

# Fly Ash Utilization for the Development of Low NO<sub>x</sub> Bed Materials

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**Abstract:** Screening tests for NO catalytic decomposition and NO catalytic reduction by CO on a series of fly-ash-derived materials have been carried out at FBC temperatures in a fixed bed quartz reactor. The samples prepared directly from biomass fly ashes appeared to have very high catalytic effects toward NO reduction by CO. Meanwhile, no activity was observed for catalytic decomposition of NO on the tested samples.

**Keywords:** Low NO<sub>x</sub> bed materials, high temperature catalyst, fly ash utilization.

## INTRODUCTION

Fluidized bed combustion (FBC) is an advanced technology of high thermal efficiency and fuel flexibility for heat and power production from solid fuels including biomass and municipal solid wastes. In an FBC plant, the combustion takes place in a bed of solid particles, fluidized by means of air blown through the bed from below. The bed is composed of sand, fuel, and ash. Due to the high heat capacity of the sand material compared to fuels and the relatively long residence time, the combustion can be completed at a relatively low temperature, typically of 800-900°C, with a high thermal homogeneity throughout the bed. In addition, additives can be easily introduced into the bed for controlling the emission of, for example, NO<sub>x</sub>, SO<sub>2</sub>, and heavy metals from the combustion process.

Recently, opportunities and challenges to develop a bed material for in-situ catalytic abatement of NO<sub>x</sub> in FBC, especially bubbling FBC plants of small and medium sizes, have been identified [1]. Various catalytic materials and processes for abatement of NO<sub>x</sub> at high temperatures were reviewed, which include De-NO<sub>x</sub> catalysis with, e.g., CO and C<sub>x</sub>H<sub>y</sub>, catalytic decomposition of NO to N<sub>2</sub>, and selective catalytic oxidation of NO<sub>x</sub> precursors (NH<sub>3</sub>, HCN) in combustion processes. In addition, direct fly ash utilization for the development appears to be a promising option of high feasibility. As a follow-up complementary step, screening tests for catalytic decomposition of NO and catalytic reduction of NO by CO on a series of fly-ash-derived materials have been carried out in a laboratory fixed-bed reactor at 750°C. This paper summarizes the first results from the tests.

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## 1. EXPERIMENTAL

### 1.1. Experimental Setup

A fixed-bed quartz reactor (Fig. 1), with an inner diameter  $d_i = 18\text{mm}$  and a length  $l = 625\text{mm}$ , coupled with heating, feeding, and analyzing devices was used for the tests. The reactor was operated at atmospheric pressure and heated by an electric tube furnace. The gas analysis was performed by means of a chemiluminescence NO<sub>x</sub> analyzer (200EH, Teledyne Instruments) and a gas chromatograph (Agilent Technology 6890N). Prior to the experiments the gas chromatograph and NO<sub>x</sub> analyzer were calibrated with certified calibration gases. The gas chromatograph was calibrated with N<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CO; the NO<sub>x</sub> analyzer was calibrated with NO.

An arbitrary gas mixture regulated mass flow controllers (Brooks 5850 E) was fed in to the reactor at a constant rate of 1800 ml/min at room temperature. The inlet concentrations of NO and CO were 300 ppmV and 2500 ppmV, respectively. These reactive gases were balanced separately by two flows of helium He-I and He-II, and met each other first just before passing the (catalyst) sample layer placed on a porous sintered quartz plate (fixed bed) located inside the reactor.

For the tests of NO catalytic reduction by CO, CO<sub>2</sub> was added to the gas mixture in order to prevent soot formation (C) from CO at elevated temperatures as the result of the Boudouard reaction (Eq. 1), which otherwise would cause bias in the measurements and graphite deposit that may block the gas line on the way from the reactor to the gas analyzers [4, 5].



### 1.2. Catalysts Preparation

The starting materials used for catalysts preparation are presented and briefly described in Table 1, of which sample

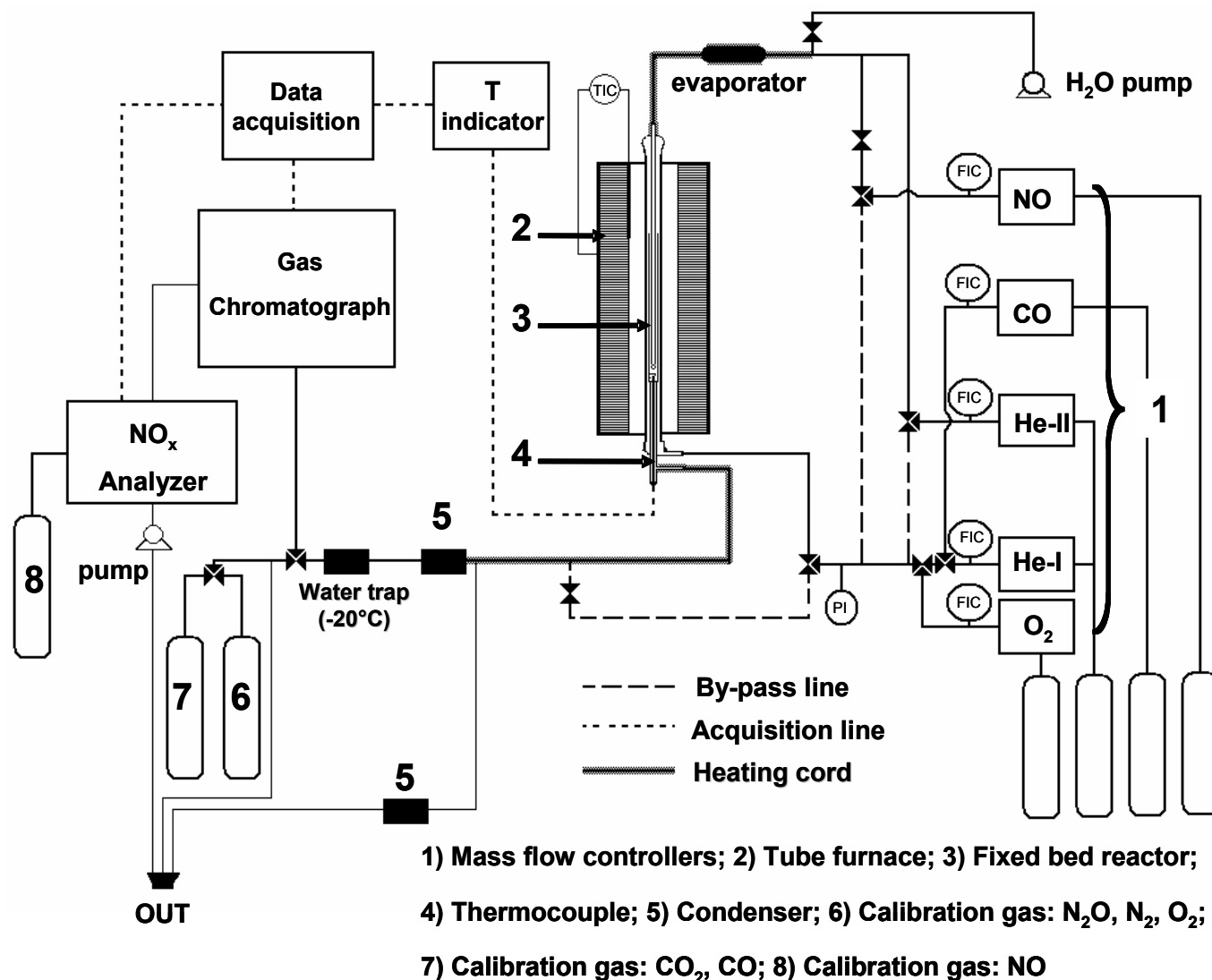


Fig. (1). The experimental set-up (Adapted from [2, 3]).

#3, NaP1-NA, was NaP1-type zeolite synthesized from coal fly ash collected from a pilot plant in Narcea, Spain. The synthesis conditions are summarized in Table 2. More details about the synthesis process can be found in the literature [6]. The chemical compositions of the fly ashes including the fly ash from Narcea are given in Table 3. Samples Elf2-4 and Elf2S3 are untreated fly ashes collected from the electric precipitator of an FBC plant in Falun, Sweden, during a research project burning wood chips without and with sulfur addition, respectively. More information about this project can also be found in the literature [7]. As can be seen in Table 3, most of the metals are present in sample Elf2-4 at a higher level than that in sample Elf2S3, which made the samples attractive to the present work.

In order to get catalysts suitable for the tests, the collected materials were sieved to obtain the portion of particle size smaller than 100  $\mu\text{m}$ , which were then pelletized at a pressure of 5 tons/cm<sup>2</sup> and calcined at 600°C for 4 hours. The pellets were subsequently crushed and sieved to obtain particles within the size range from 250  $\mu\text{m}$  to 355  $\mu\text{m}$ . An amount of 300 mg of the prepared catalysts was used for each test run.

Table 1. Tested Materials

Sample	Description
#1 Elf2-4	Fly ash from fluidized bed combustion of wood chips, from Falun, Sweden
#2 Elf2S3	Fly ash from fluidized bed combustion of wood chips similar to that of sample Elf2-4, with S addition during combustion
#3 NaP1-NA	NaP1 zeolite (Na <sub>6</sub> Al <sub>6</sub> Si <sub>10</sub> O <sub>32</sub> ·12H <sub>2</sub> O) synthesized from coal fly ash, from Narcea, Spain

### 1.3. Experimental Procedure

Before every test, the reactor loaded with 300 mg of the prepared catalysts was heated at a rate of 30°C/min under a constant Helium flow of 1800 ml/min at standard conditions in the absence of reactant gases until the catalyst reached the temperature of 900°C. Then oxygen (250 ml/min) was introduced into the reactor to support the burn-off process, eliminating combustible components of the catalysts as they

**Table 2. Experimental Conditions for the Synthesis of NaP1-NA Zeolite**

Reactor	R-410-A, stainless steel 304, 10 m <sup>3</sup>
Fly ash	2200 kg
Osmotized H <sub>2</sub> O	4400 kg
NaOH concentration	3 Molar
T, P, and t	125 °C, 3.55 kg/cm <sup>2</sup> , and 8 h
Cooling time	2 h
Filtration	Polypropylene press filters (F-406, 55 plates), 2 m <sup>3</sup> manual extraction membrane pneumatic pump (16 m <sup>3</sup> air/h), T = 90 °C, t = 1 h
Washing	T = 85 °C, t = 40 min water washing and 12 h of air drainage
Evacuation	Manual with 400 kg containers
Moisture	48% moisture content of the final product

were prepared from fly ashes and these components are not stable in the test conditions. The burn-off treatment was continued for 60 minutes and monitored by the GC, after which the oxygen was off and the system was flushed with Helium in 20 minutes. This procedure including the burn-off step has been established by previous studies at the lab [8] where the experiments of this present study were carried out. At the point when the system was ready for testing the catalyst, the reactant gases were introduced into the system in the order of NO, then CO<sub>2</sub> and CO.

**Table 3. Chemical Composition of the Starting Fly Ashes**

Element	Unit	Elf2-4	Elf2S3	Fly Ash for NaP1-NA
SiO <sub>2</sub>	%	14.7	13.4	55.2
Al <sub>2</sub> O <sub>3</sub>	%	2.28	1.9	23.3
CaO	%	36.1	32.9	4.0
Fe <sub>2</sub> O <sub>3</sub>	%	1.49	1	6.9
K <sub>2</sub> O	%	9.08	8.86	3.8
MgO	%	3.9	3.86	2.5
MnO	%	2.66	2.16	0.1
Na <sub>2</sub> O	%	1.04	0.89	0.7
P <sub>2</sub> O <sub>5</sub>	%	4.14	4.58	0.3
TiO <sub>2</sub>	%	0.08	0.07	0.9
Cl	%	1.1	1.1	NA
As	mg/kg	5.89	5.98	98
Ba	mg/kg	3270	2620	1047
Be	mg/kg	< 0.6	< 0.6	5
Cd	mg/kg	12.6	12.6	2
Co	mg/kg	8.75	8.39	30
Cr	mg/kg	67.3	41.2	177
Cu	mg/kg	134	127	86
Hg	mg/kg	0.62	0.72	NA
La	mg/kg	< 6	< 6	NA
Mo	mg/kg	9.18	< 6	6
Nb	mg/kg	< 6	< 6	NA
Ni	mg/kg	33.8	22.9	82
Pb	mg/kg	86.5	73.5	90
S	mg/kg	18000	35800	NA
Sc	mg/kg	< 1	< 1	NA
Sn	mg/kg	< 20	< 20	4
Sr	mg/kg	845	843	235
V	mg/kg	19	14.2	173
W	mg/kg	< 60	< 60	NA
Y	mg/kg	6.26	4.79	NA
Zn	mg/kg	3640	3080	171
Zr	mg/kg	37.4	28.8	NA

NA: Not available.

## 2. FIRST TEST RESULTS AND DISCUSSIONS

The concentration of NO in the off-gases was monitored and regarded as the outlet concentration of NO, which of the test at 750°C is represented in Fig. (2).

As can be seen in Fig. (2), the samples prepared directly from the biomass fly ashes (Elf2-4 and Elf2S3) appeared to have very high catalytic effects toward NO reduction by CO. Weak catalytic effects were observed for the sample prepared from the fly-ash zeolite (NaP1-NA). In addition, it has been observed that none of the tested samples showed pronounced effects on NO catalytic decomposition.

It is not surprised that none of the tested samples had catalytic effects on NO decomposition at 750°C due to the high activation energy of 364kJ/mol [9] according to Eq.2. This reaction may happen on the catalysts at higher temperatures.



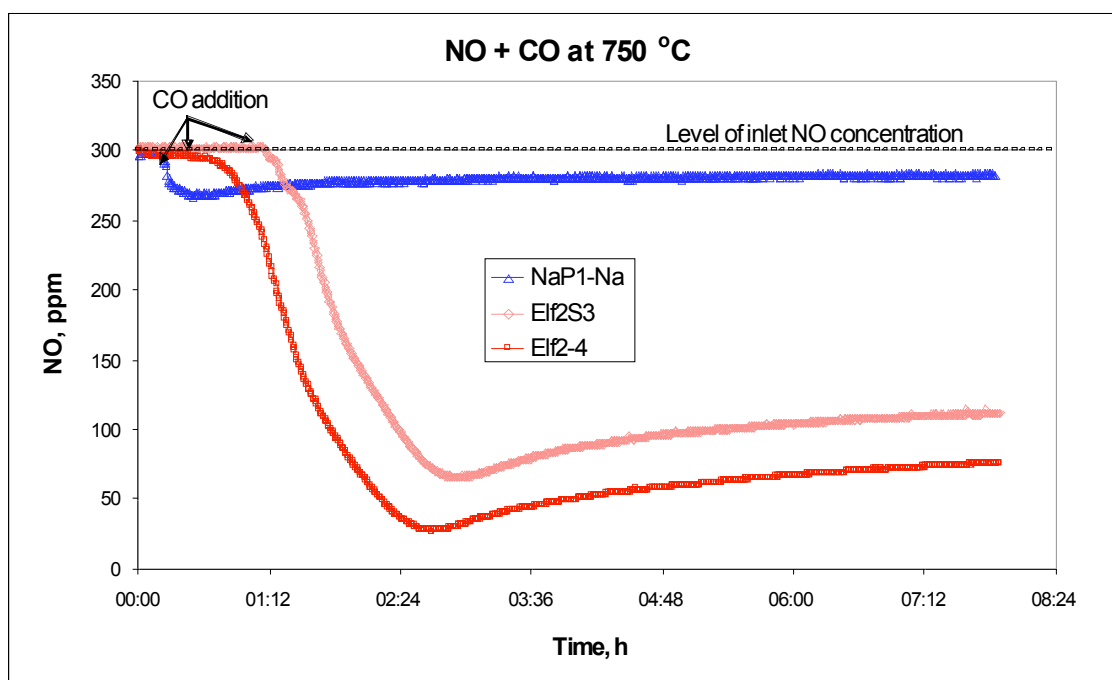
More importantly, however, all the tested samples showed catalytic effect towards the reaction of NO reduction by CO. This confirms the possibility of using fly ash as starting material for the development of low NO<sub>x</sub> bed materials.

The degree of NO conversion (X) was calculated directly from the inlet and outlet concentration of NO, according Eq.3.

$$X (\%) = [1 - [\text{NO}]_{\text{out}}/[\text{NO}]_{\text{in}}] \times 100 \quad (3)$$

The calculation showed that for samples Elf2-4 and Elf2S3 the degree of NO conversion was about 78% and 65%, respectively. In addition, the NO conversion for samples NaP1-NA was about 6% that is very close the measurement error within the order of magnitude of 3%.

In other words, the catalysts prepared directly from untreated fly ashes have showed much higher effects on catalytic reduction of NO by CO than that prepared from fly-ash zeolite. This indicates the importance of metals present on the catalysts, considering possible removals of the metals during the process of synthesizing NaIP-NA zeolite from it original fly ash, presented in Table 2. This assumption is also supported by looking at the difference in the metals content of the two samples prepared directly from fly ashes, Elf2-4 and Elf2S3. If this not the case, the observation can probably only be attributed to the difference in the content of Ba, Sr and Zn present in the original fly ashes given in Table 3,



**Fig. (2).** Catalytic reduction of NO by CO on the fly ash derived materials at 750°C.

which of the fly ash for NaP1-NA zeolite was least among the three samples.

### 3. CONCLUDING REMARKS

Three fly-ash-derived catalysts have been tested at 750°C in a fixed bed reactor operated at atmospheric pressure for NO catalytic decomposition and NO catalytic reduction by CO. It has been showed that all the samples catalyzed the reaction of NO reduction by CO, but none of them showed pronounced effects on NO catalytic decomposition. In addition, the importance of metals present on the catalysts towards NO reduction by CO was also discussed. At this stage, however, no firm conclusions have been drawn. Further investigations are therefore suggested, including catalyst characterizations and elemental analyses for the final products. The use of high-throughput-screening technology is recommended as the tests are at high temperatures and very time consuming.

This work of quick tests was to complement the previous literature study on *in situ* catalytic abatement of NO<sub>x</sub> in FBC. The work has confirmed the possibility of using fly ash as starting material for the development of low NO<sub>x</sub> bed materials.

### ACKNOWLEDGEMENT

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