

## Experimental Investigation of Endo and Exothermic Reactions Coupling in a Catalytic Microstructured Reactor

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This work reports on the experimental investigation of the performance of a microstructured catalytic reactor where simultaneous methane catalytic combustion and steam reforming occur. The reactions take place over catalytic layers deposited on the opposite faces of the same metallic slab so that combustion heat sustains the endothermic steam reforming reaction occurring on the opposite side of the slab that also separated the channels where the reactants are fed. The system may operate both in co-current (CNC) and counter-current (CTC) flow.

Under the tested conditions the best reactor performance was about 60% of methane conversion to syngas with a hydrogen yield of 3.33 when gas mean residence time in the reforming channel ( $\tau_{sr}$ ) was about 55 ms and the molar steam/methane feed ratio 3. An oxygen-lean stream (molar  $CH_4/O_2=1/1.68$  -  $O_2$  in air) was fed to the combustion channel because higher oxygen concentration negatively affected the catalytic combustion kinetics.

Even if a relatively high thermal dissipation strongly limited the thermal efficiency of the process, autothermal stability of the system was proved to occur both in CTC and CNC flow patterns when the mean residence time in the combustion channel ( $\tau_{co}$ ) was around 33 and 66 ms and the  $CH_4/O_2$  ratio 1/1.68, while in the reforming channel  $\tau_{sr}$  was about 55 ms.

### 1. Experimental setup

The experimental setup includes reactants feed, reactor and product analysis. The reactants for the exothermic and the endothermic reactions can be fed in CNC or CTC mode. Cylinder air and methane were delivered and metered by mass-flow controllers, (Brooks SL5800) while the feed water flow was regulated by a peristaltic pump (Gilson). The reactants entered the reactor at about 500°C while the reactor was pre-heated at 600°C. Electrical heaters and related temperature controllers were employed for pre-heating the reactor and the entering gas streams. The reactor exhaust products concentrations were monitored by ADVANCE OPTIMA, ABB analyzers: specifically,  $CH_4$ , CO and  $CO_2$  by a NDIR analyzer (Uras 14),  $O_2$  by a paramagnetic analyzer (Magnos 106) and  $H_2$  by a thermoconductivity analyzer (Caldos 17).

In Figure 1 a CAD-view of the catalytic plate reactor is depicted. The reactor, designed to be modular, is made of three stainless steel plates assembled together.

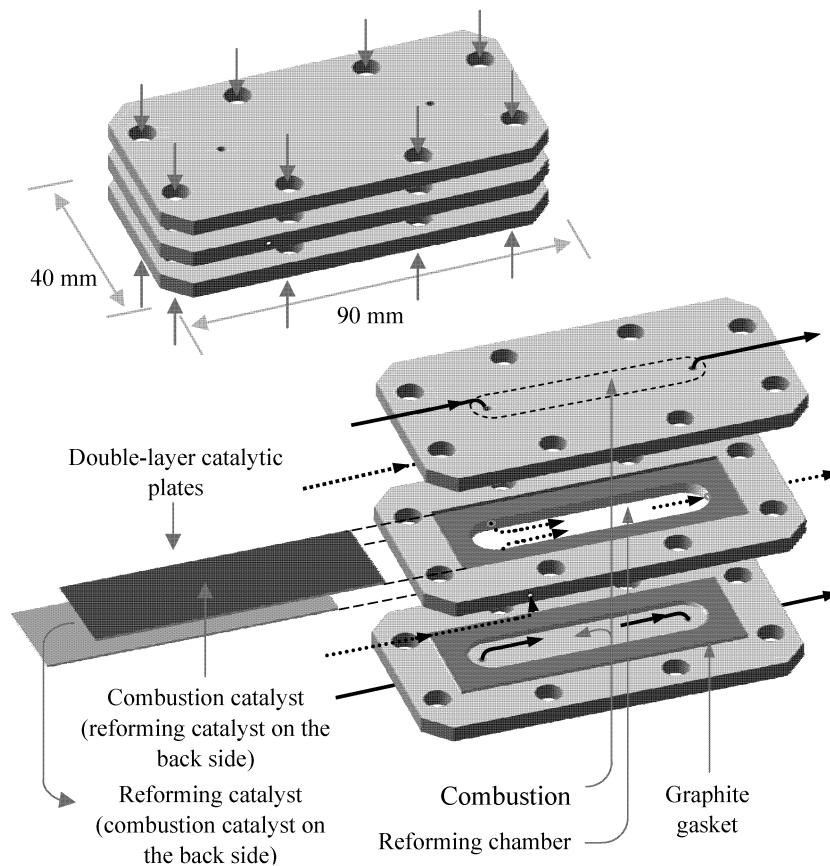


Fig. 1: Exploded and assembled reactor CAD-view. Solid arrow combustion stream – dotted arrow: reforming stream

The reforming channel (50 mm long, 10 mm wide, 3.0 mm thick) is shaped inside the inner plate while the combustion channels (50 mm long, 10 mm wide, 1.5 mm thick each) are located inside the outer plates. The channels have a parallelepiped shape with two protruding rounded edges (which makes the total channel length 60 mm) and are separated by foils (0.5 mm tick) onto which different catalysts were deposited on the opposite faces (Figure 1). The reactants flow pattern is shown in Figure 1 by arrows: solid and dotted lines represent combustion and reforming streams, respectively. Graphite foils were used as gaskets between the catalytic foils and the stainless steel plates.

0.5 mm thick aluchrom slabs (70% Fe, 25%Cr, 5% Al), supplied by ECOCAT, were used as structured metallic supports. They were formed into rectangular shape (70 x 20 mm<sup>2</sup>) to be lodged in the reactor slots and thermally pre-treated before washcoating

procedure. After cleaning with acetone, to remove the superficial impurities, an oxidative pre-treatment, for the segregation of an  $\text{Al}_2\text{O}_3$  layer on the metallic surface, was carried out at  $1200^\circ\text{C}$  for 10 min in 0.5 vol %  $\text{O}_2$  in  $\text{N}_2$  stream (Ugues, 2004).

The structured catalysts were prepared using: commercial catalytic washcoat (aqueous suspension of 38.5 wt%  $\gamma$ -alumina powder) supplied by ECOCAT,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , as active specie precursor promoting the steam reforming reaction, and  $\text{PtCl}_4$ , as active specie precursor promoting the catalytic combustion reaction both supplied by Carlo Erba Reagenti. The right amount of salt containing the noble metal species was carefully dissolved in the washcoat suspension and, then, it was deposited on the pre-treated aluchrom foils by brushing. Drying at  $60^\circ\text{C}$  for 4 hours and calcination at  $950^\circ\text{C}$  for 2.5 hours were, then, performed. The procedure was repeated for the deposition of a second catalyst layer giving a final coating about  $80\ \mu\text{m}$  thick. The complete procedure was also repeated for the deposition of the reforming catalyst on the other side of the slab. A catalytic washcoat containing 5 wt% Ni for the steam reforming reaction and a catalytic washcoat containing 3 wt% Pt for the catalytic combustion reaction were obtained.

Reforming catalyst reduction was accomplished by treatment with 20 l/h at STP of a 5%  $\text{H}_2$  in  $\text{N}_2$  stream. Mean residence times ( $\tau_{\text{co}}$  and  $\tau_{\text{sr}}$ ), in both endothermic and exothermic channels, were calculated as ratios between their volume and the gases flow rate at the average channel temperature. Methane conversions in the reforming and combustion side ( $X_{\text{CH}_4\text{-sr}}$  and  $X_{\text{CH}_4\text{-co}}$ , respectively) were calculated on the basis of the measured  $\text{CH}_4$  inlet and outlet concentrations. The  $\text{H}_2$  yield ( $\phi_{\text{H}_2}$ ) was evaluated as moles of  $\text{H}_2$  produced per mole of  $\text{CH}_4$  converted. Gas temperature were measured in each channel by three 0.25 mm diameter thermocouples, located on the reforming and combustion channels longitudinal axes, at distances from one channel edge of 10, 30 and 50 mm, respectively.

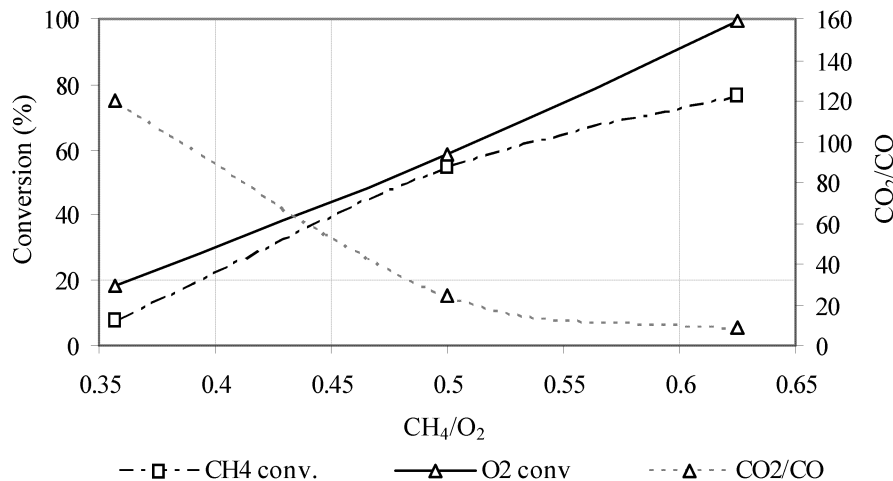


Fig.2. Effect of the  $\text{CH}_4/\text{O}_2$  molar feed ratio on conversion

## 2. Results

### 2.1 Preliminary tests of only combustion

Preliminary tests were carried out to explore the influence of the  $\text{CH}_4/\text{O}_2$  feed ratio and of  $\tau_{\text{co}}$  on the combustion catalyst effectiveness. During these tests 50 l/h of  $\text{N}_2$  at STP were fed to the reforming channel. Figure 2, where the effect of  $\text{CH}_4/\text{O}_2$  feed ratio on  $X_{\text{CH}_4-\text{co}}$  and on  $\text{CO}_2/\text{CO}$  ratio is shown, suggests that there was a sort of inhibition of the methane oxidation reaction when working with stoichiometric or excess air. The mechanistic pathways of oxidation over noble metals consider that oxygen adsorption is faster than that of methane (Frennet, 1974; Engel and Erti, 1979) and, therefore, noble metal surface is first covered with  $\text{O}_2$  and then  $\text{CH}_4$  chemisorption onto the catalyst occurs (Cullis et al 1971; Cullis et Willatt 1983; Yao, 1980). However, while in the cases of Pd and Rh catalysts this pathway allow enough room for methane adsorption (Lee et Trimm, 1995), in the case of Pt catalyst it seems to gives rise to a competitive adsorption of methane and oxygen on the available sites and, therefore, a  $\text{O}_2$ -lean feed may favour a more suitable concentration of both species adsorbed. In addition, the findings above also explains the fact that the methane catalytic oxidation kinetics under some conditions does not depends on gaseous oxygen concentration as suggested by various authors in the literature (Otto, K. 1989; Niwa et al., 1983; Cullis et al.,1983; Kolaczowski et al.,1996; Garetto et al., 2000).

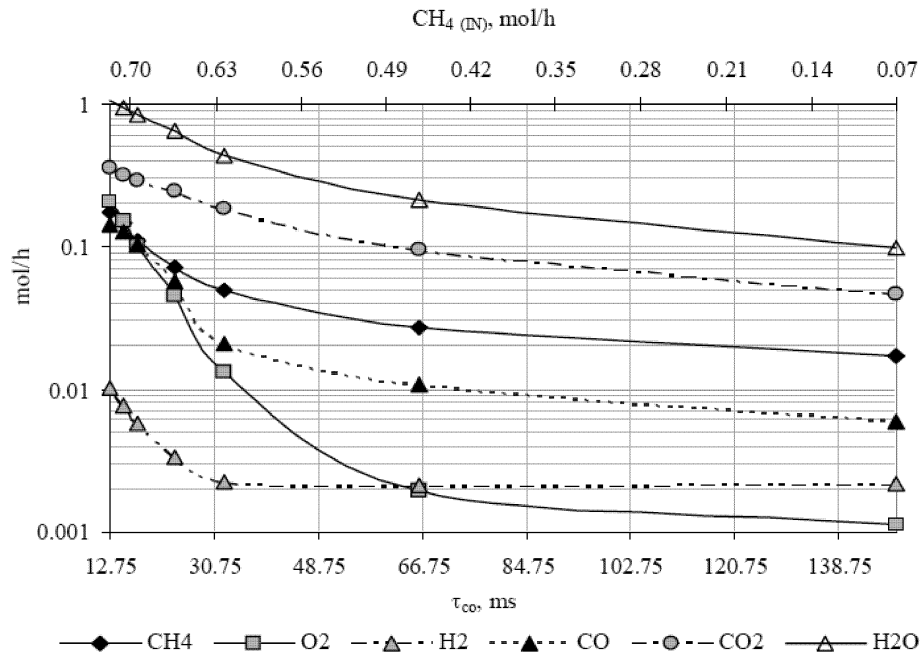


Fig. 3. Outlet stream flow rates during preliminary combustion tests as a function of  $\tau_{\text{co}}$  (ms) and the correspondent inlet methane flow rates (on secondary X-axis).

Figure 3 shows the molar flow rates of the various substances measured at the reactor outlet as a function of  $\tau_{\text{co}}$  and of the correspondent inlet methane flow rates. It is evident the presence, although at low concentrations, of CO and  $\text{H}_2$  as products of methane

partial combustion in spite of the presence of catalyst. Their presence, in agreement with the literature (Lee and Trimm, 1995) may be justified by the sub-stoichiometric inlet oxygen concentration. A mass balance of  $O_2$  on the reactor, proved that the total oxygen molar flow rate (i.e.  $O_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$ ) exiting the reactor was almost the same of the entering  $O_2$  at high flow rates, i.e. when  $36 < \tau_{co} < 13$  ms while it was only 90% of entering  $O_2$  for higher  $\tau_{co}$ 's.

## 2.2 Reforming and combustion coupled reactions

Keeping constant the inlet conditions to the reforming channel (total flow rate equal to 1.43 mol/h;  $CH_4/H_2O=1/3$ ), two different total molar flow rates  $\dot{M}_{co}$  (1.2 and 2.4 mol/h with  $CH_4/O_2=1/1.68$ ) at the inlet of the combustion channel were fed both in CNC and CTC arrangements. Under these conditions,  $\tau_{sr}$  was about 55 ms, while  $\tau_{co}$  were about 66 and 33 ms, respectively. Typical temperature patterns monitored in such tests, reported in Fig. 4, show that the temperatures inside the reforming channel were almost always higher than those detected in the combustion channels. This effect has been related to the thermal dissipation through the external walls of reactor since the heat flux across such walls induced a steep thermal gradient in the combustion channels.

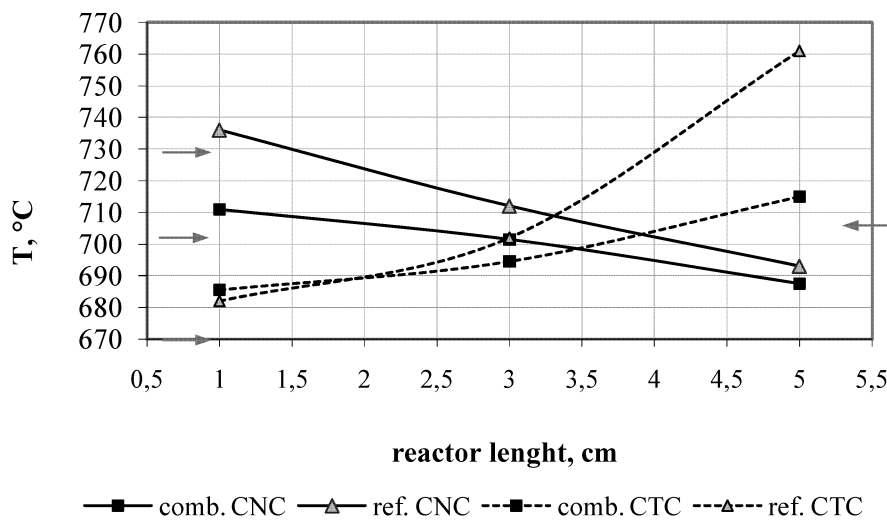


Fig.4: Temperature profiles on the channels axes in CTC and CNC mode (combustion and reforming flow rates were equal to 2.4 and 1.43 mol/h, respectively). Arrows indicate the streams orientation in the system.

In Table 1 the calculated values of  $X_{CH_4-sr}$  and  $X_{CH_4-co}$ , along with  $\phi_{H_2}$  and the  $CO/CO_2$  ratio at the reforming channel outlet, are summarized for both CNC and CTC flow patterns. It appears that in the first two tests (lower rate of combustion gas) the amount of heat generated by the combustion reaction is not enough to sustain the reforming reactions and, therefore,  $X_{CH_4-sr}$  is very low. Instead, in the third and fourth tests, where the heat generated by the combustion reaction is higher, relatively high  $X_{CH_4-sr}$  were achieved. The balance of the methane showed that the ratio between methane reacted in the reforming and the combustion channels varied from 0.33 when  $\tau_{co}$  is 66 ms to 0.94 when  $\tau_{co}$  is 33 ms in CNC mode. Similar values were found under CTC mode. These

values of such a ratio - far lower than the ideal value of 4 (assessable on the basis of the heats of reaction) - was justified considering that in both tests autothermal conditions of the system were gained; therefore, the combustion heat had to sustain not only the reforming reactions, but also the heat loss through the external walls.

The CO/CO<sub>2</sub> ratio clearly showed that the contribution of the water gas-shift reaction to the total conversion was more significant in CNC than in CTC mode. This effect may be referred to a lower average temperature in the reforming channel when operating in CNC mode, although this conclusion is based on a relatively limited number of temperature measurement points (Figure 4).

Table 1 – Test 1: Results

$\dot{M}_{CO_2}$ , mol/h	Flow pattern	X <sub>CH<sub>4</sub>-CO</sub> , %	X <sub>CH<sub>4</sub>-ST</sub> , %	φ <sub>H<sub>2</sub></sub>	CO/CO <sub>2</sub>
1.2	CNC	83.3	9.4	3.25	0.52
1.2	CTC	85.4	11.1	3.15	1.12
2.4	CNC	83.4	59.6	3.33	1.57
2.4	CTC	85.4	57.0	3.26	2.55

### Acknowledgments

The authors gratefully acknowledge the financial support of MIUR under grant PRIN n°2006094333004

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