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NH_3 oxidation during the catalytic combustion of biomasses-related fuels over Mn-substituted hexaaluminates

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The reactivity of a Mn-substituted hexaaluminate catalyst in the catalytic combustion of gasified biomasses-derived fuels is addressed. The combustion activity of the main fuel components, i.e., CO, H_2, C_2H_4 and CH_4, is investigated, along with that of NH_3 that is present in the biomasses-derived fuels. It is found that significant amounts of NO_x are formed from ammonia during the catalytic combustion process, but the occurrence of gas-phase homogeneous reactions involving NH_3 and NO in the presence of oxygen strongly reduce NO_x formation at high temperatures.

Keywords: catalytic combustion, biogas, ammonia oxidation, Mn-substituted hexaaluminate catalysts

1. Introduction

Catalytic combustion for gas turbines has been extensively investigated in recent years due to its potential to minimize NO_x, unburnt hydrocarbons and CO emissions [1]. Natural gas is so far the most widely used fuel for turbines, but the interest towards other fuels (e.g., those deriving from gasification of carbon, wastes and biomasses) is rapidly growing nowadays. In particular, the use of renewable gasified biomass would be beneficial for the reduction of the net CO_2 emissions in the atmosphere.

Biomass-derived fuels (biogas) shows a complex composition, since several compounds, including CO, H_2, CH_4 and ethylene, may be present in various amounts in a typical fuel mixture (see table 1). Also, N-containing compounds (e.g., NH_3) are typically present in small amounts. The combustion of biogas in conventional gas turbines may be difficult in view of their low heating value. In this respect, catalysts may secure effective combustion by igniting and stabilizing the reaction [2]: among the investigated catalytic materials, Mn-substituted hexaaluminates with layered alumina structure are considered promising catalysts [3,4]. The use of biomass-derived fuels may also pose emission problems related to the presence of NH_3 that may act as a potential source of unwanted fuel-NO_x.

The aim of this work was to investigate the reactivity of ammonia and of the various fuels over a Mn-substituted hexaaluminate catalyst, in order to obtain information on the role of NH_3 oxidation in the formation of NO_x emissions. Accordingly, the catalytic oxidation of NH_3 has been investigated over a $BaMn_1Al_{11}O_{19}$ catalyst, and the effect of the presence of the other fuels on the activity and selectivity of the reaction has also been addressed.

Table 1
Typical composition of gasified biomass fuel.

Species	mol%
CO	15
H_2	10
CH_4	5
CO_2	14
H_2O	11
C_2H_4	1
N_2	44
NH_3	0–0.3
H_2S	0.01

2. Experimental

2.1. Catalyst preparation and characterization

The $BaMn_1Al_{11}O_{19}$ catalyst used in this study has been prepared according to a procedure described elsewhere [5]. This procedure is based on the aqueous co-precipitation of soluble nitrates of Ba, Mn and Al at pH = 7–8 by using $(NH_4)_2CO_3$ as precipitating agent. The precipitate is filtered, washed and dried at 110 °C overnight. Upon calcination at 1300 °C of the dried precursor a monophasic sample is obtained, showing a Ba-β-Al_2O_3 structure and a surface area of 15 m^2/g (BET method).

2.2. Catalytic activity tests

Catalytic activity experiments were performed in a quartz tubular fixed-bed microreactor (i.d. 7 mm) loaded with 0.128 g of catalyst. Very small particle size ($d_p \approx 0.1$ mm) and catalyst dilution (catalyst/quartz = 2/1 w/w) were used in order to reduce diffusional limitations and temperature gradients in the reactor, respectively. The reactor

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operated at near-atmospheric pressure (P = 120–140 kPa abs. due to pressure drops in the catalyst bed) and was inserted into an electric furnace driven by a proportional-integral-derivative temperature controller/programmer (Eurotherm 812). The temperature of the catalyst was measured and controlled by means of a K-type thermocouple (o.d. = 0.5 mm) sliding in a quartz thermocouple well (o.d. = 2 mm) directly immersed in the catalyst bed. Accordingly, the reaction zone and the catalyst bed were of annular shape.

For the analysis of the exiting gases, the reactor outlet was connected in a parallel arrangement to both a quadrupole mass detector (Balzers QMS 200) and a gas chromatograph (HP 5890) equipped with a Porapak Q and a 5 Å molecular sieve capillary column connected to thermal conductivity detectors.

In a typical ammonia oxidation experiment, a stream of NH_3 (500 ppm) + O_2 (2% v/v) + Ar (3000 ppm as internal standard) in He was fed to the reactor at room temperature, with a total flow rate of 120 cm^3/min (STP). When the mass-spectrometer signals were stabilized, the catalyst temperature was linearly raised at 7 °C/min up to 950 °C, while continuously monitoring the concentration of the gases exiting from the reactor.

When the catalytic oxidation of NH_3 was investigated in the presence of the biomasses-derived fuels, a stream composed by NH_3 (500 ppm), CO (5000 ppm), CH_4 (1800 ppm), H_2 (3800 ppm), C_2H_4 (300 ppm), Ar (3000 ppm), O_2 (2%) and He (balance) was used. This composition resembles that of a "real" fuel but diluted by a factor of 7, in order to reduce the temperature gradients in the catalyst bed. Total flow rate and other experimental conditions were as those used for NH_3 oxidation. However, in addition to mass spectrometric analysis, in this case the reaction products were also periodically analyzed by on-line gas chromatography.

The following mass-to-charge ratios (m/e) were used to monitor the concentrations of products and reactants: 2 (H_2), 15 (CH_4), 17 (NH_3), 18 (H_2O), 26 (C_2H_4), 28 (N_2, CO or C_2H_4), 30 (NO), 32 (O_2), 40 (Ar), 44 (N_2O or CO_2) and 46 (NO_2). When different compounds having identical m/e ratios were present (e.g., N_2O and CO_2, or N_2 and CO) the analysis was performed by gas chromatography. The data were quantitatively analyzed by taking into account the response factors and the overlapping of the fragmentation patterns experimentally determined.

3. Results and discussion

Figure 1 shows the results obtained in the $NH_3 + O_2$ reaction over the $BaMn_1Al_{11}O_{19}$ catalyst. The concentration profiles of the gases exiting the reactor have been reported as a function of the reaction temperature. Ammonia exhibits a quite complex concentration profile, showing at first an increase due to NH_3 desorption from the catalyst surface and then a decrease due to its consumption at higher temperatures. NH_3 is converted above 300 °C, and complete ammonia consumption is attained above 500 °C. Reaction products are NO, N_2 and N_2O. Their formation is evident starting near 300 °C, with NO as the most abundant reaction product in the whole temperature range. NO concentration exhibits a maximum near 750 °C, and then rapidly decreases with temperature. The decrease in the NO concentration at high temperature is paralleled by the formation of N_2. The formation of N_2O has also been observed, with a maximum near 550 °C and a gradual decrease to 0 at 750 °C.

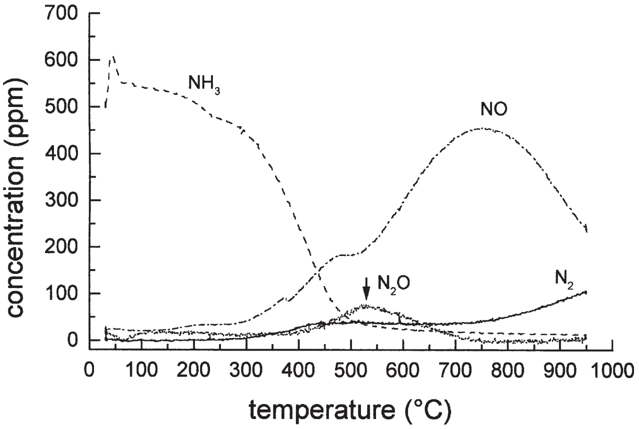


Figure 1. Product composition for ammonia oxidation reaction over the $BaMn_1Al_{11}O_{19}$ catalyst. Feed: NH_3 500 ppm, O_2 2%, He balance. Catalyst weight 0.128 g, total flow 120 Ncm^3/min.

The NH_3 oxidation has also been carried out in the presence of the fuel mixture, and results are reported in figure 2 (A) and (B). From figure 2(A) it appears that CO is the most reactive fuel, being converted starting from 250 °C, whereas the reactivity of methane is very low, being consumed only above 550 °C. These results are in line with previous data reported over the same catalytic system [5]. The concentrations with temperature of the N-containing species are shown in figure 2(B). In this case, the N_2 and N_2O concentration profiles have been obtained by interpolating the experimental points derived from the gas-chromatographic analysis, due to the overlapping with CO and CO_2, which are present in much higher amounts. The concentration profiles of the various species reported in figure 2(B) resemble those obtained in the absence of the fuel mixture shown in figure 1. Ammonia is apparently converted starting from slightly lower temperatures, i.e., above 250 °C, and also in this case NO is the most abundant reaction product in the whole temperature range, with a clear maximum near 750 °C. However, in this case the maximum in NO concentration is more pronounced, and a rapid decrease in the NO concentration is evident above 750 °C. Also, a slightly higher N_2O concentration is observed.

The results reported in figures 1 and 2 clearly show that undesired NO is the most abundant ammonia oxidation product in the whole investigated temperature range, both in the presence and in the absence of the fuel mixture. This clearly indicates a strong oxidizing capability of the $BaMn_1Al_{11}O_{19}$ catalyst surface towards NH_3, which

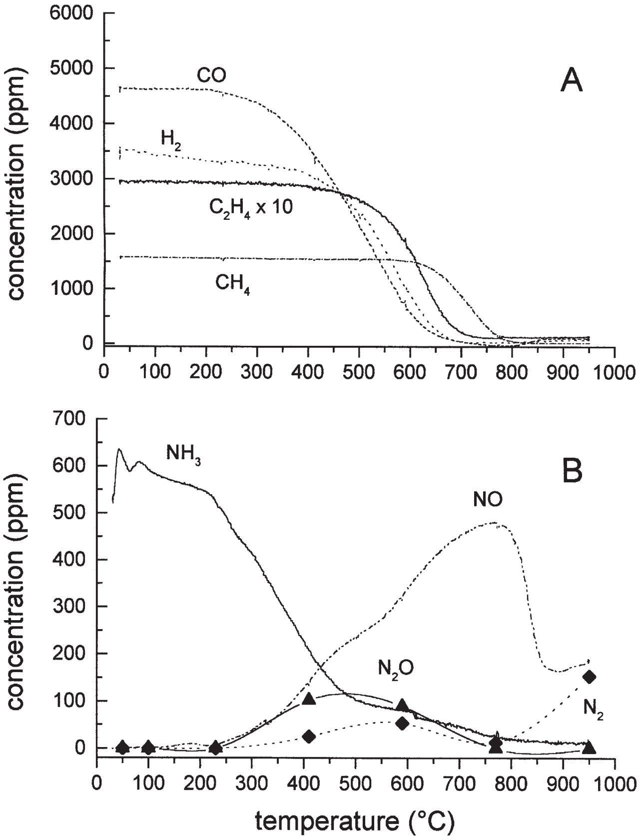


Figure 2. Product composition for ammonia + synthetic mixture oxidation reaction over the $BaMn_1Al_{11}O_{19}$ catalyst. Feed: NH_3 500 ppm, CO 5000 ppm, CH_4 1800 ppm, H_2 3800 ppm, C_2H_4 300 ppm, CO_2 5000 ppm, O_2 2%, He balance. Catalyst weight 0.128 g, total flow 120 Ncm^3/min. (A) Concentration of CO, CH_4, H_2, C_2H_4. (B) Concentration of the N-containing compounds.

is not significantly affected by the concomitant combustion of the various fuels. However, the reduction in the NO concentration that is observed at high temperatures, both in the presence and in the absence of the fuel mixture, is of particular interest in view of the potential reduction of the NO emissions during the catalytic combustion of biomass-derived fuels.

In order to gain a better understanding of the reasons leading to the observed reduction in the NO concentration profile at high temperatures, a new investigation has been undertaken. In particular, the possibility of the reduction of NO by one of the components present in the fuel mixture has been investigated. Accordingly, a series of runs have been performed by feeding NO and different reducing agents (e.g., H_2, CO, CH_4, NH_3, C_2H_4), both in the presence and in the absence of 2% v/v oxygen in the feed. The experiments have been performed both into an empty reactor, to check for the occurrence of homogeneous gas phase reactions, and in the presence of the $BaMn_1Al_{11}O_{19}$ catalyst as well. The results of these runs showed that [9]:

(i) H_2, CO, NH_3, CH_4, and C_2H_4 effectively reduce NO to molecular nitrogen at high temperatures (>600 °C) over the $BaMn_1Al_{11}O_{19}$ catalyst and in the absence of oxygen;

(ii) in the gas phase, only a slight reduction of NO by H_2 has been observed at high temperatures in the absence of oxygen;

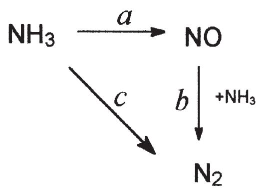
(iii) over both the $BaMn_1Al_{11}O_{19}$ catalyst and in the gas phase, when oxygen is present, H_2, CO, CH_4, and C_2H_4 are oxidized to CO_2 and H_2O, and no reduction of NO is observed;

(iv) ammonia effectively reduces NO to N_2 above 750 °C in the presence of oxygen in the gas phase (figure 3);

(v) NH_3 is not oxidized in the gas phase up to temperatures near 900 °C.

Accordingly, these results clearly indicate that in the presence of oxygen (as in the case of the experiments shown in figures 1 and 2) NO cannot be reduced to molecular nitrogen by any of the fuels present in the reacting mixture. On the other hand, the capability of ammonia to reduce NO in the gas phase above 750 °C clearly demonstrates the feasibility of the so-called selective non-catalytic reduction (SNCR) process under the investigated experimental conditions.

As a matter of fact, the following simplified reaction scheme is suggested for NO and N_2 formation over the $BaMn_1Al_{11}O_{19}$ catalyst:



Scheme 1.

In this scheme, NH_3 can be oxidized to NO via route a or to N_2 via route c and/or route b. It is noted that while route c suggests the direct ammonia oxidation to N_2, route b implies the intermediacy of NO and its subsequent reduction with NH_3.

The reaction scheme presented above neglects the formation of N_2O. The formation of this species is consistent in the low temperature region, below 700 °C. Since N_2O formation has never been observed during our gas-phase studies [9], it is likely that this species may be formed via surface-catalyzed processes, possibly involving ammonia and adsorbed nitrates and/or nitrites species. As a matter of fact, small amounts of NO_2 have been observed to be formed over the $BaMn_1Al_{11}O_{19}$ catalyst when NO is present in the feed stream, indicative of the occurrence of NO oxidation processes. The presence of adsorbed nitrates and/or nitrites species in the case of MnO_x-based catalysts has been well documented in the literature [12].

For the $BaMn_1Al_{11}O_{19}$ catalyst, the ammonia oxidation processes via routes a–c are not significantly affected

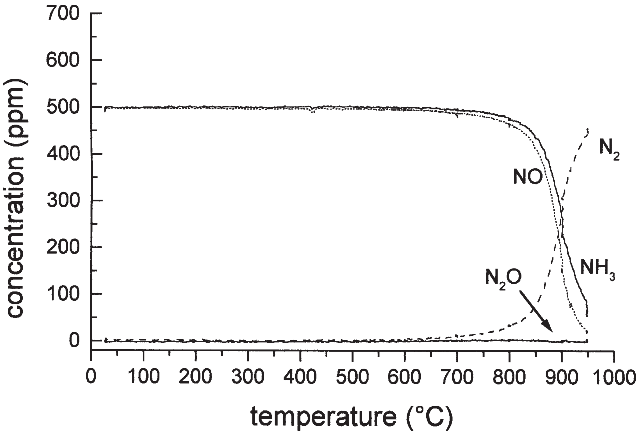


Figure 3. Product composition for ammonia+NO oxidation reaction in the empty reactor. Feed: NH_3 500 ppm, NO 500 ppm, O_2 2%, He balance. Total flow 120 Ncm^3/min.

by the ongoing oxidation reactions of the various fuels, as shown by comparing figures 1 and 2(B). At low temperatures (below 600–700 °C), where homogeneous gas-phase reactions are negligible, NH_3 oxidation is a surface-catalyzed process. Accordingly, route a represents the catalytic NH_3 oxidation to NO, whereas route b represents the well known SCR process, which is known to be catalyzed by several oxides, including MnO_x [10]. Route c, on the other hand, represents the direct NH_3 oxidation to N_2 that cannot be excluded over the catalyst surface. Over the $BaMn_1Al_{11}O_{19}$ catalyst route a prevails on route $b + c$, as pointed out by the higher amounts of NO produced if compared to N_2.

At higher temperatures, above 700 °C, homogeneous gas-phase reactions may also occur. Since no reactions have been observed with $NH_3 + O_2$ mixtures in the gas phase up to 900 °C (see previous point (v)), it is suggested that even at high temperatures the NH_3 oxidation to NO (i.e., route a) is an initially surface-catalyzed process. On the other hand, route b may effectively occur in the gas-phase, as clearly shown in figure 3. Finally, the gas-phase direct NH_3 oxidation to N_2 (route c) is generally excluded [11].

Scheme 1 thus suggests that upon the ammonia oxidation at high temperature a complex interplay does exist between heterogeneous catalyzed and homogeneous gas-phase reactions. In particular, the observation that the reduction of the NO concentration above 750 °C during the experiments shown in figures 1 and 2 is seen at the same temperatures, where the NO homogeneous gas-phase reduction by NH_3 occurs via the SNCR process (see figure 3), leads us to suggest that this route is possibly responsible for the decrease in the NO concentration at high temperatures that is observed during the catalytic combustion of gasified biomasses.

Under the operating conditions of the experiments shown in figures 1 and 2, where ammonia but no NO is fed to the reactor, the occurrence of the SNCR process obviously requires the simultaneous presence, in the gas phase and at high temperatures, of unreacted ammonia along with NO. By considering that ammonia is not present in the reactor outlet above 500 °C (see figures 1 and 2(B)), it is suggested that above 750 °C the homogeneous NO reduction by NH_3 may take place in the first part of the catalyst bed, where NO is already formed, but unreacted ammonia is still present in the gas phase.

It is noted that the more rapid decrease in the NO concentration that is observed above 750 °C, when the other fuel components are present with respect to the $NH_3 + O_2$ reaction, can be likely ascribed to the presence of fuels like CO and H_2, which are known to favor the occurrence of the SNCR process [13], as indeed observed during our homogeneous gas-phase experiments.

4. Conclusions

From the above-presented results, it can be concluded that:

(i) the catalytic combustion of biomasses-derived fuels in the presence of the $BaMn_1Al_{11}O_{19}$ catalyst leads to the formation of significant amounts of fuel-NO_x;

(ii) NO_x formation is strongly reduced at high temperatures, above 750 °C;

(iii) although the detailed mechanism of the high-temperature partial reduction of the NO_x emissions has not been clarified into details, it is likely that the observed effect is related to the SNCR process involving gas-phase ammonia and occurring in the first part of the catalyst bed. Work is currently in progress to better analyze these aspects.

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