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Catalytic activity of bed materials from industrial CFB boilers for the decomposition of N_2O

V. Barišić [a,*], F. Klingstedt [a], A. Naydenov [b], P. Stefanov [b], P. Kilpinen [a], M. Hupa [a]

[a] Åbo Akademi Process Chemistry Centre, Biskopsgatan 8, FIN-20500 Åbo, Finland
[b] Bulgarian Academy of Science, "Acad. G. Bonchev" str., bl. 11, 1113 Sofia, Bulgaria

Abstract

The correlation between the catalytic activity towards N_2O decomposition and fuel type was studied for the bed materials sampled from the bottom bed of two industrial CFB boilers, a 12 MW_{th} and a 550 MW_{th}, burning biomass fuels and wastes, alone or as a mixture. It was found that the elemental composition of the surface of the bed material particles changed according to the composition of the ash from the parent fuel. The measured catalytic activity of the bed material samples increased with the amount of the catalytically active oxides (CaO, MgO, Fe_2O_3, Al_2O_3). In the case of limestone addition, the activity of the bed material was influenced by both the elemental composition of the fuel, and the ratio between lime and sulfated lime.

Keywords: Catalytic N_2O decomposition; Circulated fluidized bed combustion; Bed material activity; Biomass fuels; Wastes; Co-firing

1. Introduction

Circulating fluidized bed (CFB) combustion is a well-proven technology for burning a variety of fuels due to its efficiency, reliability, and especially, possibility to keep low emissions of SO_2 and NO_x. However, a disadvantage of CFB is that emissions of nitrous oxide (N_2O) can be much higher as compared to other combustion technologies. During recent years, replacement of fossil fuels with biomass and biomass-derived fuels has become increasingly important due to growing concerns about global warming. Also, the combustion of various wastes has become an option for solving the problem of landfills as well as for producing electricity. Despite advantages like being a renewable source of sustainable energy, the utilization of biomass fuels and wastes in CFB might increase N_2O emissions to unacceptable levels. Emissions of N_2O from CFB are partially controlled by catalytic reactions. Based on the studies with combustion of coals, it is known that char and calcined limestone can be very active catalysts for N_2O decomposition, while ash and bed material (a mixture of sand and ash) have in general much lower activities [1–13]. However, there is limited data available in the literature regarding the catalytic activity of solids from fluidized bed during combustion of biomass fuels and wastes.

The work presented in this paper is a part of an extensive study on the catalytic decomposition of N_2O over bed materials from industrial-scale CFB boilers sampled while burning biomass fuels and wastes, alone or as a mixture. Our previous work showed that the catalytic activity of the bed material was affected by fuel type [14]. However, the observed differences could not be explained based on the analysis of elemental composition of the samples by X-ray fluorescence (XRF), and morphology and elemental composition of the surface of particles by scanning electron microscope combined with an energy dispersive X-ray analyzer (SEM/EDX). In this work, a more detailed characterization of the bed material samples by SEM/EDX, and X-ray photoelectron spectroscopy (XPS) was carried out in order to correlate the composition of the fuel to the activity of bed material towards N_2O decomposition.

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* Corresponding author. Tel.: +358 2 215 3513; fax: +358 2 215 4962.
E-mail address: vbarisic@abo.fi (V. Barišić).

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2. Experimental

The tested solids were sampled from the bottom bed of two industrial-scale circulated fluidized bed boilers while burning different fuels, or fuel mixtures. Three bed material samples were collected from a 12 MW_{th} CFB boiler: (1) Ch1, the fuel was wood pellets; (2) Ch2, the fuel was a mixture of wood pellets and mechanically dewatered municipal sewage sludge A; (3) Ch3, the fuel was a mixture of wood pellets and pre-dried municipal sewage sludge B. Details about the full-scale experiments are published by Åmand et al. [15]. Four bed material samples were collected from the second boiler, a 550 MW_{th} CFB boiler: A1, the fuel was a mixture of 25 wt.% of bark and 75 wt.% of peat; A2, the fuel was coal; A3, the fuel was bark; A4, the fuel was peat. The full-scale experiments were run within six sequential days, and limestone was added for sulfur capture together with the fuel in the samples A1, A2, and A4. The fuel data are given in Table 1.

The original samples of the bed material were sieved to a narrow size fraction, and the particle size of 125–710 μm (45–99 wt.% of the sample) was used in this work. The catalytic activity of char was not investigated in the present study, and therefore, it was burnt off in the reactor before testing (amount of char was less than 1 wt.%). Tested solids remaining after burning of the char are hereafter called ''bed material''.

The bed material samples were characterized in terms of: elemental composition by X-ray fluorescence; total BET surface area by N_2-physisorption; morphology and elemental composition of the particles by scanning electron microscope combined with an energy dispersive X-ray analyzer (SEM/EDX); and surface analysis by X-ray photoelectron spectroscopy.

The catalytic activity of the solid samples was evaluated in the previous work [14] by measuring the conversion of N_2O in a laboratory fixed bed reactor made of quartz (Fig. 1a). The reactor is a modification of a reactor designed at the Technical University of Denmark [7]. A scheme of the experimental setup is shown in Fig. 1b. The experiments were carried out under atmospheric pressure in the temperature range from 600 °C to 910 °C. The inlet concentration of N_2O was 500 ppm_v, in He (99.996%), and the total inlet gas flow was 1800 cm^3/min (STP). The catalyst bed dimensions were chosen in order to avoid the internal and external mass transfer limitations. To keep the catalytic N_2O conversion level below 20%, 1–3.5 g of sample was used. The contribution of gas-phase reactions has been taken into account when presenting the results.

3. Results and discussion

The catalytic activities of the investigated bed materials are compared in Fig. 2 in terms of the overall reaction rate of N_2O decomposition as a function of temperature. All tested bed materials showed considerable catalytic activity in the temperature range between 800 °C and 910 °C. As was

Table 1
Fuel data

	CFB boiler						
	12 MW_{th}			550 MW_{th}			
	Wood pellets[a]	Sludge A[a]	Sludge B[a]	Bark and Peat[a]	Coal[a]	Bark[a]	Peat[a]
Moisture (wt.%, ar)[b]	0	0	0	50.0	7.8	52.0	41.0
Dry matter (wt.%, ar)[c]	99.6	98.0	97.2	44.0	88.9	42.6	51.7
Ash (wt.%, dry)	0.4	46.8	42.1	6.5	11.5	2.8	6.9
Volatiles (wt.%, dry)	84.3	52.4	59.5	71.1	33.9	76.8	70.0
Carbon (wt.%, dry)	51.1	27.7	28.9	53.1	72.8	52.3	52.6
Hydrogen (wt.%, dry)	6.0	3.9	4.5	5.3	4.6	5.7	5.6
Nitrogen (wt.%, dry)	<0.1	2.8	2.8	0.9	1.9	0.2	1.3
Oxygen (wt.%, dry)	43	42	44	38	15	41	38
SiO_2 (wt.% of ash)	12.84	27.43	21.85	46.08	52.09	17.58	43.41
Al_2O_3 (wt.% of ash)	2.36	14.53	36.80	10.76	21.36	3.78	10.13
Fe_2O_3 (wt.% of ash)	1.68	22.30	5.77	8.80	6.46	2.60	7.67
CaO (wt.% of ash)	32.53	5.68	5.32	8.61	5.72	34.48	12.17
MgO (wt.% of ash)	5.39	1.24	1.10	1.84	2.02	3.91	2.14
P_2O_5 (wt.% of ash)	2.81	15.67	13.61	2.29	0.84	3.76	5.98
Na_2O (wt.% of ash)	0.71	0.14	0.12	0.15	0.21	0.19	0.37
K_2O (wt.% of ash)	12.95	1.65	1.23	3.52	2.30	7.31	2.27
SO_3 (wt.% of ash)	3.81	4.96	3.80	6.53	6.30	3.39	6.51
Cl^- (wt.% of ash)	1.00	0.10	0.09	0.54	0.08	0.46	0.58
CO_2 (wt.% of ash)	~24	3.92	1.72	4.51	6.38	10.48	4.25
Sum	100.08	97.62	91.41	93.63	103.76	87.94	95.48

ar, as received. Elemental composition of ash is given as oxides.

[a] Fuel.

[b] Dried at room temperature.

[c] Dried at 105 °C for 2 h.

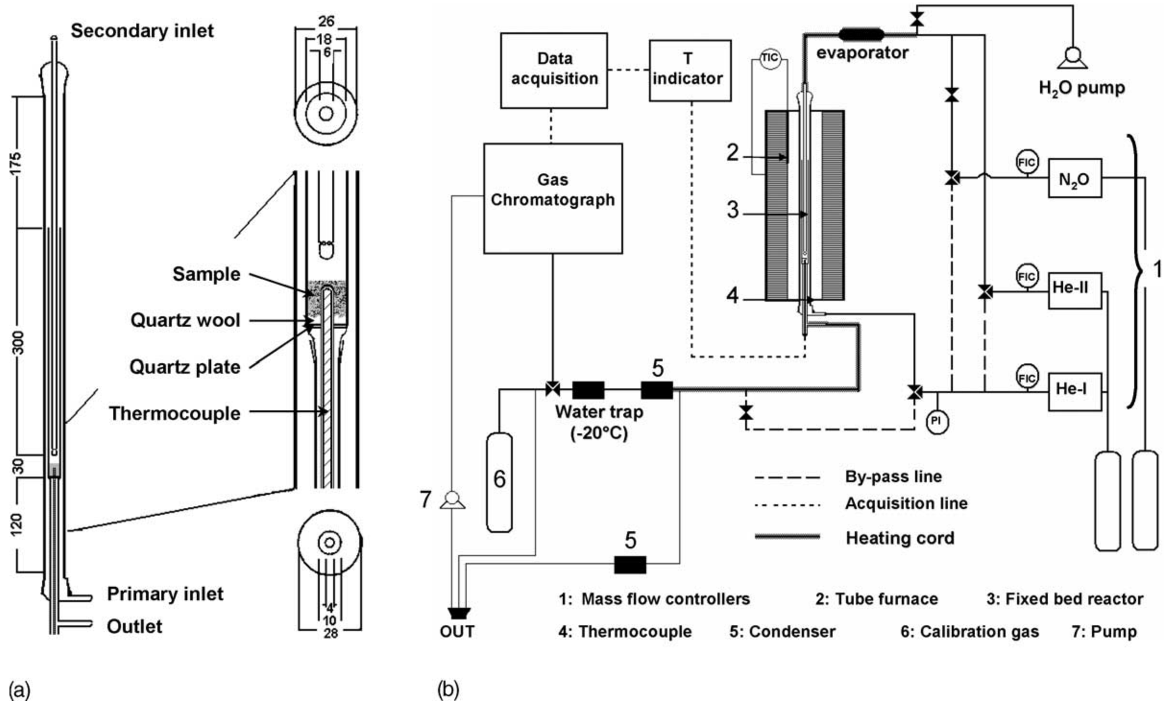

Fig. 1. (a) Laboratory quartz reactor modified after the design at Technical University of Denmark [7] and (b) experimental setup [14].

concluded in the previous work [14], the activities of bed materials were affected by the type of fuel. Addition of sludge A to wood pellets decreased the activity of the bed material Ch2 by about half, while the addition of sludge B caused the increase in activity of the bed material Ch3 by about half, as compared to the sample Ch1 (wood pellets) (Fig. 2a). Change of the fuel in the case of samples A1 (bark and peat) and A2 (coal) did not result in a significant difference in the activity of the bed materials (Fig. 2b). However, when bark was used the activity of the bed material A3 towards N_2O decomposition decreased by half as compared to samples A1 and A2. When the bark was switched to peat, the activity of the bed material A4 increased approximately five times compared to the sample A3. In addition, it can be noticed that when fuels were mixed, the catalytic activity of the bed material A1 (bark, 25% and peat, 75%) was not a result of a simple addition of catalytic activities observed for the bed materials when individual fuels were burnt, A3 (bark) and A4 (peat).

The XRF analysis of the elemental composition of the bed material samples showed that the composition of bed materials from the 12 MW_{th} boiler varied in such a way that the highest amount of the catalytically active oxides (CaO, MgO, Fe_2O_3, Al_2O_3) was measured for the sample Ch3 (wood pellets and sludge B), and the lowest for the sample Ch2 (wood pellets and sludge A). The measured catalytic activity of the 12 MW_{th} bed material samples can be correlated to the amount of the catalytically active oxides. On the other hand, the composition of bed materials from the 550 MW_{th} boiler was quite similar even though the ash

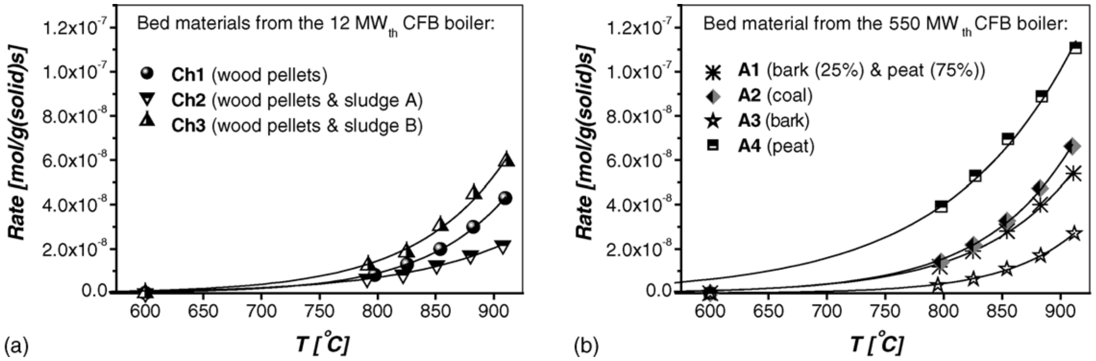

Fig. 2. The overall rate of N_2O decomposition over the bed material from: (a) the 12 MW_{th} boiler and (b) the 550 MW_{th} boiler. Sample particle size = 125–710 μm; atmospheric pressure; inlet gas composition: N_2O = 500 ppm_v, He balance, the total gas flow: 1800 cm^3/min.

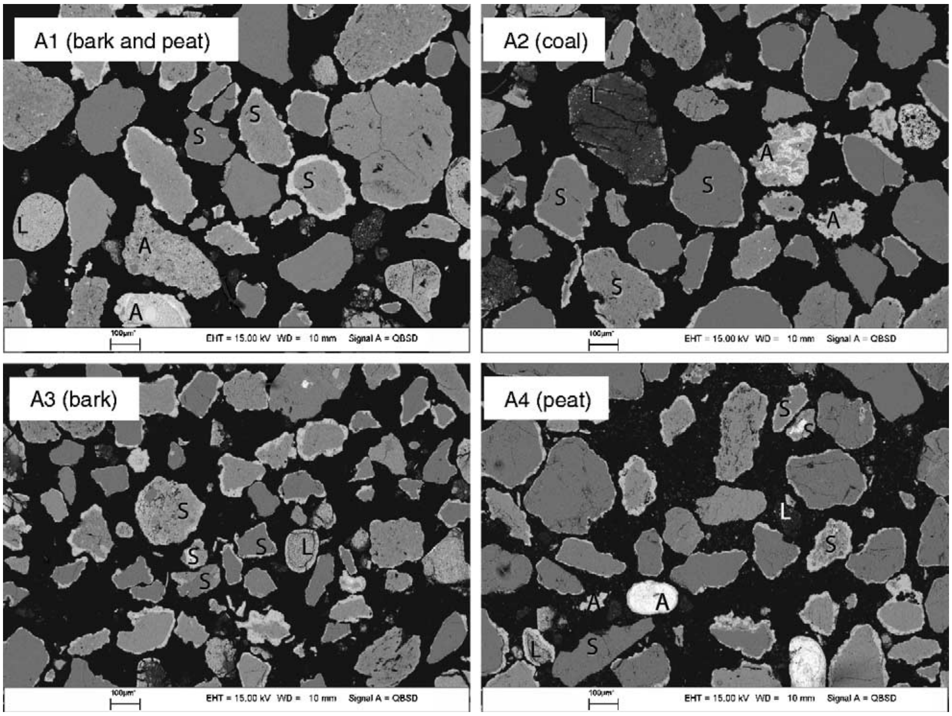

Fig. 3. SEM images showing cross-sections of the bed material samples: A, ash particles; S, sand particles; L, particles originating from limestone.

composition differed among the investigated fuels. Different activities for N_2O decomposition observed for these samples could not be attributed to the variation in the elemental composition [14].

The total BET surface area of the samples was measured by the means of N_2-physisorption, and it varied between 2.0 m^2/g and 2.9 m^2/g. The highest surface area was measured for the sample Ch3 (wood pellets and sludge B) and A4 (peat), which showed the highest activity among the samples from the12 MW_{th} and the 550 MW_{th} boilers, respectively.

The SEM/EDX analysis of the morphology and elemental composition of the surface of the particles, indicated that three types of particles could be distinguished: an ash particle, which is ash that remains after burning off the fuel; a sand particle, which consists of a quartz core coated with a layer originating from ash; and particles which were partially sulfated lime originating from limestone particles (only for samples from the 550 MW_{th} boiler). The composition of the surface layer of the ash particles resembled the composition of the fuel ash. In the case of samples from the 12 MW_{th} boiler, the elemental composition of the surface of the sand particle changed according to the composition of the ash from the parent fuel. In the case of samples from the 550 MW_{th} boiler, the changes in the elemental composition of the surface of sand particle with the fuel type were noticeable. However, those changes could not always be attributed to the composition of the ash from the parent fuel, and even more they did not correspond to the measured change in the activity of the bed material for the N_2O decomposition.

Further on, more detailed SEM/EDX analysis was carried out with the bed material samples from the 550 MW_{th} boiler. The samples were embedded in epoxy, cross-sectioned, and polished. The resulting cross-sectional areas are shown in Fig. 3 together with an average of a number of spot analyses taken at the surface of sand particles (Fig. 4). Clearly, three types of particles were distinguished: ash particles, sand particles, and particles originating from limestone. The amount of the ash particles was much smaller than the amount of the sand particles. In the case of the samples A1 (bark and peat) and A3 (bark), the ash type of particles originating from bark were not found probably due to small amount of ash in this fuel (Table 1). As in the case of the surface (above), the composition of the ash particles from cross-sections analysis, found in samples A1, A2 and A4,

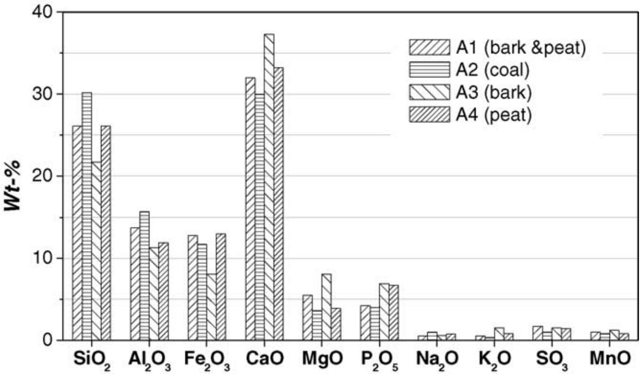

Fig. 4. Average of a number of spot analyses taken at the surface of sand particles.

resembled the composition of the parent fuel ash. In addition, cross-sectional analysis of the sample A2 (coal) showed the presence of ash particles originating from the fuel previously burnt, probably peat, which were covered with the new ash. The ash particles found in the sample A4 (peat) had a notable presence of iron (bright particles), which is typical for the peat fuel. These enriched iron containing particles may be partly responsible for the high activity of the A4 sample.

EDX analysis of the sand particle cross-sections showed the presence of two types of cores: quartz sand, around 99% of quartz (SiO_2); and natural sand, sodium and potassium aluminosilicate. Besides, agglomerates were found, mostly in the sample A3 (bark). The thickness of the coating layer on the sand particles was typically less than 10 μm, and rarely up to 40 μm, as shown in Fig. 4. A number of spot analyses were made randomly on coating layers of the sand particles, and an average is given in Fig. 4. Noticeably, the elemental composition of the coating layer of the sand particles (Fig. 4) changed according to the composition of the ash from the parent fuel (Table 1). The same trend was observed when measuring the surface composition by XPS analysis. The only exception was calcium, which was highest for the sample A4 (peat).

Even though limestone was not added during the full test experiments to the sample A3 (bark), particles originating from the calcined limestone were found in all four samples. However, the sulfation degree differed. In the samples A1, A2 and A4, both calcium sulfate particles and particles of calcium oxide with a layer of calcium sulfate were found. Samples A2 (coal) and A4 (peat) had a higher amount of calcium oxide particles than the sample A1 (bark and peat). In the sample A3 (bark), only calcium sulfate particles were found, and even more, some of them were covered with the ash.

The surface analysis of all the samples by XPS reveals that silicone is in the form of SiO_2. Both on the surface and in the subsurface layer (2–3 nm), calcium and magnesium were present as Ca^{2+} and Mg^{2+} ions while aluminum as Al^{3+} ions. Iron on the surface was a mixture of Fe^{3+} and Fe^{2+} ions while in the subsurface layer (2–3 nm), only Fe^{2+} ions were found. Sputtering may have caused the reduction.

The results obtained with cross-section analysis gave better understanding of the samples properties in terms of their catalytic activities. The activity of the bed material samples from the 550 MW_{th} boiler is most likely directed by the presence of lime (CaO). The presence of very porous lime particles was neither obvious from the elemental analysis, nor from the SEM/EDX surface analysis of particles, which showed only the presence of $CaSO_4$. The activity reported for lime is at least an order of magnitude higher than the activity of $CaSO_4$, for which the reported activity is similar to ash [1,6–12]. However, sulfation of freshly formed lime during the fluidized bed combustion is an on-going process, which causes a constant change in the activity of the bed material. The results obtained imply that in the case of no limestone addition, the elemental composition of the bed material, mostly sand particles, gives good correlation with the activity. In the case of limestone addition, besides the elemental composition of the sand particles, the rate of sulfation and the activity of the limestone are needed for building-up the correlation between the fuel properties, i.e. ash composition and the activity of bed material towards N_2O decomposition.

4. Conclusions

In order to correlate catalytic activity towards N_2O decomposition to the fuel type, a detailed characterization of the bed materials sampled from the bottom bed of two industrial CFB boilers burning biomass fuels and wastes was carried out. The bed materials consist of three types of particles, ash particles, sand particles, and particles originating from limestone, but the prevailing ones were the sand particles. The highest surface area was measured for the samples which showed the highest activity among the samples from the 12 MW_{th} and the 550 MW_{th} boilers. For all investigated samples, the elemental composition of the coating layer of the sand particles changed according to the composition of the ash from the parent fuel. In the case of no limestone addition, the elemental composition of the bed material, mostly sand particles, gave good correlation with the activity. The measured catalytic activity of the bed material samples increased with the increased amount of the catalytically active oxides (CaO, MgO, Fe_2O_3, Al_2O_3). Both on the surface and in the subsurface layer (2–3 nm), Ca^{2+}, Mg^{2+}, and Al^{3+} ions were present. Iron on the surface was a mixture of Fe^{3+} and Fe^{2+} ions while in the subsurface layer (2–3 nm), only Fe^{2+} ions were present. In the case of limestone addition, besides the elemental composition of the sand particles, the rate of sulfation and the activity of the limestone are needed for the correlation between the fuel properties and the activity of bed material towards N_2O decomposition.

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