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Catalytic combustion of CO–H_2 on Manganese-substituted hexaaluminates

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Abstract

This work is devoted to a preliminary study on the feasibility of catalytic combustion for syngas fuelled gas turbines equipped with Mn-substituted hexaaluminate catalysts. Results of catalytic activity tests on combustion of CO–H_2 over $BaMn_1Al_{11}O_{19}$ and $La_{0.8}Sr_{0.2}Mn_1Al_{11}O_{19}$ are reported and analyzed by means of a mathematical model of the catalyst section of a hybrid combustor. Experimental activity levels are shown to be close to the operating requirements of the combustor.

Keywords: CO–H_2 combustion; Mn-substituted hexaaluminate catalysts

1. Introduction

Catalytic combustion for gas turbine (GT) applications has received much attention in recent years due to its potential to achieve ultra low emissions of NO_x and very high combustion efficiencies [1,2]. The severe operating conditions of GT combustors poses demanding requirements on catalytic materials [2] that have to be extremely heat resistant and very active towards complete fuel oxidation. Accordingly, many efforts have been placed on the design of new combustor configurations aimed at the reduction of the catalyst thermal stresses and at the development of new catalytic materials. The hybrid combustor [3] appears as a valuable compromise between combustor reliability and emission abatement efficiency. It is based on the coupling of a catalytic and a homogeneous section. Only a fraction of the fuel is fed to the catalyst, controlling its concentration to limit the adiabatic reaction temperature at 1000°C. The remaining fraction is fed downstream to a premixed homogeneous combustor where gas phase reaction is stabilized at low temperature by the hot gas stream exiting the catalyst.

Among the proposed catalysts, Mn-substituted hexaaluminates seem to be particularly promising in view of their excellent thermal stability [4]. A major drawback for the practical use of these materials in catalytic combustors is their limited catalytic activity. Extrapolation by mathematical model has shown that the experimentally observed activity level in CH_4 combustion are 1–2 orders of magnitude lower than those necessary to meet the operating requirements of natural gas fuelled gas turbines.

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Most of the studies described in the literature are concerned with the use of natural gas, i.e., the most common fuel in current GT. Fuels from gasification of coal or biomass are a perspective alternative to NG for GT in the next years. These fuels mainly consist of CO–H_2 mixtures that typically possess a reactivity towards oxidation higher than methane, thus potentially overcoming the limits on catalytic activity mentioned above. This work is devoted to a preliminary investigation on the feasibility of catalytic combustion of CO–H_2 mixtures over Mn-substituted hexaaluminates. Catalytic activity tests have been performed on powder materials and the experimental results have been analyzed by means of a mathematical model of the catalyst section of the hybrid combustor.

2. Experimental

Catalytic activity tests have been performed on $BaMn_1Al_{11}O_{19}$ (BMA) and $Sr_{0.8}La_{0.2}Mn_1Al_{11}O_{19}$ (SLMA). The catalyst samples have been prepared via coprecipitation in aqueous medium of carbonates, hydroxides and hydroxicarbonates of the constituents [5] and calcined at 1300°C for 10 h. The results of XRD analyses, N_2 BET adsorption and Hg-porosimetry show that both the catalysts are monophasic with a layered alumina structure showing a high sintering resistance. A Ba–β-Al_2O_3 with 17 m^2/g of surface area, an average pore radius of 700 Å and a magnetoplumbite with 10 m^2/g of surface area and an average pore radius of 700 Å have been observed for BMA and SMLA, respectively.

Catalytic activity tests have been performed on powder catalysts (d_p = ca. 0.1 mm). Test conditions were as follows: 1.35% of fuel in air (fuel: CO, H_2, CO/H_2 = 1/1) was fed to the reactor (GHSV = 54000 Nml/g_{cat} h) at ambient pressure. The analyses of reactants and products have been performed by means of GC chromatography.

3. Results and discussion

3.1. Catalytic activity tests

In Fig. 1, the experimental conversion curves of CO, H_2 and CH_4 on BMA and SLMA are reported. CO and H_2 conversion data refer to CO–H_2 fuel mixtures, however experiments with pure H_2 and CO on BMA have not shown any significant variation associated with mixture effects. Both catalysts show the following order of oxidation reactivity: CO > H_2 > CH_4. In line with literature indications, CH_4 requires much higher temperatures than CO and H_2 to be oxidized to a significant extent. A 10% conversion of CH_4 is obtained at about 200 and 300°C above the temperature required to achieve the same conversion level of H_2 and CO, respectively. According to this strong difference of reactivity, calculated activation energies for CO and H_2 oxidation, 13000 and 15500 cal/mol, respectively, are markedly lower than the value of 21000 cal/mol calculated for CH_4. The comparison between BMA and SLMA results shows that the latter is more active in the oxidation of all the investigated fuels. The activity enhancement of SLMA is more marked for CH_4 and CO but these differences are far less strong than those observed between the reactivity of the different species over the same catalysts.

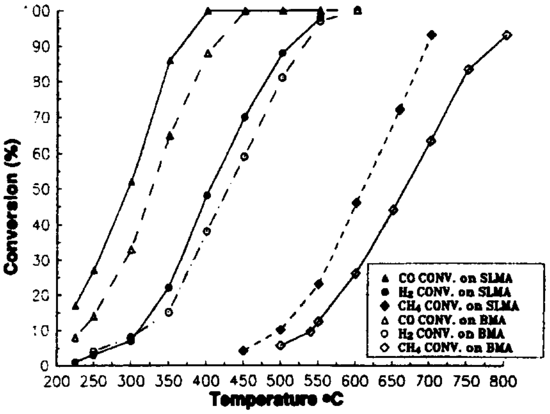

Fig. 1. Catalytic activity in CO, H_2 and CH_4 combustion of Mn-substituted hexaaluminates. 1% CH_4 in air, GHSV = 48000 h^{-1}.

3.2. Mathematical model analysis

The experimental results described above refer to a pure chemical regime, while the combustor performances are determined by both physical and chemical phenomena occurring in the monolith catalysts that are actually used to achieve GT constraints on pressure drops. Mathematical models of the monolith combustor are a tool for preliminary scale-up of the laboratory data. A distributed parameter model has been used for this purpose. The model, whose detailed description is reported elsewhere [6], refers to steady state conditions and laminar flow in circular channels and accounts for homogeneous and heterogeneous oxidation reactions, diffusion and convection of heat and mass in the gas phase, diffusion in the catalyst pores and gas property variation with temperature. The effects of solid conduction, radiation and hydrodynamical development have been neglected according to the results of a previous work devoted to CH_4 combustion [6]. Kinetic expressions for the heterogeneous reactions have been derived from experimental data on Mn-substituted hexaaluminates (BMA) assuming a first order dependence on CO and H_2 concentration. For the homogeneous reactions, simple molecular kinetic expressions have been derived from the literature [7,8].

With reference to the hybrid combustor configuration relevant design parameters, i.e., the temperature of the gas exiting the catalyst (T_{out}) and the maximum temperature of the catalyst ($T_{W\ max}$) have been calculated as a function of operating parameters such as the CO/H_2 feed ratio, inlet gas temperature and fuel concentration. Due to laminar flow assumption, a linear gas velocity corresponding to the lowest values of the operating range of the hybrid combustor has been considered within the preliminary scope of our analysis. A reactor configuration consisting of four ceramic monolith segments of 2.5 cm length each with circular channels of 1.2 mm diameter and an open frontal area of 0.68 has been assumed.

Fig. 2a shows the calculated T_{out} as a function of the $H_2/(H_2 + CO)$ feed ratio for different values of gas inlet temperature (T_{in}). A design target of 1073 K has been assumed in line with the literature indications for NG fuelled hybrid combustors. At $T_{in} = 723$ K, the activity of BMA is high enough to ignite the fuel-air mixture near the monolith inlet thus achieving the target level on T_{out}. For the low gas velocity assumed in the simulations, this value is largely exceeded for a wide range of feed compositions also due to the important contribution of the homogeneous reaction that, except for pure CO, is responsible for about 50% of the total fuel conversion. It has to be remarked that the high homogeneous reactivity of CO and H_2 may also affect the design target on T_{out} that was chosen on the basis of the experience on hard oxidizing NG. T_{out} diminishes on decreasing T_{in}. For pure H_2, it markedly

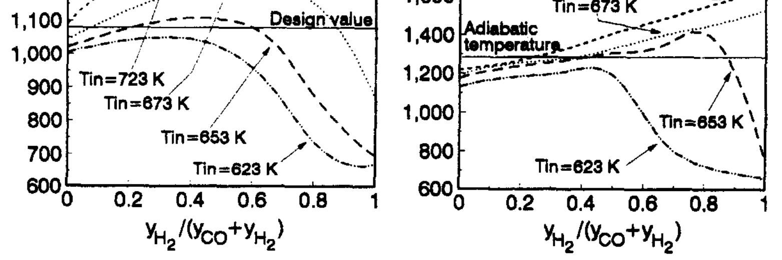

Fig. 2. Calculated T_{out} and $T_{W\ max}$. Conditions: $\upsilon^0 = 7.75$ m/s and $P = 10$ atm.

drops well below the target value already at $T_{in} = 673$ K, due to the lower heterogeneous reactivity of H_2 oxidation on BMA. However, at this temperature also small fractions of CO in the fuel can secure a fast ignition of the combustion mixtures. Notably, T_{out} does not monotonously grow with CO content in the fuel but shows a smooth maximum for intermediate fuel compositions. The presence of a maximum in T_{out} is related to the following opposing factors: (i) the lower heterogeneous reactivity of H_2 that limits the ignition of the rich fuels; (ii) the higher homogeneous reactivity of H_2, at least in water free environment; and (iii) the high diffusion rate of H_2, that enhances the heterogeneous reaction rate of H_2 oxidation in the diffusion controlled region downstream the catalytic light-off. A further decrement of the inlet temperature progressively blows out the ignition front, starting from H_2-rich fuel. At $T_{in} = 623$ K (i.e, a typical value of the outlet temperature from air compressors), the design target is not achieved for any fuel composition.

The peculiar diffusion rate of H_2 may cause severe problems to the combustor. Hegedus [9], studying overtemperature phenomena in catalytic mufflers, experimentally verified that the solid temperature can exceed the adiabatic reaction temperature at steady state in monolith catalysts during H_2 oxidation. This phenomenon arises from the steady state balance of heat production by reaction, controlled by the extremely fast H_2 diffusion rate and heat release from solid to gas phase that is determined by the intrinsically slower heat diffusion.

Model predictions confirm the possibility of solid temperatures exceeding the adiabatic reaction temperature. In Fig. 2b the predicted maximum temperature of the wall ($T_{W\ max}$) is plotted as a function of $H_2/(H_2 + CO)$ feed ratio. For high enough T_{in} to completely ignite the combustion mixture, $T_{W\ max}$ increases with the H_2 content in the fuel. Noteworthy for some conditions the predicted values exceed the adiabatic reaction temperature (1273 K has been chosen as the limit temperature for stable long term operation of the catalyst) by several hundred degrees. It has to be remarked that these predictions are very sensitive to the model parameters (i.e, kinetic parameters, operating conditions); moreover this phenomenon, being driven by the diffusion behaviour of H_2, may significantly change in transitional and turbulent regimes that are likely to prevail in the channels of the combustor monolith; finally, backward heat transmission by wall conduction, that has herein been neglected, may significantly smooth the overtemperature peak. However, these results definitely indicate that catalyst overtemperature may be a severe problem when dealing with H_2-containing fuels.

A possible solution to achieve acceptable thermal stresses of the catalyst, also when overtemperature occurs, is the reduction of the adiabatic reaction temperature by decreasing the fuel inlet concentration for the catalyst section

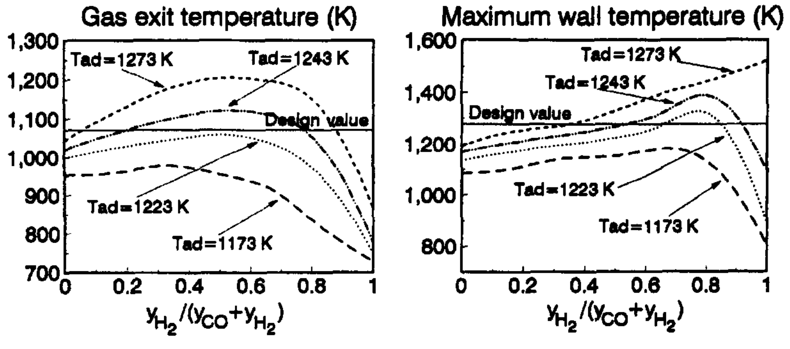

Fig. 3. Calculated T_{out} and $T_{W\ max}$. Conditions: $\upsilon^0 = 7.75$ m/s, $P = 10$ atm and $T_{in} = 673$ K.

of the hybrid combustor. Model simulations have been performed to check the possibility to meet both the design constraints on T_{out} and $T_{W\ max}$. In Fig. 3a and Fig. 3b, respectively, T_{out} and $T_{W\ max}$ are reported as a function of the H_2 content in the fuel for different values of the adiabatic reaction temperature. As expected, both these temperatures decrease on diminishing the adiabatic reaction temperature for any fuel composition. Due to kinetic and thermal effects the decrement of fuel inlet concentration delays and smooths the ignition of the reaction and can finally cause the blow out of the reaction front. Moreover, gas heating is also slowed by reducing the fuel inlet concentration due to the lower solid temperature and to the minor contribution of the gas phase reactions. Eventually, as shown in Fig. 3a and Fig. 3b, appropriate values of the adiabatic reaction temperature can be found to achieve both the design targets, at least for H_2/CO ratios in the range 0.5–1.5, that correspond well to those reported for syngas from coal and biomass gasification.

4. Conclusions

Catalytic activity tests have demonstrated that Mn-substituted hexaaluminates are very active in $CO-H_2$ combustion. By means of mathematical modelling these activity levels have been shown to be comparable to those necessary to meet the operating requirements of syngas fuelled hybrid combustors. Simulation results have evidenced that H_2-containing fuels may also cause severe problems to catalyst stability due to overtemperature phenomena.

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