

KINETICS OF HIGH PRESSURE CATALYTIC COMBUSTION OF CH₄, H₂ AND CO

P.S. Barbato*, G. Landi**, G. Russo*

landi@irc.cnr.it

* Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II, P.le Tecchio 80, Napoli

** Istituto di Ricerche sulla Combustione-CNR, P.le Tecchio 80, Napoli

Abstract

Up to date, catalytic combustion has been predominantly studied at atmospheric pressure, even if the extension of these results at higher pressure is not trivial, due to the several phenomena simultaneously occurring during catalytic combustion. Moreover, catalytic combustion appears very appealing if the new trends of producing energy from coal and/or biomass derived syngas, eventually added with methane, are considered. In this work we report an isothermal (kinetic) study on the catalytic combustion of CH₄, H₂ and CO on a perovskite catalyst in the range of pressures 1-12 atm. Experiments have been carried out at different temperatures, fuel concentrations and oxygen/fuel ratios for each fuel. Several reaction rate have been tested in order to identify the models best reproducing the experimental data. Fractional models, generally derived from Mars-van Krevelen or Langmuir-Hinshelwood mechanisms, are suitable for kinetic description of catalytic combustion of H₂, CO and CH₄ over a perovskite catalyst in a wide range of operating conditions. The kinetic parameters derived from this study are fundamental for the development of more complex models, representing reactors under self-sustained operation.

Introduction

Catalytic combustion has been extensively studied as an alternative route to produce power with low environmental impact. As a matter of fact, catalytic combustion should allow to convert light hydrocarbons at relatively low temperatures, thus eliminating or at least reducing NO_x formation, and with very high combustion efficiency, thus avoiding CO and HC emissions. As a consequence, catalytic combustion for power generation has been generally related to the development of burners for gas turbines (GT). Three main classes of active phases have been studied: i) noble metals, ii) metal oxides, iii) hexaaluminates. Amongst different types of metal oxides, perovskites (general formula ABO₃) have been extensively considered as total oxidation catalysts. Moreover the robustness of the structure permits the partial substitution of A and B cations with metals with a different oxidation state (A_xA'_{1-x}B_yB'_{1-y}O_{3-δ}). The partial substitution results into the profound modification of the activity since it leads to the formation of structural defects promoting catalytic activity of the material [1]. To date, formulations in which A sites are occupied by La or La-Sr and B sites are occupied

by Co, Fe, o Mn are the most active phases for methane combustion, Mn-based perovskite showing the best performance [2]. Notwithstanding several efforts, up to date a single catalytic system is unable to fulfil all process requirements in the case of NG-fuelled GT. Actually a suitable active phase should combine high reactivity at low temperature (close to those of compressor outlet 290-450°C depending on load), and stable operation at relatively high temperature (at least 900°C-1000°C, or even higher). Due to the above mentioned materials limitations, complex process designs including additional homogeneous or catalytic stages have been proposed and, in turn, a wide diffusion of catalytic combustion in power and heat production was limited [3]. On the other hand, in the last decades a huge interest towards Integrated Gasification Combined Cycle (IGCC) plants, in which several liquid (such as residual oils) or solid (biomass or coal) fuels are converted into “synthesis gas”, has increased the attention towards the study of the combustion of fuel mixtures containing hydrogen and/or carbon monoxide at gas turbine conditions relevant for power generation [4]. It should be noted that the partial or total replacement of methane, representative of natural gas, with low calorific fuels, such as H₂ and CO, is usually accompanied by a reduction of fuel mixture dilution thus resulting in adiabatic temperature and NO_x production increase even for established technologies such as gas turbines. In this context, catalytic combustion has been proposed as an alternative route to the homogeneous combustion of low BTU mixtures. As previously reported, a huge number of papers has been devoted to catalytic combustion at atmospheric pressure and under very diluted (i.e. isothermal) conditions. Notwithstanding, “it is not unusual to hear of catalysts that appear to have worked well in a laboratory environment but do not so when installed in a High Pressure pilot-scale rig” [5], suggesting that the relative ratio amongst the several phenomena simultaneously occurring during catalytic combustion (external and internal mass transfer of both reactants and products, heat transfer from and to the surface and along the catalyst, surface and homogeneous kinetics) could be altered by changing the working pressure, as reported by Carroni et al. [6]. Nevertheless, in the last 15 years very few studies have been devoted to high pressure with respect to atmospheric combustion and generally concern noble metal catalysts [7].

The aim of the work is to obtain relatively simple rate equations valid in a wide range of operating conditions and including the effects of pressure, temperature, fuel concentration and equivalence ratio for the catalytic combustion of methane, hydrogen and carbon monoxide on a perovskite-based catalyst.

Experimental

Structured catalysts in form of platelets have been prepared according to the procedure reported in [8]. The final active layer loading corresponds to about 0.026 g of a 20wt% LaMnO₃ supported onto La-stabilized γ -Al₂O₃. Chemical composition of the active layer has been measured by means of inductively coupled plasma (ICP) analysis, performed on an Agilent 7500 ICP-MS instrument, while

the adhesion of the active layer has been tested by ultrasound treatment (30 min) in a ultrasonic bath (Quantex 90H, L&R Manufacturing) in order to evaluate the resistance to mechanical stresses. ICP analysis revealed that catalyst composition is very close to the theoretical one. No significant weight difference between so prepared and ultrasound-treated sample has been measured, suggesting that high mechanically resistant structured catalyst can be prepared by the preparation method described above.

A stainless steel reactor has been used to house the catalytic platelet and to obtain a 1 mm gap above the platelet thus creating the combustion chamber. At the two edges of the rectangular chamber, two circular housing have been obtained and used for the allocation of SiC foams in order to well distribute the mass flow of the gas in correspondence to the inlet and the outlet of the catalyst and, at the same time, to block the platelet in the appropriate position. The thermal profile along the axial direction and the temperature difference between upside and downside (i.e. below the platelet) wall of the chamber have been measured.

Diluted CH₄, H₂ and CO mixtures were used for the assessment of the more appropriate kinetic law and the temperature dependence of the kinetic parameters. The catalyst was previously aged in air at 800°C for at least 12 hr, thus providing stable performance [8]. Some tests repeated at selected reaction conditions revealed the repeatability of experiments.

In table 1, the operative conditions adopted for the combustion tests under pressure are summarized.

Table 1. Operative conditions adopted for the tests under isothermal condition.

	CH ₄	H ₂	CO
Fuel, %	0.15-1	0.25-1	0.25-1
O ₂ , %	8.5	2-8.5	2-8.5
Q _{TOT} , slph	55-80	75	75
τ, g·l(STP)·s ⁻¹	1.7-1.2	1.25	1.25
Temperature range, °C	555-620	470-530	470-530

Different reaction rates, both power laws and equations derived from kinetic models, have been tested in order to find the best model representing the combustion rates of CH₄, H₂ and CO over LaMnO₃ perovskite catalyst.

Results and discussion

Fig.1 shows methane conversion as a function of the pressure parametric in the inlet methane concentration $y^{\circ}_{\text{CH}_4}$ at a fixed O₂ content (8.5 vol%) for some selected tests carried out at 555°C.

It clearly appears that the conversion increases by increasing the pressure but decreases by increasing methane concentration. This effect is more pronounced at

higher pressures. The estimated reaction orders with respect to pressure are all lower than unity and higher in the case of the lower methane content. For example at 620°C are equal to 0.63, 0.57 and 0.55 respectively for 0.2 %, 0.5% and 1% $y^{\circ}_{CH_4}$.

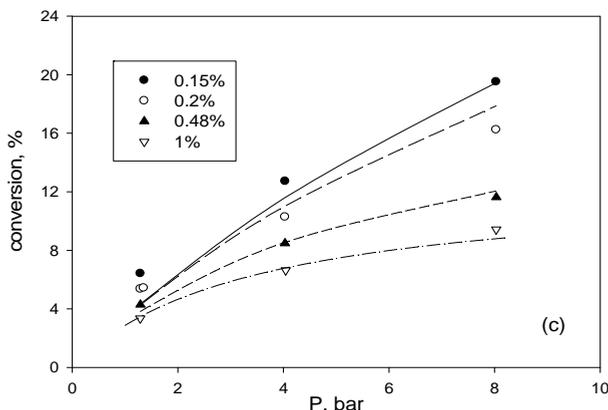


Figure 1. CH_4 conversion as a function of total pressure. $T=620^{\circ}C$, total flow rate= $80 \text{ dm}^3/\text{h}$ (STP). Symbols: experimental data; lines: predicted conversion according to reaction rate reported as equation 2.

Several reaction rate expressions have been tested in order to identify the model best reproducing experimental data. Two models showed best results and the corresponding rate expressions are reported in equations 1 and 2. Equation 1 corresponds to a reaction rate based on a Mars-van Krevelen mechanism and it has been also proposed by Auer et al. [9] for a La-Ce-Co perovskite catalyst, gives a fairly good data fitting. Kinetic constants (not reported) showed a value of k_1^* at least two orders of magnitude higher than the other constants, thus suggesting a very fast oxygen dissociation.

$$r = \frac{k_1 k_2 P_{CH_4} P_{O_2}}{(k_2 P_{O_2} + 2k_1 P_{CH_4}) \left(1 - \frac{k_1}{k_1^*} P_{O_2} \right)} \quad (1)$$

$$r = \frac{k P_{CH_4}}{1 + K P_{CH_4}} \quad (2)$$

Also the second model shows a very good fitting of the experimental data, even if it is based on a simple reaction rate showing only two parameters, as it is visible in figure 2, where fittings of models based on equations 1 and 2 are compared. Actually, the model 2 could be derive from a Langmuir-Hinshelwood model by assuming that the number of oxidized sites is fairly constant, thus implying that the re-oxidation rate is very fast. This assumption is consistent with the estimated reaction constant of model 1 as previously explained.

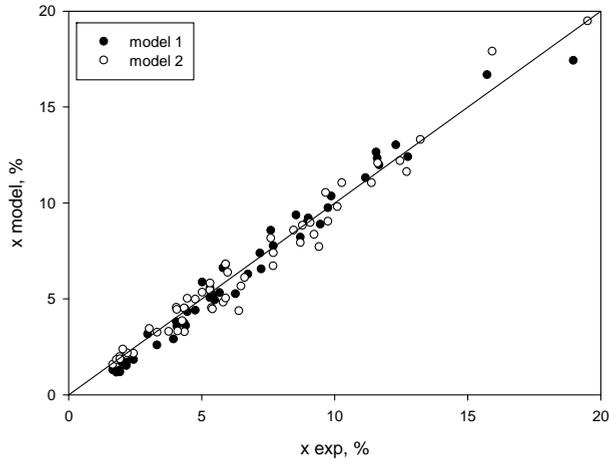


Figure 2. Predicted versus experimental conversion values for CH₄ combustion.

About CO combustion, in line with the results of methane, the pressure effect on the fuel conversion is positive and less than linear (not reported). Moreover the conversion decreases by increasing fuel concentration at fixed pressure and $y_{O_2}^0$. Changing oxygen concentration in the gas feed results in a slight but not negligible modifications of CO conversion, suggesting that variation of oxygen coverage due to steps including oxygen adsorption and surface transfer cannot be neglected.

The results of the mechanistic models tested for the carbon monoxide combustion showed that the following reaction rate expressions allows to well reproduce experimental data.

$$r = \frac{k_1 k_2 P_{CO} P_{O_2}}{(k_2 P_{O_2} + 2k_1 P_{CO})} \left(1 - \frac{k_1}{k_1^*} P_{O_2} \right) \quad (3)$$

$$r = \frac{k_1 k_2 P_{CO} P_{O_2}}{(k_2 P_{O_2} + 2k_1 P_{CO} + (k_1 k_2 / k_3) P_{CO} P_{O_2})} \quad (4)$$

Differently from CO and CH₄ combustions, H₂ combustion resulted linear with respect to fuel concentration in the whole range of the investigated experimental conditions, thus suggesting that this reaction is based on a different mechanism. On the other hand, the effect of oxygen partial pressure is similar to that observed during CO combustion. This difference with respect to CH₄ combustion is due to the different temperature range investigated. As a matter of fact, at temperatures lower than 550°C oxygen mobility over perovskite catalysts is reduced and, as a consequence, O₂ adsorption, dissociation and transfer cannot be neglected.

According to the above considerations, the reaction rate best reproducing the experimental data corresponded to a modified Langmuir-Hinshelwood model, reported in the equation 5. In this case, the rate limiting step is the surface reaction occurring between adsorbed O-atom and a weakly adsorbed hydrogen molecule.

$$r = \frac{kP_{H_2}K_{O_2}P_{O_2}}{(1 + K_{O_2}P_{O_2})^2} \quad (5)$$

Conclusions

Catalytic combustion of methane, hydrogen and carbon monoxide have been studied over a perovskite catalyst at variable pressure. CH₄ and CO adsorptions result limiting at increased fuel partial pressure, resulting into less than linear kinetics with respect to the fuel. On the contrary, hydrogen reaction rate is linear with respect to the fuel. Reaction rates depend on oxygen partial pressure only at relatively low temperature, i.e. if lattice oxygen mobility is limited. The kinetic parameters derived from this study are fundamental for the development of more complex models, representing reactors under self-sustained operation.

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