

Research on catalytic combustion burners and products selectivity of the heterogeneous oxidation of methane*

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Abstract: The pollutant emissions characteristics of the combustion of ultra-lean methane-air mixtures in some precious metals (Pt and Pd) based honeycomb monoliths were investigated in Catalytic Combustion Burners. Especially, temperature profiles inside the monoliths channels were measured and the best location of the precious metal in monolith was found. The operating conditions verified 'near zero' pollutant emissions that only a catalytic combustion process can achieve at present. The chemistry at this process was then investigated using fundamental experimental reactor, namely the stagnation point flow reactor or SPFR. These showed the extent of the phenomenon of inhibition of gas phase ignition and how catalytic combustion is a clean process.

Keywords: catalytic combustion, CH₄ conversion efficiency, products selectivity

1. Introduction

The main characteristics of catalytic combustion are that by burning fuel lean mixtures, the combustion temperatures and NO_x emissions are low compared to those of a conventional flame, and that a portion of the incoming energy from the fuel is emitted as thermal radiation. Conventional combustion can only exist within well-defined fuel to air ratios, known as the flammability limits. Catalytic combustion is not so constrained and can offer fewer limitations on reactor design.

There are large world reserves of methane in the form of natural gas. Catalytic combustion is the most attractive choice to oxidize methane completely without the concurrent formation of pollutants such as NO_x, CO, and UHC (unburnt hydrocarbons). Whereas conventional homogeneous combustion processes always generate variable amounts of nitrogen oxides (NO and NO₂), carbon monoxide, and unburnt fuel, heterogeneous catalytic combustion allows the combustion of ultra-lean hydrocarbon-air mixtures below the lean flammability limit and in conditions of near zero pollutant emissions.

In the types of combustion processes that incorporate a solid catalyst, one can distinguish three. These are catalytic combustion, catalytically stabilised thermal (CST) combustion, and coupled heterogeneous-homogeneous combustion. In the first, the complete conversion of the fuel to CO₂ occurs via (solid-gas)

heterogeneous reactions, this can only happen at low temperatures. In the second, the heat released by heterogeneous reactions is used to stabilise homogeneous combustion reactions [1]. In the third, simultaneous heterogeneous and homogeneous oxidation reactions occur at intermediate temperatures [2].

About the previous work, the temperature profiles inside the monoliths channels were measured and investigation of the best location of the precious metal (Pd) in monolith was carried out. The maximum temperature were reached within the first 15mm of the monolith. On the strength of the results from the 15 mm long monolith, it was clear that the catalyst was essential not only at ignition, but also during steady-state conditions, where its role was to ensure the complete heterogeneous

conversion of the CH₄ to CO₂ and simultaneously inhibit gas phase ignition [3].

The combustion of ultra-lean methane/air mixtures in precious metal based catalytic honeycomb monolith burners remained heterogeneous at temperatures high enough to have supported homogeneous combustion. This was concurrent with near zero pollutants emission and high stability. This phenomenon was examined in more controlled conditions in a stagnation point flow reactor (SPFR), paired with its theoretical model making use of global and detailed coupled heterogeneous-homogeneous chemistry[4,5].

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For the present work, the combustion of ultra-lean methane-air mixtures in some precious metals (Pt and Pd) based honeycomb monoliths were investigated as well as the CH_4 conversions inhibition of gas phase ignition phenomenon, as will be seen later, and CO selectivities for the fuel-lean and rich concentrations in the SPFR.

2. Experimental set-up

A schematic diagram of the experimental set-up is shown in Fig. 1.

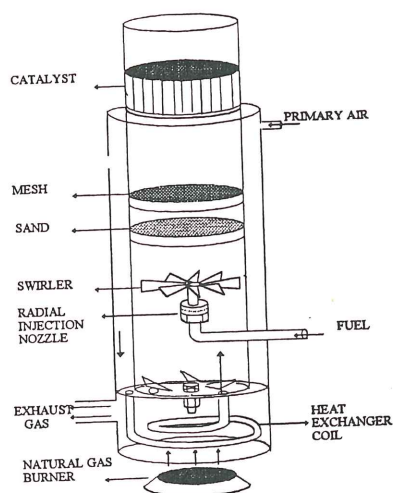


Fig. 1 Catalytic burner

The monoliths studied were 101.6 mm (4 in) in diameter and 50.8 mm (2 in) in length, with square shaped cells at 400 cpi² (cell per inch square) corresponding to cells of 1.27 mm side length. The monoliths contained various loadings of precious metals (Pt and Pd), deposited on approximately 6250 m² of washcoat supported on a cordierite honeycomb structure. No reduction or oxidation treatment was imposed on the monolith prior to the experiments.

To activate the catalyst prior to the combustion, the air was preheated in a heat exchanger.

After That, a mixture of methane and air, rich enough to achieve a blue flame above the monolith was then injected radially below the swirler. The blue flame gradually disappeared, while the catalyst started glowing red internally as the temperatures inside the monolith increased. The flow of methane was then adjusted to the desired ultra-lean mixture composition while the catalyst reached steady-state.

O_2 and CO/CO_2 were measured with a paramagnetic and an infra-red absorption on-line

analyzers respectively.

Thermocouple temperatures were also measured. For temperatures inside the monolith, two type K thermocouples of diameters 0.5 mm and 1 mm were inserted in central channels separated by 3 clear channels.

For the SPFR, Fig. 2, showed the diagram of the reactor.

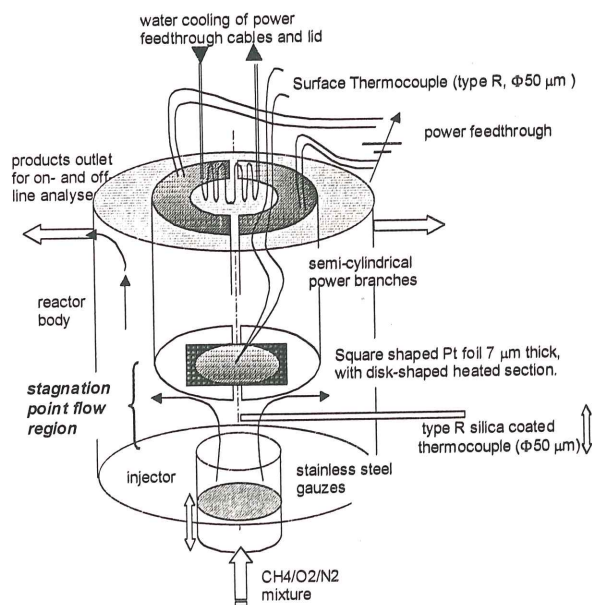


Fig. 2 Stagnation point flow reactor

In it, the geometry was now almost entirely axisymmetric as required. The foil of Pt catalyst was square shaped, but as it came into contact with the semi-cylindrical aluminium electrical power connectors via a thin insulating sheet of mica, to which it lost heat, the high temperature region of the foil was effectively round-shape, matching the injector's cross section.

The thick Pt polycrystalline foil of 99.95 % purity was heated between 300 K and 1800 K. The respective flows of CH_4 , O_2 and N_2 reactants were ensured by mass flow controllers. The readings were then corrected for water vapour content during the processing of the results, yielding the fuel conversion and CO selectivity.

The fuel mixture strength by varying the parameter α given by

$$\alpha = \frac{\dot{V}_{\text{CH}_4}}{(\dot{V}_{\text{CH}_4} + \dot{V}_{\text{O}_2})}$$

where $\dot{V}_k$ is the input volume flow rate of the relevant species k, α was varied from 0.1 to 0.2, the N_2 mole fraction for the SPFR in the reactant mixture, X_{N_2} (0.87).

2. Results and discussion

Fig. 3. shows the profiles of the bulk gas and catalyst wall temperatures inside centrally located channels of 50 mm long Pd and Pt monoliths.

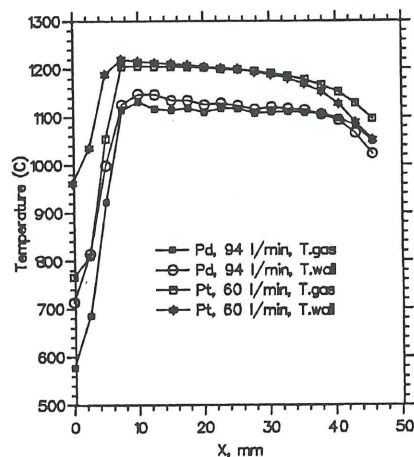


Fig.3 Gas and wall temperature profiles inside 50 mm long monoliths (Pt catalyst with 5.5% CH₄ in air, total flow rate 60 l/min STP, and Pd catalyst with 5% CH₄ in air, total flow rate 94 l/min STP)

The total flow rates used were 94 L/min (STP) with 5 % CH₄ for the Pd monolith, and 60 L/min with 5.5 % CH₄ for the Pt monolith. Higher temperatures were observed in the more fuel-rich concentration used with the Pt catalyst than with the Pd catalyst, as the adiabatic temperature was increased. However, the reaction zones (evidenced by the sharp temperature increase reaching a peak, with higher wall temperatures than for the bulk gas) indicated that the reaction took place at the bottom of the catalyst and must have occurred at the walls. The final dip in the temperature was due to the heat losses by radiation from the downstream surface of the catalyst to its laboratory surroundings. In all the runs, complete conversion of the methane to CO₂ and H₂O was observed, with no detection of CO nor NO_x.

Fig. 4. shows the profiles of the bulk gas and catalyst wall temperatures inside centrally located channels of 50 mm long Pd and Pt monoliths.

The total flow rates used were 60 L/min (STP) with 5 % CH₄ for the Pd monolith, and with 5 % and 5.5 % CH₄ for the Pt monolith. Higher temperatures were observed with the Pt catalyst than with the Pd catalyst, as the adiabatic temperature was increased due to the higher fuel concentration used.

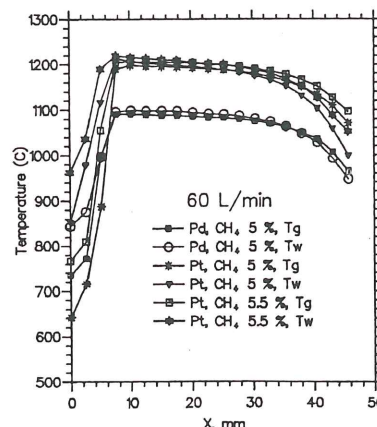


Fig. 4 Gas and wall temperature profiles inside 50 mm long monoliths (Pt catalyst with 5 and 5.5% CH₄ in air, total flow rate 60 l/min STP, and Pd catalyst with 5% CH₄ in air, total flow rate 60 l/min STP)

Fig. 5a,b show the CH₄ conversions and CO selectivities for the three ultra-lean values of α (0.1, 0.15, and 0.2) and XN₂ (0.87,) obtained with the reactor. The temperature for the formation of CO was higher than 1350K.

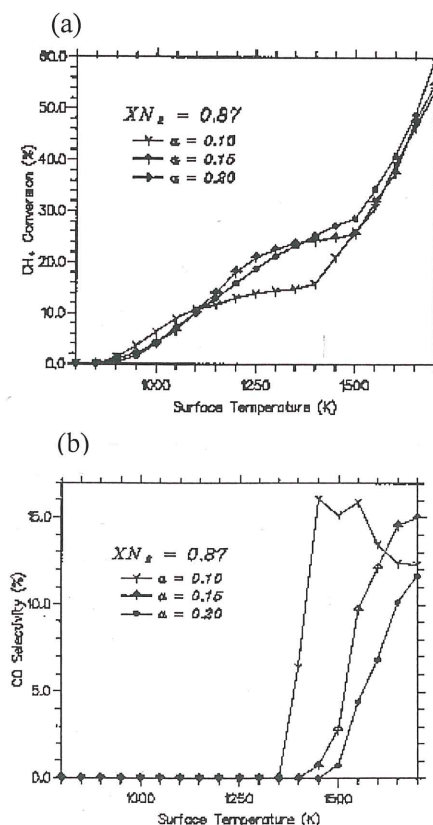


Fig. 5a,b CH₄ conversions and CO selectivities for the three ultra-lean values of α (0.1, 0.15, and 0.2) and XN₂ (0.87,)

The intermediate species C₂H₄, C₂H₆ and C₃H₈ measured by off-line Gas Chromatography-TCD analysis of samples were collected in 5 L Tedlar bags(not shown here). In particular the formation of

C_2H_6 with the CO selectivity supports the theory of its involvement in the mechanism of inhibition of homogeneous ignition.

For the previous work, the result also showed the optimised mechanisms predictions with their experimental counterparts beyond homogeneous ignition [6].

Figures 6a,b show the CH_4 conversions inhibition of gas phase ignition phenomenon, as will be seen later, and CO selectivities for the fuel-rich concentrations of α (0.35, 0.4, 0.45, 0.5 and 0.58) and X_{N_2} (0.91), i.e. conditions of partial oxidation on Pt foil for the SPFR.

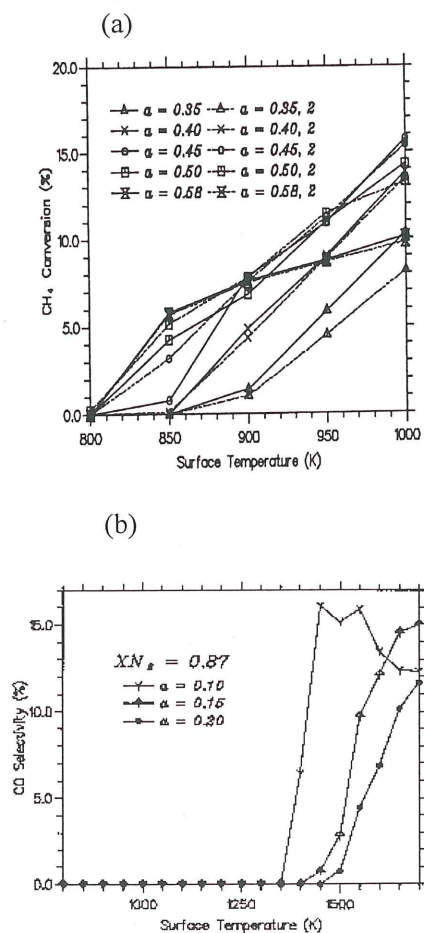


Fig. 6a,b CH_4 conversions inhibition of gas phase ignition phenomenon, and CO selectivities for the fuel-rich concentrations of α (0.35, 0.4, 0.45, 0.5 and 0.58) and X_{N_2} (0.91), i.e. conditions of partial oxidation.

The main results from these runs are the large CO selectivities (more than 10 %) obtained at low catalyst temperatures (800-1000 K). No amounts of C_2H_4 and C_3H_8 were detected and negligible concentrations of C_2H_6 were detected (lower than 8 ppm).

4. Conclusions

In most conditions studied here, a greater proportion of the CH_4 feed must have completely oxidised on the catalyst at the very entrance of the monolith. The results showed that Complete conversion of the lean methane to CO_2 and H_2O was observed, with no detection of CO nor NO_x .

Studies with other gas fuels such as natural gas will follow and the fuel-rich experiments on Pt foil with appearance of CO in the exhausts at low temperatures will provide valuable data for the more fuel-rich concentration in the monolith.

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