

SHORT CONTACT TIME CATALYTIC PARTIAL OXIDATION OF CH₄-H₂ MIX OVER Ni FOAMS

S. Cimino*, L. Lisi*, G. Mancino*, M. Musiani**,
L. Vázquez-Gómez**, E. Verlato**

stefano.cimino@cnr.it

* Istituto Ricerche sulla Combustione – CNR – P.le V. Tecchio 80, Napoli – Italy

** Istituto per l'Energetica e le Interfasi IENI - CNR, Corso Stati Uniti 4, Padova, Italy

Abstract

The catalytic partial oxidation (CPO) of methane - hydrogen mixtures in air, intended for the first stage of hybrid radiant catalytic burners, was investigated under self-sustained short contact time conditions on commercial Ni foam catalysts eventually modified with Rh and Pt. The modified catalysts were prepared by a simple novel method based on the spontaneous deposition of noble metals via metal exchange reactions onto those Ni foam substrates. Modification with noble metals enhances stability and reducibility of the Ni foam whereas the overall CPO performance is not significantly improved. Safe operation of the CPO reactor with up to 70% vol. H₂ in the fuel mixture has been achieved by properly increasing the feed equivalence ratio to avoid catalyst overheating, while guaranteeing high methane conversions and a persistent net hydrogen production.

Introduction

The catalytic partial oxidation (CPO) of various fuels has been proposed as a preliminary conversion stage in hybrid burners for gas turbines with ultra low-NO_x emissions [1 and ref. therein]. Recently the concept has been extended to develop a novel class of hybrid catalytic gas burners, with integrated interstage heat removal by IR radiation from the hot structured catalytic partial oxidation reactor/radiator [2,3], showing significant improvements with respect to the state-of-the-art fully premixed or blue-flame diffusive natural gas burners for domestic condensing boilers [2]. Since the fuel-air mixture fed to the burner is generally above its upper flammability limit, this technology is intrinsically safe and can be considered as a promising candidate also for hydrogen-hydrocarbon blends, although only a few data are available.

Structured CPO catalysts based on noble metals (particularly Rh, Pt) supported onto ceramic and metallic honeycombs, foams or gauzes have shown high syn-gas yields when operated under auto-thermal conditions at very short contact times with hydrocarbon feeds from methane up to jet-fuels, and bioderived liquids.

Among structured carriers for such a fast, diffusion-limited, highly exothermic process, metallic foams represent the most advantageous choice in order to reduce hot spot formation and the size/weight of the reactor needed to reach high

conversions for their outstanding gas-to-solid heat- and mass-transfer characteristics and high specific geometric surface areas.

Metallic foams are generally used as support structures for high-surface-area ceramic supports [4,5] such as γ -Al₂O₃ which are used to disperse the active metal phase. However the deposition of a thin uniform washcoat layer of refractory oxides firmly anchored to the metal struts is not a trivial matter, but is of paramount importance in order to guarantee long catalyst durability. On the other hand metallic foam/gauze itself can be made of an active catalytic element as for the case of copper, nickel and their alloys as well as noble metals.

In the present paper, we set out to investigate for the first time the catalytic partial oxidation of methane - hydrogen mixtures with air over metallic Ni foam catalysts intended as the first conversion stage in radiant hybrid catalytic burners and operated under self-sustained high temperature, short contact time conditions.

Experimental

Ni, Pt-Ni and Rh-Ni catalysts were produced using as substrates Ni foam discs (with a 18 mm diameter) cut from grade 50 INCOFOAMTM sheets 0.17 cm thick. The apparent density of the foam was 0.22 g cm⁻³, corresponding to a void volume fraction of 0.975, an average pore size of ca. 500 μ m and strut diameter of ca. 60 μ m. The preparation of modified catalysts, was performed via the spontaneous deposition of noble metals (Pt or Rh) onto those Ni foam substrates, obtained through the direct immersion of the foam in a solution of complex noble metal ions (PtCl₆²⁻ or RhCl₆³⁻) at controlled time and pH. The noble metal loadings in Pt-Ni and Rh-Ni catalysts employed for the CPO tests were respectively 0.68 % and 0.26 % w./w.

Catalytic Partial Oxidation tests were performed with two identical catalytic discs (d=18mm, total length 1.7 \times 2 = 3.4mm), stacked between two mullite foam monoliths (45 ppi, L=12mm) as heat shields, and fitted with ceramic paper in a quartz tube reactor (I.D.= 20mm) which was inserted in an electric furnace. High-purity gases (CH₄, O₂, N₂, H₂) calibrated via mass-flow controllers, were pre-mixed and fed to the reactor at a gas hourly space velocity (GHSV) comprised between 1.1 to 3.4 $\times 10^5$ h⁻¹ corresponding to a minimum contact time (based on the solid volume of the foam) of 0.27 ms at standard conditions. Catalytic partial oxidation tests were run under self-sustained high temperature conditions at fixed preheating (200°C) and an overall pressure of P=1.1 bar, using simulated air as the oxidant. In view of the partial substitution of methane with hydrogen in a hybrid combustion device, CPO tests with CH₄-H₂ mixtures with variable H₂ contents (yH₂ up to 70% vol. of the fuel) were run at fixed nominal power and equivalence ratio of the feed (ϕ = 3.2, 3.6, 4.0 always above the upper flammability limit for the fuel mix in air at room conditions).

Results and Discussion

SEM images of Pt-Ni and Rh-Ni catalysts show that, besides some 100-nm nuclei of noble metals, the surface is rather homogeneously covered by much smaller needle-like crystals. Since SEM analysis do not allow to quantitatively assess the relative size of Pt and Rh nanocrystals, electrochemical methods were employed to determine the noble metal surface area [6]. For comparable loadings, the Rh deposits have larger surface areas and smaller dimensions than the Pt deposits. The typical specific surface area per unit noble metal mass in the Pt-Ni and Rh-Ni foam samples used for CPO tests were respectively 3 and 40 m² g⁻¹.

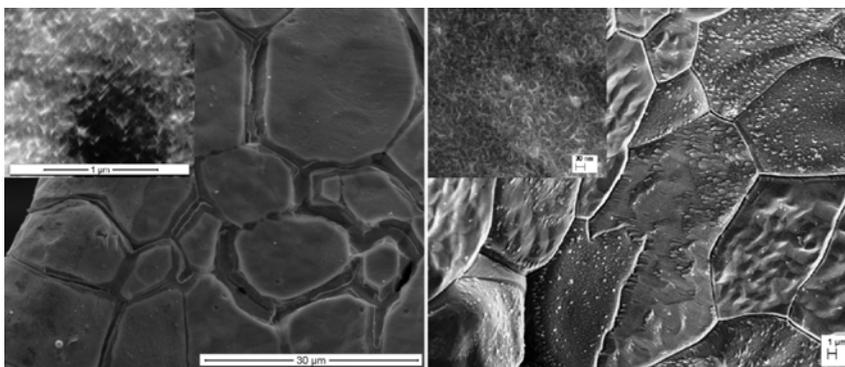


Figure 2. SEM images of a Pt-Ni catalyst (left) and a Rh-Ni catalyst (right).

Ni foam based catalysts showed a remarkable activity for the catalytic partial oxidation of pure methane. Our experiments were run under self-sustained high temperature conditions (>800°C), with limited preheating (200°C) and very short contact times, always giving complete O₂ conversion, and high selectivities to CO and H₂. After an initial stabilization, which was shorter for doped catalysts, the methane CPO performance curves of Rh-Ni, Pt-Ni and unmodified Ni foam catalysts were superimposed within experimental accuracy. In particular methane conversion, and selectivities to CO and H₂ followed the trends of adiabatic equilibrium calculated excluding solid carbon formation, departing from them due to heat losses from the hot catalytic foam that enhanced the kinetic limitation of the steam reforming reaction path. On the other hand, the water gas shift reaction always proceeded fast enough to closely approach its equilibrium at the exit gas temperature, even at the shortest contact times tested. In general the thermal efficiency of the lab-scale reactor, estimated comparing the temperatures recorded in the gas leaving the catalytic stage with the corresponding temperature calculated from the actual composition of the product stream assuming adiabatic conditions [7], varied between 0.78 and 0.85. It should be considered that testing under non-adiabatic conditions is required in view of the use of structured CPO reactors as radiant elements in hybrid catalytic burners, where a large fraction of the nominal input power can be transferred by direct IR-radiation from the hot catalyst [2,3].

CPO experiments with methane-hydrogen mixture were run by increasing the H_2 content in the fuel blend, at fixed equivalence ratio and nominal input power: steady state catalytic performances for the unmodified Ni foam and for Pt- or Rh-modified catalysts were almost identical, as shown in Fig. 2 a-d for the case of $\phi=4$. The partial substitution of methane with H_2 caused a progressive increase of the temperature of the catalytic foams (in Fig. 3a for Pt-Ni catalyst) and of the product syn-gas, in agreement with the trend of the adiabatic equilibrium temperature (Fig. 2a), that increases because of the higher heat of combustion of H_2 per mole of oxygen [8] and the lack of endothermic chemistry with respect to methane. Methane conversion (Fig. 2b) increased progressively with increasing the hydrogen content in the fuel mix, due to higher temperatures on the catalyst and higher partial pressures of water speeding up the kinetically limited steam reforming reaction. CO selectivity (Fig 2c) raised slightly approaching the equilibrium value for the highest hydrogen contents.

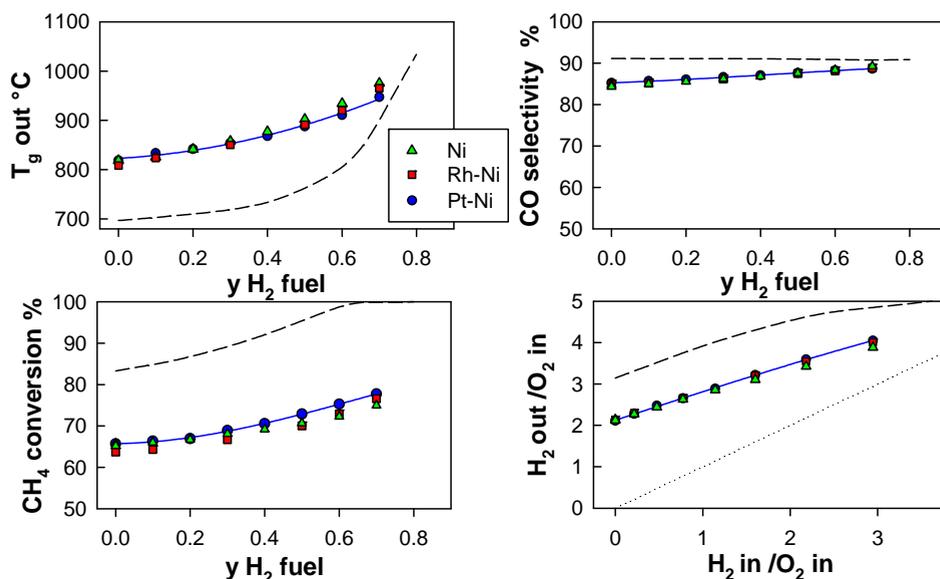


Figure 2. Effect of the H_2 content in CH_4 - H_2 fuel blends during the CPO in air at fixed input power (0.38 kW) and equivalence ratio ϕ (4.0) over pure Ni foam, Rh- and Pt-modified catalysts: a) temperature of the gas leaving the catalyst, b) CO selectivity, and c) methane conversion as a function of yH_2 ; d) hydrogen production expressed as H_2 out / O_2 in vs. H_2 in / O_2 in . Dashed lines represent thermodynamic equilibrium values (p , H =constant).

Fig. 3a,b illustrate the qualitative analogy in the trends of methane conversion and surface temperatures observed at three levels of the feed equivalence ratio as a function of yH_2 in the fuel. As expected, lower values of ϕ , corresponding to higher quantities of oxygen (the limiting reactant) in the feed, were responsible for

higher methane conversions and catalyst temperatures; this circumstance imposed a progressive reduction in the maximum value of y_{H_2} to avoid catalyst overheating. In other words, fuel mixtures very rich in H_2 or even pure hydrogen can be safely handled in a hybrid catalytic burner by increasing the feed equivalence ratio, whose minimum allowable value, set by the thermal resistance of the catalyst, will depend directly on the efficiency of heat removal from the CPO reactor [2,3].

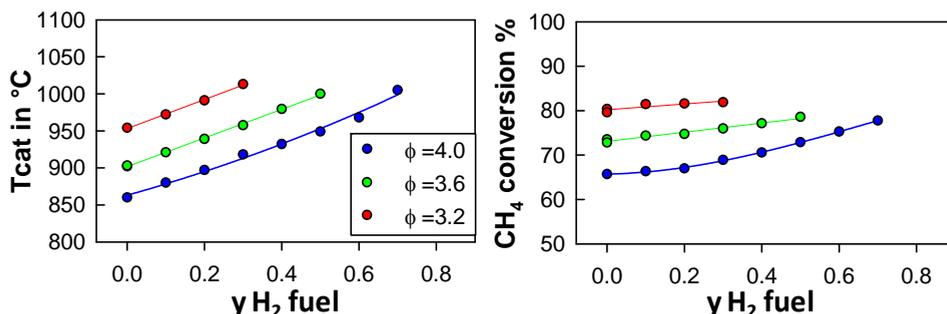


Figure 3. Effect of the H_2 content in CH_4 - H_2 fuel blends during the CPO in air over Pt-Ni foam catalyst at three levels of feed equivalence ratio ϕ (4.0, 3.6, 3.2): a) temperature on the front face of the catalyst, b) methane conversion.

A net hydrogen production was observed across the CPO reactor for all the inlet compositions explored: as seen in Fig. 2d more H_2 was produced than fed up to an inlet H_2/O_2 ratio of 3. The progressive substitution of CH_4 with H_2 shifted the process O-selectivity towards H_2O rather than CO and CO_2 , with a distribution among the three oxygenated products which was rather unaffected by the specific level of the inlet equivalence ratio ϕ . In fact the WGS reaction reached equilibrium on all the three catalysts even with the addition of large quantities of H_2 in the feed. In spite of the lack of experimental data for CH_4 - H_2 mixtures, several literature reports have shown the effectiveness of H_2 as sacrificial fuel in the CPO of ethane over Pt- based structured catalysts to boost ethylene production via homogeneous oxy-cracking of C_2H_6 [8,9 and ref. therein]. In particular it was found that H_2 is rapidly and preferentially oxidized instead of ethane in the first part of the catalytic reactor due to its higher reactivity with respect to the hydrocarbon, causing a marked increase in the catalyst temperature in this zone [9]. Further downstream the reactor H_2 is produced again via ethane dehydrogenation and steam reforming [9]. Apart from the obvious lack of homogeneous oxy-dehydrogenation chemistry, a similar mechanism can be argued also for hydrogen addition to methane on Ni-based foam catalysts, also in view of the lower reactivity of methane with respect to ethane.

Although the contribution from the homogeneous combustion of H_2 cannot be excluded from the present data of integral CPO reactor performance, flashback and ignition of the fuel-air mixture upstream of the catalyst were never observed even

at the highest hydrogen contents because of the high values of the feed equivalence ratio.

References

- [1] Bairda B, Etemad S, Karim H, Alavandi S, Pfefferle W. Gas turbine engine test of RCL catalytic pilot for ultra-low NO_x applications. *Catal. Today* 155: 13-17 (2010).
- [2] Cimino S., Russo G., C. Accordini, G. Toniato, "Development of a hybrid catalytic burner", *Combust. Sci. Tech.* 182: 380-391 (2010).
- [3] Cimino S., Allouis C., Pagliara R., Russo G., "Effect of catalyst formulation on the performance of a natural gas hybrid catalytic burner", *Catal. Today* 171: 72-78 (2011).
- [4] Giani L, Groppi G, Tronconi E. Mass-transfer characterization of metallic foams as supports for structured catalysts. *Ind Eng Chem Res* 44(14):4993–5002 (2005)
- [5] Coleman L, Croiset E, Epling W, Fowler M, Hudgins R. Evaluation of Foam Nickel for the Catalytic Partial Oxidation of Methane. *Catal Lett* 128: 144 (2009)
- [6] Verlato E, Cattarin S, Comisso N, Gambirasi A, Musiani M, Vázquez-Gómez L. Preparation of Pd-modified Ni Foam Electrodes and their Use as Anodes for the Oxidation of Alcohols in Basic Media. *Electrocatalysis* 3: 48-58 (2012)
- [7] Beretta A, Groppi G, Lualdi M, Tavazzi I, Forzatti P. Experimental and modelling analysis of methane partial oxidation: transient and steady state behavior of Rh-coated honeycomb monoliths. *Ind Eng Chem Res* 48: 3825-3836 (2009).
- [8] Cimino S, Donsì F, Russo G, Sanfilippo D. Olefins production by catalytic partial oxidation of ethane and propane over Pt/LaMnO₃ catalyst. *Catal Today* 157: 310-314 (2010).
- [9] Michael BC, Nare DN, Schmidt LD. Catalytic partial oxidation of ethane to ethylene and syngas over Rh and Pt coated monoliths: Spatial profiles of temperature and composition. *Chem Eng Sci* 65: 3893-3902 (2010).