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Catalytic combustion of gasified biomasses over Mn-substituted hexaaluminates for gas turbine applications

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Abstract

The catalytic combustion of gasified biomasses over Mn-substituted hexaaluminates with high thermal stability is addressed. Combustion activity tests of the main fuel components, i.e. CO, H_2, C_2H_4 and CH_4, have been performed, and the effects of H_2O and CO_2 on the fuel combustion have been investigated. The reactivity of NH_3 in the catalytic combustion has also been studied in view of its potential source of undesired fuel-NO_x. Lab-scale data have been preliminarily scaled up through mathematical modeling. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; Gasified biomasses fuels; $BaMnAl_{11}O_{19}$ catalyst; Ammonia oxidation

1. Introduction

Catalytic combustion for gas turbines (GT) has been vigorously investigated in recent years due to its unique potential to minimize NO_x, unburned hydrocarbons (UHC) and CO emissions [1]. The interest has been focused on natural gas as the most widely used fuel for GT; however other fuels, such as those deriving from gasification of carbon, wastes and biomasses, will be likely used in future years. In particular, the use of renewable gasified biomass would be beneficial for the reduction of CO_2 emissions in the atmosphere. The combustion of such biomass-derived fuels (see typical composition in Table 1) in conventional GT may be difficult in view of their low heating value. Catalysts may secure effective combustion by igniting and stabilizing the reaction [2].

Among the investigated materials Mn-substituted hexaaluminates with layered alumina structure [3] are considered promising catalysts. The use of such materials in natural gas fueled catalytic combustor was experienced by Osaka Gas [4]. Pilot scale tests proved:

1. the possibility to produce monoliths with the required geometrical and mechanical properties by direct extrusion of hexaaluminate powders;
2. the stability of catalytic performances for hundreds of hours under actual operating conditions;
3. the resistance to thermal shocks during transients secured by proper sizing and arrangement of the catalyst.

However, due to their poor activity in CH_4 combustion, Mn-substituted hexaaluminates were only used as finishing segments in the final hot part of the catalyst bed, whereas to ignite the fuel mixture at relatively low gas inlet temperature (450°C) very active Pd-based catalyst segments were used at the entrance. In gasified biomasses, the presence of substances much more reactive than CH_4, such as CO and H_2, may partly overcome such ignition problems. On

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Table 1
Typical composition of gasified biomass

Species	CO	H_2	CH_4	CO_2	H_2O	C_2H_4	N_2	NH_3	H_2S
mol%	15	10	5	14	11	1	44	0–3000 ppm	100 ppm

the other hand, it has been reported that other compounds present in significant amounts in the fuel mixture (such as CO_2 and H_2O) may have an inhibiting effect on the catalytic combustion. Finally, we note that the presence of *N*-containing compounds (i.e. NH_3) in the fuel mixture may pose additional problems as potential source of undesired fuel-NO_x.

The purpose of this work was to investigate the potential of Mn-substituted hexaaluminates in catalytic combustion of gasified biomasses. Accordingly the following properties have been tested over a reference $BaMn_1Al_{11}O_{19}$ catalyst:

1. activity in CO, H_2, CH_4 and C_2H_4 combustion;
2. kinetic effects of CO_2 and H_2O;
3. reactivity of NH_3 in the catalytic combustion.

Finally, to get a better comprehension of the results, lab-scale data have been scaled up through mathematical modeling.

2. Experimental

A $BaMn_1Al_{11}O_{19}$ catalyst was prepared according to a procedure described elsewhere [5], based on aqueous co-precipitation of soluble nitrates by $(NH_4)_2CO_3$ addition. Upon calcination at 1300°C of the filtered and dried precursor a monophasic sample was obtained, showing a Ba-β-Al_2O_3 structure and 15 m^2/g of BET surface area.

Combustion tests on both single- and multi-component fuel were performed over catalyst powders loaded in a quartz microreactor equipped with a sliding thermocouple. Very small particle size ($d_p \cong 0.1$ mm) and catalyst dilution (catalyst/quartz=2/1 w/w) were used in order to avoid diffusional limitations and to reduce temperature gradients in the reactor. A layer of quartz granules (6 cm high) was placed above the diluted catalyst bed to preheat the reactants and to minimize the dead spaces in the reactor. In single component fuel experiments, 1% (v/v) of CO, H_2 and CH_4 in air and 0.1% (v/v) of C_2H_4 with 2% (v/v) O_2 in helium were fed to the reactor at GHSV=54 000 Ncc/g h. The following feed composition (molar basis) was instead used in multi-component fuel experiments: 0.33% H_2, 0.51% CO, 0.15% CH_4, 0.40% CO_2, 0.45% H_2O, 2.25% O_2, balance N_2. Analysis of reactants and products were performed by on-line gas chromatography. The effect of CO_2 and H_2O was investigated in the same apparatus by co-feeding either CO_2 or H_2O (through a saturator) to CO/air and CH_4/air mixtures in order to obtain CO_2 or H_2O concentrations up to 7% (with fuel concentration fixed at 1% and air to balance).

A similar experimental setup was used to investigate the NH_3 combustion reaction over the same catalyst. The NH_3 concentration was set in this case at 500 ppm+2% (v/v) of oxygen, He balance. Analysis of reactants and products has been performed by a quadrupole mass detector (Baltzers QS 200) and gas chromatography (HP 5890 gas chromatograph) connected in a parallel arrangement. In a typical experiment, the catalyst temperature is linearly increased at 7°C/min up to 850°C, while continuously monitoring the outlet product concentration.

3. Results and discussion

3.1. Fuel combustion activity

In Fig. 1 are reported the conversion curves obtained for the different fuels in single component experiments. The following order of combustion reactivity has been observed: $CO > H_2 \geq C_2H_4 > CH_4$. The difference of reactivity is very marked, the temperature required to achieve 10% conversion at the experimental conditions herein adopted ranges from 250°C for CO to 550°C for CH_4. Apparent activation energy was calculated assuming a first order dependence on fuel concentration for kinetics and plug flow isothermal behavior for the reactor. Typical values of 13–15 kcal/mol were obtained for CO and H_2, 19 kcal/mol for C_2H_4 and 22–24 kcal/mol for CH_4. These

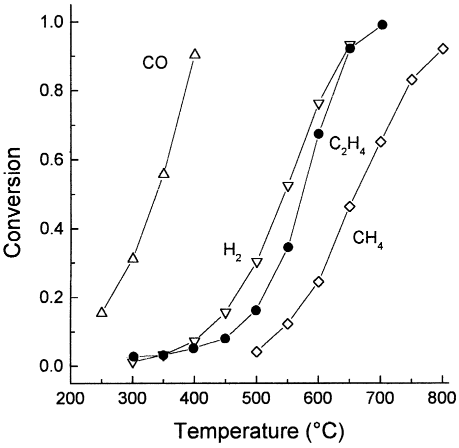

Fig. 1. Conversions of CO, H_2, C_2H_4 and CH_4 obtained over $BaMnAl_{11}O_{19}$ catalyst.

values are in line with the observed activity trend, except for CO that despite of its markedly higher reactivity shows an apparent activation energy very similar to that of H_2. A possible explanation for this deviation is related to competitive adsorption effects that may unevenly affect the combustion kinetics of the investigated species due to different temperatures at which significative conversions are obtained.

In multi-component fuel experiments, the same reactivity order was obtained. However, a slight decrease of conversion for all the investigated fuels was observed with respect to single component experiments. This behavior can be tentatively related to the presence of small amounts of CO_2 and H_2O in the feed. Accordingly, the effect of these substances was separately investigated.

3.2. *Effect of CO_2 and H_2O on fuel combustion activity*

In Fig. 2 the conversion of CO and CH_4 obtained at constant temperature for different CO_2 and H_2O concentrations in the feed are reported. Due to their large reactivity gap, different temperatures were considered for CO and CH_4 (300°C and 600°C, respectively), in order to obtain proper conversion levels. Experimental results show that CO conversion decreases on increasing both CO_2 and H_2O concentration in the feed. Inhibition effect of H_2O appears slightly stronger than that of CO_2 and is particularly marked in the 0–3.5% concentration range, whereas it progressively levels off at higher H_2O concentration. The difference between the effects of CO_2 and H_2O is much more evident in the case of CH_4 combustion. H_2O inhibition is still well evident although less marked than for CO combustion, whereas CH_4 conversion is only slightly affected by the presence of CO_2 in the feed also at high concentration levels. The differences observed between CO and CH_4 likely arise from the wide temperature difference in the experiments. The high temperature required by CH_4 combustion results in a markedly smoothing of inhibition that is reasonably

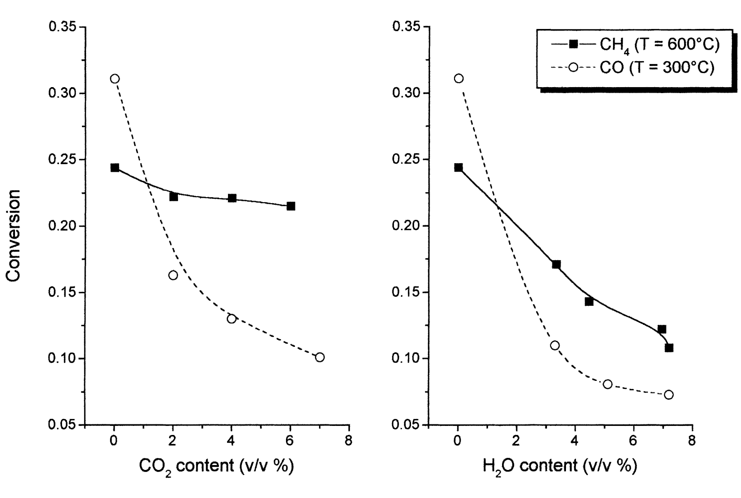

Fig. 2. Effects of CO_2 and H_2O in the feed on CO and CH_4 combustion.

associated with competitive adsorption effects. It is worth stressing that data on CH_4 combustion were collected at 600°C, i.e. a temperature of practical importance for Mn-substituted application in gas turbine combustors. Similar data concerning H_2O inhibition over the same catalytic systems were collected by Johansson et al. [6] who observed a significant shift towards higher temperatures of the CH_4 light-off temperature upon addition of water in the feed. Accordingly, the effects of H_2O inhibition, which is not presently considered in the literature [7], should be included in kinetic expressions for combustion over Mn-substituted hexaaluminates.

3.3. NH_3 combustion activity

The reactivity of NH_3 in the absence of the $BaMn_1Al_{11}O_{19}$ catalyst was investigated at first (blank experiment). It was observed that ammonia is converted starting from ~500°C, with formation of NO and of N_2 as reaction products. The NH_3 conversion does increase on increasing the reaction temperature and is close to 70% at 850°C. In the *T*-range 500–700°C the concentration of N_2 prevails, whereas above 700°C the relative amount of NO increases up to 50% *N*-selectivity. No formation of additional reaction products (e.g. N_2O and NO_2) has been observed in the whole investigated temperature range.

A different situation is observed when the NH_3 oxidation reaction is performed in the presence of the $BaMn_1Al_{11}O_{19}$ catalyst. The NH_3 concentration profile is complex due to its desorption from the catalyst surface at the beginning of the temperature programming and due to its consumption at higher temperature. The formation of the NH_3 oxidation product (i.e. NO, N_2 and N_2O, Fig. 3) is observed starting from 250°C, and almost complete NH_3 consumption is attained at 500°C. Accordingly the NH_3 oxidation reactivity is only slightly lower with respect to the most reactive fuel, i.e. CO (see Fig. 1). The NO concentration increases with temperature and shows a maximum near 750°C. Nitrogen formation, on the other hand, exhibits a complex behavior: it monotonically increases with temperature and shows a shoulder near 400°C. The concentration profile of N_2O, on the other hand, shows a maximum in correspondence of the N_2 shoulder and then decreases for further temperature increases. The N_2O formation is negligible above 700°C. The formation of the NH_3 oxidation products is accompanied by water evolution.

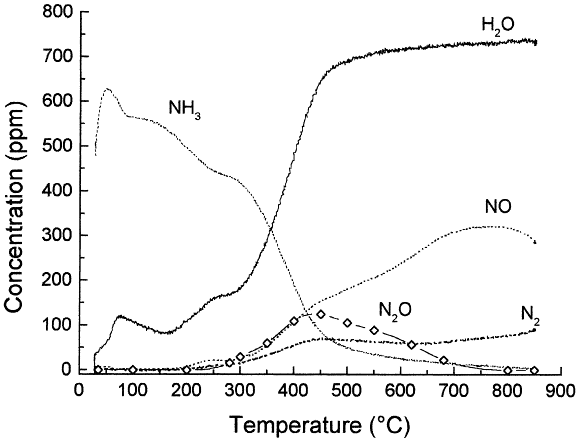

Fig. 3. Results of NH_3 oxidation over $BaMnAl_{11}O_{19}$ catalyst. Feed: NH_3 500 ppm, O_2 2%, He balance.

The results shown in Fig. 3 clearly indicate that undesired NO is the most abundant ammonia oxidation product in the whole investigated temperature range, even if in terms of *N*-selectivity its relative amount is reduced. To check whether the NO formation could be lowered by the presence of the reducing agents present in the fuel mixture (i.e. CO, H_2, CH_4, or C_2H_4), the reactivity of ammonia in the presence of the various fuels has been investigated. Accordingly, tests of catalytic oxidation of NH_3 in the presence of a fuel mixture representative of gasified biomasses (Table 1) has been performed. The results obtained in the case of a dry feed are reported in Fig. 4. The fuel behavior (not reported in the figure) closely resembles that of the single components shown in Fig. 1. For what is concerning the behavior of NH_3 present in the synthetic mixture, it is noted that below 750°C the formation of the various reaction products (i.e. N_2, N_2O and NO) is similar to that observed in the case of the NH_3+O_2 mixture already shown in Fig. 3. At higher temperatures, above 750°C, a significant reduction in the formation of NO is observed, with a corresponding increase in the formation of N_2. In particular, at 850°C the N_2 concentration is higher with respect to that of NO, near 150 ppm. This result is of particular interest in view of the potential reduction of the NO emission deriving from fuel-NO_x. Accordingly, these aspects have been investigated more into details, and the

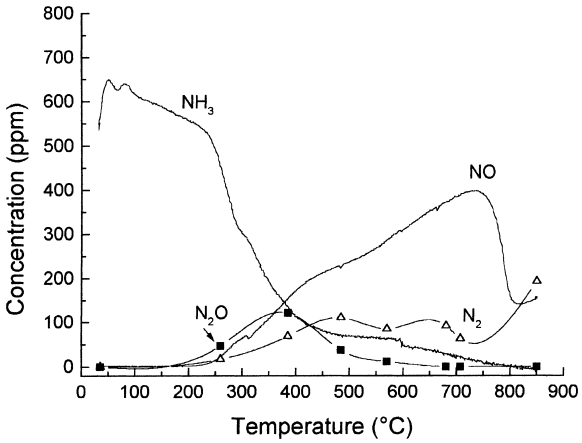

Fig. 4. Results of simultaneous NH_3 and fuel mixture oxidation over $BaMnAl_{11}O_{19}$ catalyst. Feed: NH_3, 500 ppm; CO, 5000 ppm; H_2, 3800 ppm; CH_4, 1800 ppm; C_2H_4, 300 ppm; O_2, 2%; He balance.

reaction of a synthetic mixture having the same composition of that used in Fig. 4, but containing NO instead of NH_3 has been studied in order to check the possible reduction of NO by the fuel. These results however indicate that NO is not reduced in the whole investigated *T*-range, apparently ruling out a possible role of the various fuels in the high-*T* NO reduction observed in Fig. 4. A possible explanation of the effect observed in Fig. 4 is that ammonia, in the presence of the fuel mixture, is directly oxidized to N_2 instead of NO at high temperature. Alternatively, the involvement of homogeneous gas-phase reactions may be invoked. However, these aspects have not been completely clarified yet and work is currently in progress.

3.4. Mathematical model analysis

Mathematical modeling was used to scale-up the results obtained in the lab [8] in order to preliminarily assess the potential of Mn-substituted hexaaluminates under actual GT conditions. Mathematical models of a single monolith channel were developed for this purpose accounting for:

1. convective heat and mass transfer in the gas–phase;
2. heat and mass gas–solid transfer by diffusion: a 2D description has been adopted for laminar flow conditions, whereas under transitional and turbulent flow, a 1D description based on correlations for heat and mass transfer coefficients derived from heat transfer literature [9] has been used;
3. mass transfer in the solid by intra-porous diffusion through calculation of the effectiveness factor under the assumptions of first order kinetics and isothermal catalyst thickness;
4. conductive heat transfer in the solid phase;
5. heterogeneous and homogeneous reactions.

In particular kinetic expressions for heterogeneous reactions to be implemented in model equations have been derived from the data of combustion experiments of single component fuel, assuming a first order dependence on fuel concentration. Although this approach neglecting inhibition effects of H_2O is not conservative, it has been adopted because of the preliminary purpose of the analysis and because of the absence of reliable kinetic expression including the effect of water. An extensive kinetic investigation on this effect is currently in progress in order to implement more comprehensive kinetic expression in model equation. Concerning kinetics of homogeneous reactions simple literature expression based on molecular approximation have been adopted [10,11].

A similar analysis was previously performed for combustor fueled with CH_4 [8] and pure CO/H_2 mixtures [12]. The results showed that Mn-substituted hexaaluminates can only be used as finishing segments in natural gas fueled combustors (as actually experienced in pilot scale tests by Osaka Gas [4]), whereas, they possess activity levels close to satisfy the operating requirements with fuel that only contains CO and H_2 as reactants. In this latter case it was also evidenced that, under adiabatic operation of the combustor, light-off of the more reactive CO was able to promote the ignition of the less active component up to very high H_2 content (e.g. 50% of the fuel fraction), thus enhancing the catalyst performances.

The case of gasified biomasses appears as intermediate. Indeed despite of the relatively low CH_4 concentration, this species is responsible for about $\frac{1}{3}$ of the heating value, due to its high combustion enthalpy. 2D model simulation results plotted in Fig. 5 shows that on increasing CH_4 concentration at fixed overall heating value the ignition is progressively delayed and smoothed. Eventually, Mn-substi-

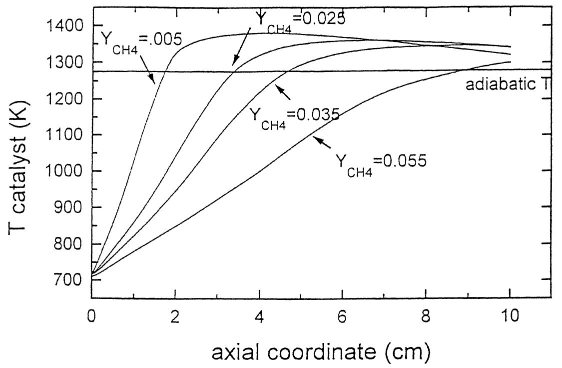

Fig. 5. Effect of CH_4 concentration in the fuel on the catalyst temperature. Operating conditions: $T=330°C$, $G_{air}=2.8$ kg/s, $T_{ad}=1000°C \Rightarrow G_{fuel}=0.5$ kg/s, $P=10$ bar. Catalyst configuration: $L=10$ cm, $d_{eq}=1.2$ mm, $\epsilon=0.68$.

tuted hexaaluminates are not active enough to secure the necessary fast ignition under all the relevant conditions. Indeed their activity in CH_4 combustion is so poor that ignition of the more reactive CO/H_2 fraction is not able to promote the light-off of the whole fuel mixture, so that CH_4 actually behaves similarly to an inert diluent. Several simulations have been performed aiming to identify the catalyst activities required to achieve effective ignition. Results in Fig. 6 were obtained with a 1D model and refers to full load conditions of a 2.9 MW gas turbine but for an adiabatic temperature limited at 1000°C in order to reduce catalyst thermal stresses. A reactor configuration has been considered, consisting of four finishing hexaaluminate-type segments and two igniting segments with catalytic activity higher than that of hexaaluminates by a 7 factor in CO and H_2 combustion and by a 100 factor in CH_4 combustion. Such activity levels are widely matched by Pd-based catalyst. Enhanced activities of the first two segments provide effective catalyst ignition that results in an intense heating of the gas-phase that in turn allows for ignition in less active hexaaluminate-type catalysts. Eventually, the gas outlet temperature is high enough to secure stable combustion to complete fuel consumption in a downstream homogeneous section.

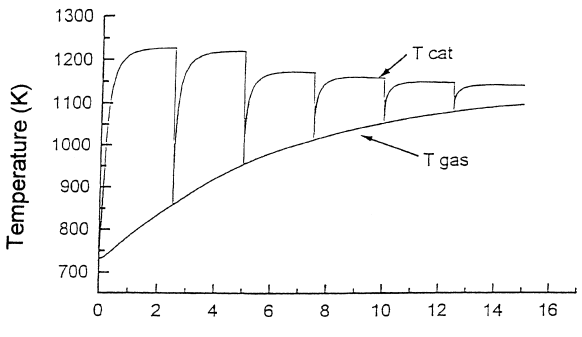

Fig. 6. Calculated temperature profile in the catalyst section. Operating conditions: Full load of a 2.9 MW gas turbine. Catalyst configuration: $L=6\times2.5$ cm, $d_{eq}=1.2$ mm, $\epsilon=0.68$.

Similar results were obtained considering parameter values corresponding to partial load operations. Accordingly mathematical model simulations indicate that the operating requirements can be matched by using a couple of very active noble metal-based segments at the bed entrance.

4. Conclusions

The following conclusions can be drawn from the present study on catalytic combustion of gasified biomasses over Mn-substituted hexaaluminates:

1. The different fuels present in the gasified biomasses exhibit the following reactivity order: $CO>H_2\geq C_2H_4>CH_4$.
2. Scale-up of the activity data by means of mathematical modeling shows that $BaMnAl_{11}O_{19}$ is not active enough to satisfy the operating requirements of catalytic combustors fueled by gasified biomasses. This is due to the high methane content of the fuel that requires noble metal based-catalysts for ignition at low temperatures.
3. CO_2 and H_2O inhibit CO and CH_4 combustion: the inhibition effect of water is still evident at high temperature (600°C), and accordingly it should be accounted for in reliable kinetic expressions. On the other hand, the CO_2 inhibition effect is only observed at temperatures below those of practical application of these systems.
4. The $BaMnAl_{11}O_{19}$ catalyst is very active in the oxidation of ammonia, with NO as the major reaction product observed in the whole investigated temperature range. In the presence of the fuel mixture, at high temperatures ($T>750°C$) a

decrease of the NO formation is observed, paralleled by N_2 production. These aspects deserve further investigation, being relevant to the possible reduction of undesired fuel-NO_x.

Acknowledgements

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