and H_2 will be delivered to ICE vehicles while the produced H_2 will be delivered to FC vehicles. The project is sustained by the European Union and includes twins initiatives in Germany and in Italy. In Mantova the H_2 will be produced through an air blown SCT-CPO reformer designed for being tightly integrated with the multi-fuel station needs and characteristics.

5. Conclusions

Simple and in some cases qualitative pictures have been given with the purpose of providing information on the reasoning that has linked science and technology issues in a field that has appeared as one of the most promising in high temperature catalysis. The story has not been concluded yet but the fundamental understanding is clearly consolidating into technological objects that are not far from the final industrial realisations.

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