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Experimental and modeling analysis of the effect of catalyst aging on the performance of a short contact time adiabatic CH_4-CPO reactor

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Abstract

Catalytic partial oxidation of methane at short contact time was studied in a lab-scale packed bed reactor over a 0.5 wt% Rh/A_2O_3 catalyst. Experiments were focused on the investigation of catalyst stability and durability upon repeated start-up/shut-down tests at different inlet temperatures and flow rates. Measurements of the axial temperature profiles evidenced a high sensitivity of the steady state thermal behavior of the reactor on catalyst activity: a decrease of the intrinsic catalytic activity was interpreted as the cause of a progressive over-heating of the bed which, in turn, moderated the loss of methane conversion and syngas productivity. At sufficiently high flow rate the observed temperature rise spread along the whole catalytic bed. Under such conditions both steady state and dynamic reactor performances were affected by the progressive decay of catalyst activity. A rationalization of the observed results was pursued by applying a one dimensional (1D) heterogeneous model of the reactor to the quantitative analysis of experimental results. Model predictions revealed the occurrence of operating surface temperatures up to 1100 °C and allowed to quantify the progressive worsening of reactor performances in terms of a loss of reforming activity localized in correspondence of the catalyst hot spot.

Keywords: Catalytic partial oxidation; Methane; Rh catalyst; Deactivation; Adiabatic reactor; 1D model analysis

1. Introduction

On-board fuel reforming for the production of hydrogen or synthesis gas faces several challenges. Among them, there is the need of a compact reformer unit, with fast response to load changes. Catalytic Partial Oxidation (CPO) offers in this respect the advantages of an autothermal operation and small reaction volumes; indeed partial oxidation has been proven in the literature as a successful technology for the conversion of liquid hydrocarbons into CO and H_2 mixtures in milliseconds contact time reactors [1,2]. The compactness and simplicity of a single-step CPO reformer could also allow an efficient conversion also of CH_4 for both the small-scale distributed generation of hydrogen and mobile applications [3–5].

Among noble metals, Rh has been mostly studied for the partial oxidation of natural gas and liquid hydrocarbons because of its high activity and selectivity, low tendency to C formation and low volatility [6,7]. Autothermal operation is characterized by extremely high temperatures (even higher than 1000 °C) which can compromise long-term catalytic performances. To counterbalance possible activity losses, due for instance to thermal sintering of the metal clusters [8] or volatilization of the active species, relatively high metal loadings (from 2 to 10% by weight) have been proposed in the literature [1,9].

Data concerning catalyst durability under conditions of continuous operation are reported by Basini et al. [10] who observed stable reactor performances for a time on stream of 500 h; however, the reactor operated at low GHSV close to conditions of thermodynamic equilibrium. Mitri et al. [9] studied the behavior of a reverse flow reactor upon aging of 3–5 wt% Pt, Rh and Ir based catalysts. Within a time on stream of

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25 h they found that Rh did not suffer significant deactivation phenomena. In this work, pieces of evidence were collected on the behavior of a CH_4-CPO reformer, operating under quasi-adiabatic conditions with a 0.5 wt% Rh/Al_2O_3 catalyst within an overall time on stream of 150 h. The low Rh content allowed to better investigate the impact of catalyst activity on the overall performance of the reactor. The stability of the catalyst was monitored within series of repeated start-up/shut-down experiments at different reaction temperatures and flow rates (in the range of tenths of ms contact times) with the aim of identifying critical operating conditions associated to the decay of catalyst activity. The effects of catalyst aging over the behavior of the reactor were investigated in terms of both steady state conversion/productivity and evolution of axial temperature profiles (so far scarcely investigated in the literature). The impact of catalyst deactivation on the start-up dynamics of the process was also studied. A quantitative analysis of the observed deactivation phenomena was pursued by applying a complete model of the adiabatic reformer [11] which incorporates an indirect kinetic scheme of the reaction process based on previous work discussed in ref. [12] and accounts for the combined effect of heat and mass transfer.

2. Experimental

2.1. Lab-scale assembly

The process of CH_4 partial oxidation was studied on a 0.5 wt% Rh/Al_2O_3 catalyst (BET surface area $\sim$40 $m^2\,g^{-1}$) prepared by grafting of alumina powders with $Rh_4(CO)_{12}$ dissolved in *n*-hexane [13,14]. After drying, the catalytic powders were dispersed in an aqueous solution of nitric acid and a slurry was prepared via 24-h ball milling of the dispersion. A thin (20 μm) and mechanically resistant catalyst layer was deposited by dipping over solid alumina spheres with an average diameter of 3.4 mm. A packed bed of coated spheres (about 17 g) was placed inside a quartz tube reactor between two beds of uncoated spheres acting as thermal shields to prevent axial heat dispersion by radiation. A layer of mullite particles upstream from the spheres bed was used to realize the preheating of reactants and to optimize their premixing. Radial insulation of the reacting zone was realized by wrapping a layer of ceramic insulator around the quartz tube in correspondence of the packed bed. The reactor, equipped with an axial sliding thermocouple, was located inside a tubular furnace for the preheating of the system. A detailed description of the geometry and features of the reactor are reported in ref. [15]. Tests were performed at atmospheric pressure with CH_4/air feeds (O_2/CH_4 ratio = 0.56).

2.2. Start-up and shut-down procedures

The process was started-up by delivering at time zero of the dynamics (t_0) the reactant mixture to the reactor previously heated to the initial desired temperature (reported in the following as $T(t_0)$) under static N_2 atmosphere. The temporal evolution of the outlet stream composition was acquired by means of a continuous ABB AO2000 analyzer, able to measure CH_4, O_2, CO, CO_2 and H_2 volumetric percent; water concentration during dynamics was estimated by closing the oxygen mass balance. Under steady state conditions the analysis of products was repeated by gas chromatography, which also allowed a direct measurement of H_2O. Atomic mass balances to converted C, O and H were closed within 3%.

The reaction was shut-down by diluting progressively the reactant stream with N_2 and, eventually, the reactor was cooled down to initial conditions under pure N_2 flow. Catalytic runs (1.5–2 h long each) were operated daily; by night the reactor was left under static N_2 atmosphere at room temperature. The autothermal behavior of the reactor was investigated in 4–5 h long experiments by switching off the heating furnace after reaching the stable ignited state.

3. Reactor modeling

A previously developed one dimensional (1D) dynamic heterogeneous model of an adiabatic packed bed reactor was applied to the analysis of experimental data. Model equations and assumptions are fully discussed in refs. [12,15]. The model implements a molecular indirect kinetic scheme independently derived over a 0.5 wt% Rh/α-Al_2O_3 catalyst with a surface area of $\sim$4 $m^2\,g^{-1}$ [12]; the model parameters were modified (after a sensitivity analysis developed in ref. [15]) to account for the higher value of surface area (40 $m^2\,g^{-1}$) in the present experiments. To study the effect of localized deactivation phenomena the possibility to assign an axial activity profile of the catalytic bed was herein implemented in the model, which extended the analysis of kinetic sensitivity mentioned above.

The heat exchange between the oven and the reactor along the preheating zone as well as the heat dispersion in the catalytic portion were described by including in the gas phase energy balance a heat transfer term with an overall heat transfer coefficient.

4. Results and discussion

4.1. Steady state performances: experimental results

The reproducibility of the reactor performances upon exposure of the catalyst to different operating conditions was tested by performing experiments in which the preheating temperature was alternatively set at 380 and 610 °C and the flow rate was increased from 140 N L h^{-1} (representative of an important thermodynamic control on the product mixture, with a significant role of heat dispersion) to 240 N L h^{-1} (representative of a more kinetically controlled, almost adiabatic operation) [15]. Catalyst stability with time at constant preheating temperature and flow rate was investigated by performing series of consecutive start-up/shut-down experiments, for an overall time on stream of about 150 h.

Concerning steady state results, Fig. 1a and b reports the evolution of CH_4 conversion and of H_2 and CO molar fractions, respectively, observed during the sequence of experimental runs. The conversion of O_2 was complete under all operating

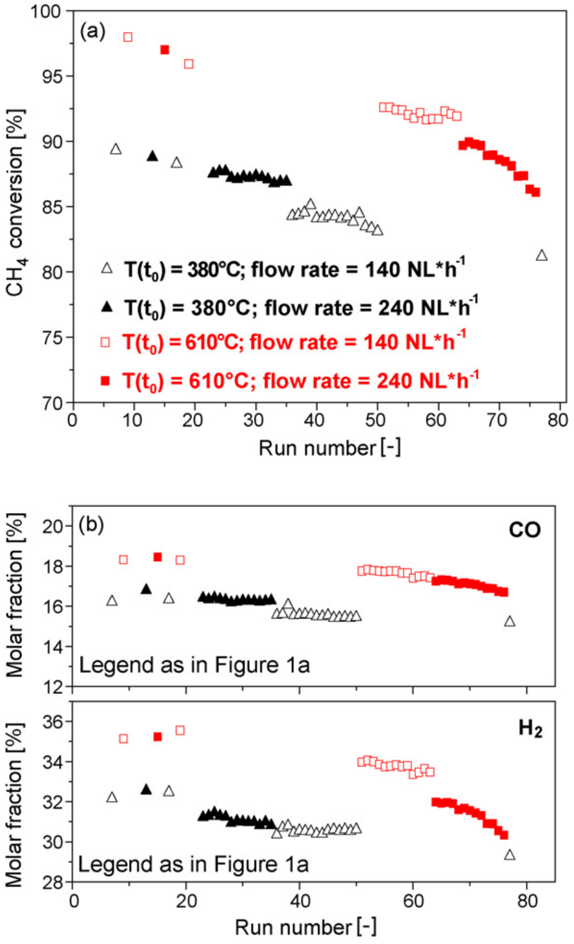

Fig. 1. Observed steady state conversion (a) and H_2/CO percent molar fraction (b) within the sequence of start-up/shut down experiments performed at different preheating temperature [$T(t_0)$] and flow rate. Feed: CH_4/air, $O_2/CH_4 = 0.56$; atmospheric pressure.

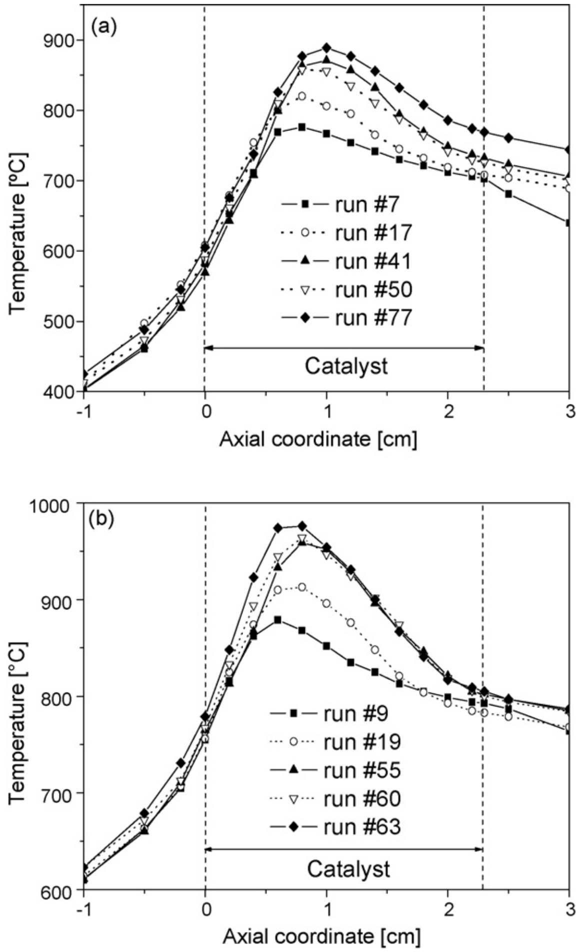

Fig. 2. Evolution of steady state temperature profiles measured in the runs performed at flow rate = 140 N L h^{-1} and preheating temperature of 380 °C (a) and 610 °C (b). Feed: CH_4/air, $O_2/CH_4 = 0.56$; atmospheric pressure.

conditions. At the flow rate of 140 N L h^{-1} the conversion of methane was 89% at $T(t_0)$ = 380 °C (run #7) and grew to 98% at $T(t_0)$ = 610 °C (run #9). The corresponding axial temperature profiles, reported in Fig. 2a and b, were characterized by the presence of a maximum which reached 776 and 879 °C, respectively. Reactor performances corresponded to those predicted by thermodynamic equilibrium calculated at the outlet measured temperature. At both preheating temperatures, by increasing the flow rate to 240 N L h^{-1} the catalyst heated up, mainly due to the enhanced thermal efficiency of the reactor [15] and, to a lower extent, to the lower selectivity to synthesis gas [11]; in fact, CH_4 conversion had small decreases (lower than 1%) due to the kinetic effect of the reduced contact time. Peak temperatures were 800 °C at $T(t_0)$ = 380 and 901 °C at $T(t_0)$ = 610 °C (runs #13 and 15 in Fig. 3a and b, respectively).

Within the following series of start-up/shut-down runs performed at 240 N L h^{-1} flow rate and $T(t_0)$ = 380 °C both methane conversion and synthesis gas production kept rather constant (with just 1% of conversion drop), evidencing an apparent stability of reactor performances. Still, the inspection of the corresponding axial temperature profiles (Fig. 3a) reveals that a progressive evolution of the thermal behavior of the reactor occurred. Indeed, the catalytic bed progressively heated up and the temperature peak shifted towards the centre of the catalytic zone. The temperature rise was mainly localized in correspondence of the temperature maximum which reached 890 °C, with an increase of 90 °C with respect to that initially measured, while at the outlet of the bed the temperature grew of about 30 °C. An analogous behavior was observed at 140 N L h^{-1} in both series of runs at low and high preheating temperature. The conversion of CH_4 had a very slight decreasing trend with variations lower than 1% and substantially kept around 84% at $T(t_0)$ = 380 °C and 93% at $T(t_0)$ = 610 °C, about 5% lower than measured over the fresh catalyst in runs #7 and 9, respectively; such a moderate difference of reactant conversion mainly affected the molar fraction of H_2 while the concentration of CO had minimum deviations from the initial reference. Contrarily, a marked increase of the peak temperature of 90–95 °C was recorded (runs #50 and 63 in Fig. 2a and b, respectively) against a significantly lower increase of the outlet temperature which did not exceed 25 °C.

By re-establishing the high flow rate and the high preheating temperature (the most severe operating conditions) the

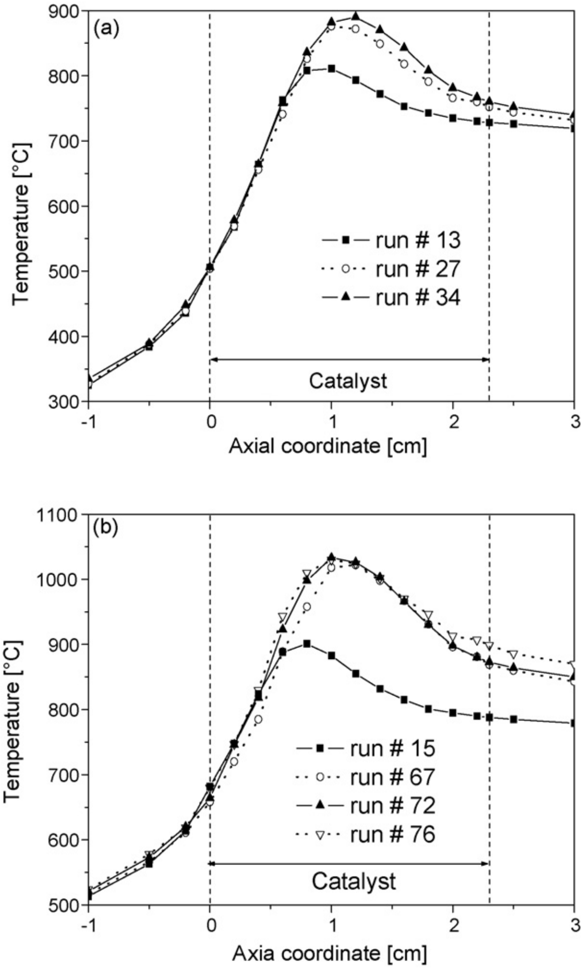

Fig. 3. Evolution of steady state temperature profiles measured in the runs performed at flow rate = 240 N L h^{-1} and preheating temperature of 380 °C (a) and 610 °C (b). Feed: CH_4/air, $O_2/CH_4 = 0.56$; atmospheric pressure.

conversion of CH_4 and the molar fraction of H_2 and CO were, respectively, 7%, 3% and 1% lower than the initial references. Correspondingly, the peak temperature reached 1022 °C (run #67 in Fig. 3b) with an increase of more than 120 °C with respect to the initial profile. Notably, differently from the other cases previously introduced, such a marked over-heating was extended to the whole length of the catalytic bed. In parallel, a progressive decrease of both CH_4 conversion and H_2/CO productivity was observed within the series of start-up/shut-down runs. Methane conversion suffered a drop of about 4% between the first and the last run of the series (runs #64 and 76, respectively), accompanied by a reduction of H_2 molar fraction around 2%. In line with previous findings, the concentration of CO was less sensitive to variations of catalytic performances and decreased no more than 0.5%. The decreasing trends of CH_4 conversion and syngas production were associated to a further temperature rise localized along the inlet portion of the catalyst bed and at the catalyst outlet of about 50 and 25 °C, respectively.

The decay of catalyst activity was confirmed in a final run (#77 in Fig. 1) at 140 N L h^{-1} flow rate and 380 °C preheating temperature wherein a further 2–3% decrease of CH_4 conversion and of H_2 molar fraction was observed with respect to tests performed in the start-up/shut-down series at the same operating conditions. The comparison between the corresponding temperature profile and those measured in previous runs (Fig. 2a) evidences that the loss of catalytic performances was associated to a further rise of temperatures which predominantly occurred along the downstream portion of the bed.

Analogous effects of catalyst aging on reactor behavior were observed in thermally self-sustained runs, realized by removing the furnace heat supply after stabilization of the ignited state. Within the present experimental campaign two tests were realized under these conditions: one before (run #20) and the other after (run #35) the start-up/shut-down series at 240 N L h^{-1} flow rate and 380 °C preheating temperature representative, respectively, of the performances of a fresh catalyst and of a partially aged catalyst. In both cases upon removal of the preheating the process kept ignited and a stable production of syngas was observed as long as the reaction could be monitored (4–5 h). After aging a slight decrease of CH_4 conversion was observed, accompanied by a temperature rise extended to the central and outlet portion of the catalytic bed.

4.2. Steady state performances: model analysis

A quantitative interpretation of the observed trends was pursued by means of the 1D mathematical model of the reactor. The model analysis was applied to experimental results collected at the flow rate of 240 N L h^{-1}, that is under conditions of close approach to adiabatic behavior of the reactor.

The experimental evidence enlightened that the thermal behavior of the reactor was much more sensitive, thus more informative, on the activity loss than the reactant conversion and the product distribution. In Fig. 4a and b the temperature profiles measured at $T(t_0) = 380$ °C before and at the end of the start-up/shut-down series (run #13—fresh catalyst and run #34—aged catalyst, respectively) are compared to model predictions of the solid phase and of the gas phase temperatures, respectively. As reported in ref. [15] the simulation of the reactor behavior in the presence of the fresh catalyst evidences a tight correspondence between thermocouple measurements and the calculated gas phase temperature. The predicted hot spot of the solid phase is closer to the catalytic bed entrance with respect to the gas temperature profile, and along the inlet zone the solid temperature is significantly higher, with peak values close to 890 °C. Such high surface temperatures (which at the preheating temperature of 610 °C increase up to 950–1100 °C) could represent critical conditions for catalyst stability because of reduction of the alumina surface area, sintering of Rh particles and/or possible loss of Rh by volatilization [8].

In order to analyze the observed effect of aging on the reactor performances a sensitivity study was performed by perturbing the activity of portions of the catalytic bed. In particular we varied the rate of the steam and dry reforming reactions whose predominant role in determining the steady state behavior of the reactor had been shown in ref. [15]. At this

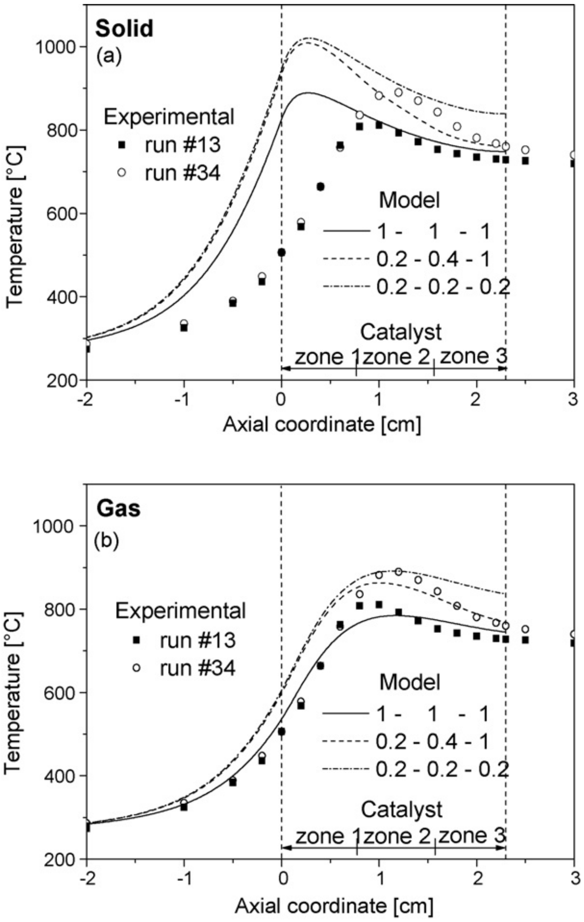

Fig. 4. Comparison between measured temperature profiles (symbols) and model predictions (lines) of the solid (a) and gas (b) temperature calculated by assuming progressively decreased intrinsic kinetics of reforming. Preheating temperature = 380 °C, flow rate = 240 N L h^{-1}.

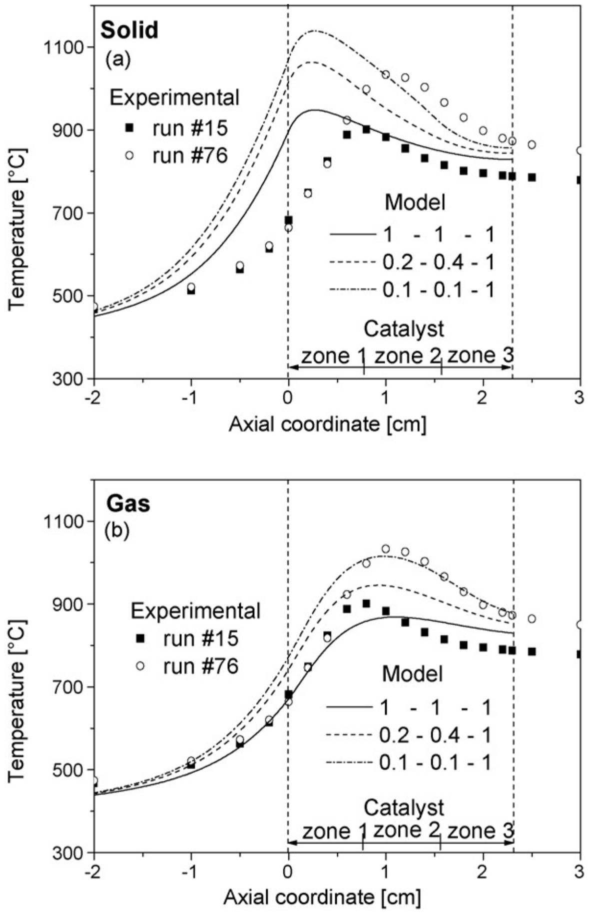

Fig. 5. Comparison between measured temperature profiles (symbols) and model predictions (lines) of the solid (a) and gas (b) temperature calculated by assuming progressively decreased intrinsic kinetics of reforming. Preheating temperature = 610 °C, flow rate = 240 N L h^{-1}.

purpose the catalytic bed was split in three zones, each equal to one third of the bed length; a stepwise activity profile was assigned by relaxing both the reference reaction rates of steam- and CO_2-reforming (i.e. those referred to the fresh catalyst) by factors related to the axial position (reported in Figs. 4 and 5 as three-digits sequences).

The observed temperature rise upon catalyst aging suggested the occurrence of a reduction of the heat consumption rate by endothermic reactions, that is a decrease of the reforming rates which tends to shift the product distribution towards CO_2 and H_2O making the process more exothermic. Indeed, by reducing the rates of the reforming reactions to 20% of reference values (profile 0.2–0.2–0.2 in Fig. 4b), i.e. adopting the original kinetics found over a stable catalyst supported over a low surface area α-Al_2O_3 [12], the predicted temperatures shifted to higher values and simulations captured the measured peak temperature (run #34). Still, such a uniformly distributed reduction of activity resulted in a significant overestimation of temperatures at both the inlet and the outlet zone of the catalytic bed. Model predictions better approached the measured temperatures by assuming a non-uniform 0.2–0.4–1 activity profile which is in line with the hypothesis of a progressive activity loss at increasing catalyst surface temperatures. Under these conditions the calculated conversion of CH_4 and molar fractions of H_2 and CO were 85%, 31% and 16%, respectively, in good agreement with experimental data (Table 1).

Notably, the predicted peak temperature of the solid phase approached 1000 °C, which evidences a self-promoting nature of the aging phenomena. The predicted temperature increase of the solid was significantly higher than that observed for the gas phase, which evidenced how the occurrence of critical conditions for catalyst stability could be missed by thermocouple measurements. We also remark that deviations of predicted temperatures from those observed after aging along

Table 1
Observed and simulated reactor performances at the flow rate of 240 N L h^{-1} after catalyst aging

	Experimental		Model	
	$T(t_0)$ = 380 °C	$T(t_0)$ = 610 °C	$T(t_0)$ = 380 °C	$T(t_0)$ = 610 °C
CH_4 conversion (%)	87	86	85	88
H_2 molar fraction (%)	31	30	31	33
CO molar fraction (%)	16	17	16	17

the inlet portion of the catalyst could not be reduced according to the present simplified schematization.

Experimental data showed that aging phenomena were enhanced by operating at high preheating temperature ($T(t_0) = 610$ °C) since such conditions promoted the exposure of the catalyst to surface temperatures even exceeding 1000 °C that is the maximum calculated solid temperature at which stable reactor performances were eventually observed at $T(t_0)$ equal to 380 °C. Model predictions show (Fig. 5a) that at $T(t_0) = 610$ °C even in the presence of a fresh catalyst (run #15) surface temperatures could reach values up to 950 °C. Due to such critical conditions the reduction of the reforming activity was expected to be more significant and extended to a wider portion of the catalytic bed than occurred at lower preheating temperature. Indeed, with respect to the reference kinetics (corresponding to the activity profile 1–1–1) a 90% decrease of reforming reaction rates (profile 0.1–0.1–1 in Fig. 5b) had to be invoked along both the first and second portion of the catalytic bed to match the measured temperature profiles after aging (run #76). According to model predictions, in line with the results at lower preheating temperature the reforming activity of the downstream catalytic zone apparently kept unchanged with respect to the fresh catalyst. The calculated conversion of CH_4 and H_2/CO molar fractions were 88%, 33% and 17%, respectively, in agreement with the experimental results. Correspondingly, a maximum temperature of the catalyst surface close to 1140 °C was predicted (Fig. 5a). As a whole experimental results and model analysis of steady state performances point out the key role of the kinetics of reforming reactions on the control of catalyst temperature profile. Either poorly active or deactivated catalysts may guarantee good conversion and selectivity performances only at the expense of extremely marked hot-spots that, in turn, may endanger the catalyst. Similar control effects of catalyst activity on steady state temperature profiles have been reported in ref. [16] by comparing the performances of Rh supported catalyst with different metal dispersion under adiabatic, short contact time conditions characteristic of gas turbine combustors.

4.3. Start-up dynamics: experimental results

A detailed description of the transient behavior of the reactor upon ignition of the process has been discussed in ref. [15]. For the sake of clarity the main features reported therein are summarized below.

At 380 °C preheating temperature and 240 N L h^{-1} flow rate, start-up dynamics were characterized by the presence of a 4 min induction time during which a slow heating of the catalytic bed occurred, associated to a low conversion of CH_4 and O_2 into H_2O and CO_2. After that, the reactor lit-off with a fast increase of reactants conversion accompanied by the formation of syngas and a hot spot at the back-end of the catalytic bed; the hot spot then rapidly propagated upwards through the reactor (back end ignition). Steady state was reached within 10 min. At 610 °C preheating temperature no induction time was observed (Fig. 6). A net production of H_2 and CO was recorded since the initial moments following the delivery of the feed into the reactor. The catalytic bed heated up uniformly and reached the highest temperatures within 3–4 min (front end ignition).

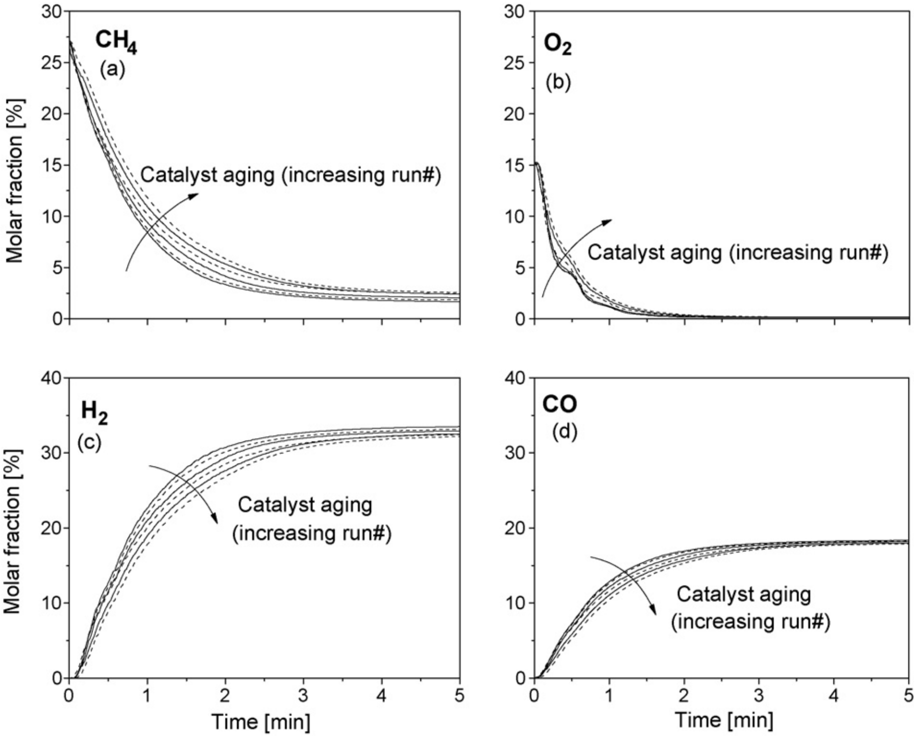

Fig. 6. Observed evolution of ignition dynamics within the series of start-up/shut-down experiments performed at preheating temperature of 610 °C and flow rate of 240 N L h^{-1}.

In the present study the effects of catalyst aging on the transient behavior of the reactor were investigated. At the preheating temperature of 380 °C the overall duration of start-up dynamics kept roughly constant with time on stream and no significant trend associated with a loss of activity was found.

Fig. 6 reports the dynamics of the outlet concentration of reactants, H_2 and CO measured within the series of start-up/shut-down experiments at $T(t_0) = 610\ ^\circ C$ and flow rate 240 N L h^{-1}. Start-up dynamics at high preheating temperature were so fast to be disguised by the intrinsic response delay of the continuous analysis system. This was clearly evidenced by the measured outlet concentration of O_2 whose signal approached zero only 2 min after the reactants injection. Indeed, at such a high preheating temperature an instantaneous complete consumption of oxygen would be expected as also confirmed by model predictions [15]. Still, being constant the response delay of the analyzer, the observed variations of light-off dynamics with time on stream were relevant for analyzing the impact of catalyst aging over the ignition transient of the process. According to the temporal sequence of consecutive runs a systematic trend was evidenced consisting in a progressive slow down of methane consumption (Fig. 6a) and of synthesis gas formation (Fig. 6c and d), feasibly correlated to a progressive reduction of the reforming activity. Such a behavior was accompanied by a small decrease of the asymptotic concentration values which corresponded to the slight worsening of steady state performances upon catalyst exposure to high temperature discussed above (runs #64–76).

4.4. Start-up dynamics: model analysis

The intrinsic response dynamics of the continuous analyzer had to be accounted for to have a reliable quantitative comparison with the measured light-off dynamics of the process. At this purpose a specific experimental campaign was devoted to the characterization of the analyzer dynamic response to fast variations of concentration in the sample stream. By applying basic dynamic models (first order response, second order response, delay time) to the rationalization of the observed results a transfer function of the continuous analyzer was derived which was coupled to the output of the 1D model of the reactor. Thus, simulations reported in the following accounted for the combined effect of the analyzer and reactor dynamics. A detailed discussion dedicated to this issue will be given in a future work.

Concerning the light-off dynamics at 380 °C starting temperature a sensitivity analysis (not reported) evidenced that variations of the intrinsic kinetic of the reforming reactions did not affect the predicted induction time. Thus, the simulated start-up of the process was governed by the reaction rate of combustion, which confirmed the considerations derived from the inspection of experimental dynamics. Given the back-end ignition occurring under these operating conditions, a major role of the combustion activity of the outlet section of the catalytic packing was expected. Indeed, model simulations predicted that the induction time was markedly more sensitive to variations of the kinetics of oxidation in the outlet zone than in the upstream zones of the catalytic bed. At the light of these findings, the observed invariance of the induction time within

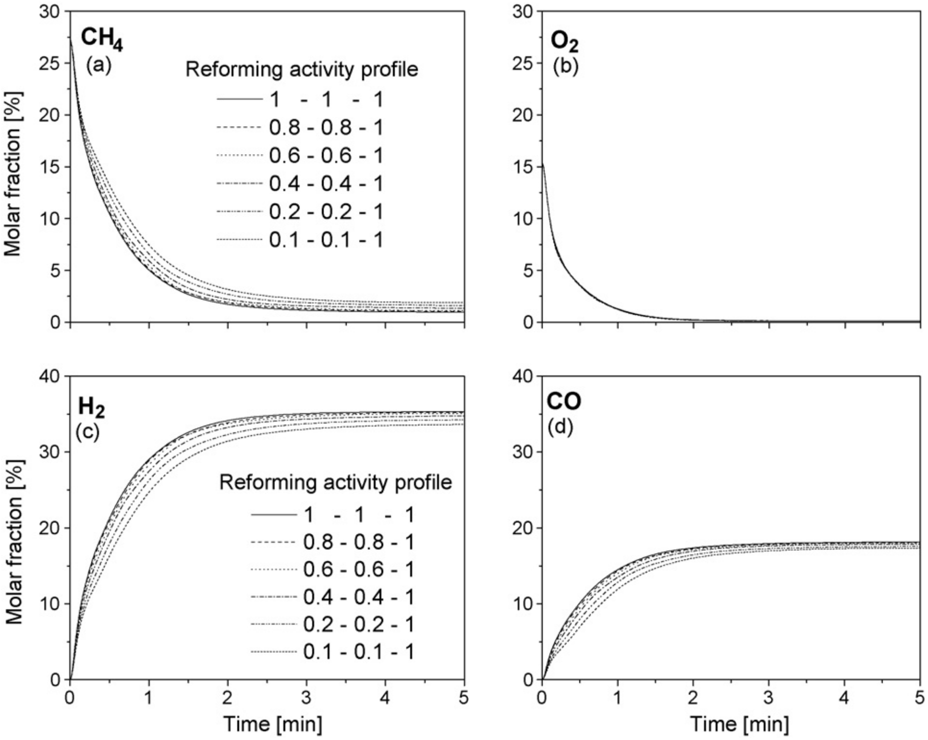

Fig. 7. Predicted effect on ignition dynamics of decreasing intrinsic kinetics of reforming (according to the multiplicative factors reported in figure—see caption of Fig. 4); preheating temperature = 610 °C, flow rate = 240 N L h^{-1}.

the series of start-up dynamics measured at $T(t_0) = 380\ ^\circ\mathrm{C}$ could be reasonably associated with the persistence of a fresh catalyst activity of combustion at the back-end of the catalytic bed.

Fig. 7 reports the start-up dynamics, simulated at $T(t_0) = 610\ ^\circ\mathrm{C}$ by progressively decreasing the activity of reforming in the inlet and central zone of the catalytic bed. Calculated trends captured well the slow down of methane consumption and synthesis gas formation observed upon repetition of experiments at high preheating temperature and flow rate, albeit the calculated dynamics were moderately faster than the measured ones. Such deviations could be ascribed mainly to the high sensitivity of the light-off dynamics on the starting temperature (an effect enhanced at high reactor preheating) whose experimental value was determined as the arithmetic average of the axial temperature profile measured at time zero (with deviations from the average value within $\pm 5\ ^\circ\mathrm{C}$). As expected, the progressive reduction of the intrinsic rate of reforming did not affect the predicted dynamics of O_2 consumption (Fig. 7b) whose observed evolution could be definitely associated to a decrease of the oxidation activity. No informative evidence is available concerning the induction time at high preheating temperature.

5. Conclusions

Because of the low Rh content and the high support surface area of the catalyst tested in the present study and the high GHSV conditions at which the reactor operated, kinetic effects of catalyst aging could be evidenced and relevant pieces of information on the impact of catalyst deactivation on the overall behavior of the reactor were collected.

The observed evolution of steady state temperature profiles within the series of repeated start-up/shut down runs revealed that catalyst deactivation was associated with a marked temperature rise in correspondence of the hot spot of the catalytic bed. At lower reaction temperature such overheating tended to compensate the loss of activity leading to a roughly constant conversion of methane and production of syngas. No significant effects of catalyst deactivation were evidenced on the low temperature start-up dynamics. Remarkably, both before and after catalyst aging under these conditions, stable thermally self-sustained syngas production was observed upon preheat removal by switching off the furnace.

The exposure of the catalyst to extremely severe reaction conditions realized at $T(t_0) = 610\ ^\circ\mathrm{C}$ and flow rate $240\ \mathrm{N\ L\ h^{-1}}$, with measured temperatures exceeding $950\ ^\circ\mathrm{C}$, caused a decrease of activity extended to a wider portion of the catalyst packing, evidenced by a temperature rise along the whole bed, accompanied by a progressive worsening of both steady sate and dynamic performances of the reactor. The temporal evolution of the observables demonstrated that the temperature rise had a self-promoting effect on catalyst deactivation.

Model analysis revealed that the decrease of the observed catalyst performances was associated with a reduction of the intrinsic rate of reforming reactions localized at the bed entrance, where the catalyst was exposed to the maximum surface temperatures. The close correlation between high surface temperature and aging phenomena was confirmed by the predicted finding that neither the activity of reforming nor that of oxidation decreased in the back-end zone of the catalytic bed, wherein surface temperatures were moderated by the endothermic reaction.

Remarkably, the adopted indirect kinetic scheme was able to capture satisfactorily the bulk of both steady state and dynamic observed trends.

Model analysis confirms the low sensitivity of conversion/selectivity to deactivation but also stresses the occurrence of a self-promoting effect associated with marked enhancement of the hot spot temperature that poses a warning for long-term operation under severe conditions.

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