Nitrogen oxides removal from flue gases using sodium bicarbonate

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Introduction

A coal accounts for nearly 60% of energy consumption in Poland. According to the Central Statistical Office in 2011, more than 79 million tons of coal was used, of which the biggest part accounts for power plants and thermal power plants [1]. The combustion of this material is associated with emissions of many substances harmful to health and to the environment. The permissible emissions are regulated by the Regulation of the Minister of Environment from 22nd of April 2011. The nitrogen oxides, in addition to sulfur dioxide, are especially undesirable substances in flue gases, hence the current emphasis is related with NO_x reduction, almost as high as with sulfur dioxide reduction. For coal-fired plants with a nominal thermal power of less than 50 MW, NO_x emission standards calculated to nitrogen dioxide are 400 mg/m^3 [2]. Such a low level of emissions often requires additional purifying system. The solution is a dry flue gas cleaning method in which dry sorbent is injected into the flue gases. In contrast to the wet method, dry method does not require a great deal of capital or conversion of installation and it is possible to be implemented in both: new and existing buildings. Sodium bicarbonate is a successfully used substance in this method, which beside of SO_2 removal, has the ability to remove other acidic pollutants, such as NO_x.

In the seventies of the last century there was an interest in the reaction chemistry of sodium bicarbonate in the solid phase with nitrogen oxides. The first studies on $NaHCO_3$ reactivity with NO_x have been published by Knight (1977) [3], which conducted the laboratory tests on reactivity of both: sodium carbonate and sodium bicarbonate with NO_x in flue gases. He claimed that the reaction with NO occurs only in the presence of free oxygen, in contrast to NO_2. He showed that sodium carbonate reacts with NO_2, without oxygen to form sodium nitrate:

$$Na_2CO_3 + 3NO_2 \rightarrow 2NaNO_3 + NO + CO_2 \qquad (1)$$
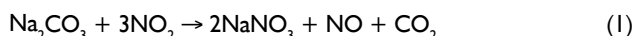
This reaction was verified by Bland [4], which in addition to the reaction of sodium bicarbonate with NO_x without SO_2, allowed the other reaction pathway, i.e. he adopted the reaction of sodium bicarbonate with nitrogen dioxide in the presence of SO_2. According to Bland, Na/SOx intermediate compound forms in this reaction, depending on the temperature. Below 120°C, which is a temperature below $NaHCO_3$ decomposition, the reaction runs according to the following scheme (2):

$$2NaHCO_3 + SO_2 \rightarrow Na/SO_x \text{ intermediate} + CO_2 + H_2O \qquad (2)$$

The resulting Na/SO$_x$ intermediate can be converted here into a final sodium sulfite product, according to the scheme (3):
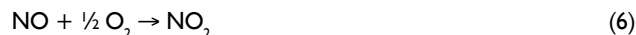
$$Na/SO_x \text{ intermediate} \rightarrow Na_2SO_3 \qquad (3)$$
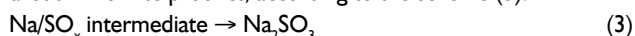
At the temperature above 120°C the decomposition of $NaHCO_3$ to sodium carbonate occurs:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \qquad (4)$$
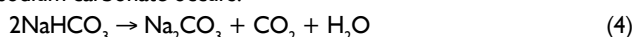
In this temperature range, according to Bland, sodium carbonate reacts with SO_2 to form Na/SO$_x$ intermediate :

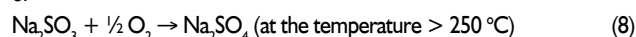$$Na_2CO_3 + SO_2 \rightarrow Na/SO_x \text{ intermediate} + CO_2 \qquad (5)$$
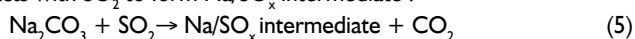
Intermediate Na/SO$_x$ produced in that stage catalyzed heterogeneously oxidation of nitrogen oxide to nitrogen dioxide:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad (6)$$

Na/SO$_x$ intermediate may also be converted into sodium sulfite or sodium sulfate, depending on the temperature:

$$Na/SO_x \text{ intermediate} \rightarrow Na_2SO_3 \text{ (at the temperature} < 150\,°C) \qquad (7)$$

or

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \text{ (at the temperature} > 250\,°C) \qquad (8)$$
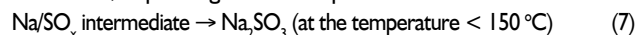
Nitrogen dioxide formed in reaction (6) reacts with sodium carbonate, according to reaction scheme (1) approved by Knight.

The authors [3, 4] argued that there is dependence of sodium nitrate formation obtained by thermal activation of sodium bicarbonate, on the degree of development of surface area. The amount of obtained sodium nitrate increased with development of surface area and decreased with increasing temperature.

Tests on laboratory scale carried out on the circulating fluidized bed were conducted by Verlaeten and others [5] and demonstrated the effectiveness of sodium bicarbonate in the nitrogen oxides removal at the level of 60%, while SO_2 removal at the level of 90%. The most effective nitrogen oxides removal were observed in the temperature range 127–160°C, above which the NO_x removal is significantly reduced. Such as high efficiency is related to the decomposition of sodium bicarbonate to sodium carbonate, as shown in the reaction (4), which, according to several authors [6, 7, 8, 9, 10] takes place at temperatures of 67–125°C, depending on the partial pressure of CO_2 and H_2O. The resulting sodium carbonate apparently changes its microstructure on porous material and its surface area increases from less than 1 m^2/g up to 7–10 m^2/g after decomposition.

The effectiveness of sodium sorbents in NO_x removal from gaseous products of combustion, similarly as in dry desulfurization processes [11], can be assessed by one of the criteria: NO_x removal efficiency in time, determined as:

$$\frac{\text{amount of } NO_x \text{ removed from flue gases}}{\text{amount of } NO_x \text{ introduced with flue gases}} \cdot 100\%$$

The value of this criterion is affected by several parameters associated with both the purified gas and sorbent used. These parameters are: process temperature, the contact time of the sorbent with the purified gas, NO_x concentration in the purified gas, sodium sorbent particle diameter, surface area. To increase the sorption ability of sodium sorbents, the mechanical activation (mainly grinding) before entering it into the gas stream is used [12].

The laboratory results presented in this paper show the effect of mechanical activation of chosen sodium sorbents on NO_x removal efficiency from the model gases, depending on the process temperature: at 300°C and at 850°C.

Experimental

Materials

The materials used in the studies were: sodium bicarbonate in the form of baking soda of standard class and intermediate product

obtained during production of sodium carbonate by Solvay – raw bicarbonate. Sodium bicarbonate was characterized by a purity of 99.9% and an average grain diameter of 126 microns, while raw bicarbonate contained 2.75% of ammonium compounds, mainly in the form of NH_4HCO_3 and the average grain diameter of 140 microns. The ammonium compounds present in the sorbent should positively impact on the process of NO_x removal from flue gases.

Analytical methods and apparatus

Studies of sorption ability of sodium sorbents in nitrogen oxides removal were carried out at temperatures of 300 and 850°C, what corresponds to the temperature in the second stage of the boiler on the outlet of flue gases in combustion plants and to the temperature in combustion chamber in fluidized bed boilers. Before sorption tests sodium sorbents were activated mechanically by grinding on fine impact mill. Raw bicarbonate before milling was dried at the temperature of 50–60°C, in which decomposition of sodium bicarbonate does not occur and the decomposition of ammonium compounds is limited. The 160 UPZ mill from Hosokawa-Alpine was used for impact milling, where the grinding process depends on impact of the steel tines spaced on the shield and on the spinning rotor. Particle size distribution of grounded products was measured on a Beckman Coulter laser analyzer LS 13320, using a wet measuring module. Applied method was consistent with ISO requirements on particle size analysis by laser scattering method [13].

Mechanically activated sodium products, ungrounded sodium bicarbonate and raw bicarbonate were then subjected to analysis of active surface area, using the method of Brunauer, Emmett, Teller (BET). Investigated sorbents were degassed in a vacuum with helium, in order to remove impurities, which include moisture. Tests were carried out on the Gemini VII 2390 a type surface area analyzer, which measures the volume of gas adsorbed at the temperature of -196°C in the relative pressure range of 0.05–0.3. The surface area, which comprises surface of solid, surface of open pores (m^2/g), have allowed the classification of the material in accordance with IUPAC (International Union of Pure and Applied Chemistry). This parameter was determined before and after mechanical activation of sorbents and after their thermal decomposition at the temperature of 250°C.

The impact of structural parameters on the sorption ability of sorbents with respect to NO_x from model gases was verified by laboratory tests carried out on the test bed, as shown in Figure 1.
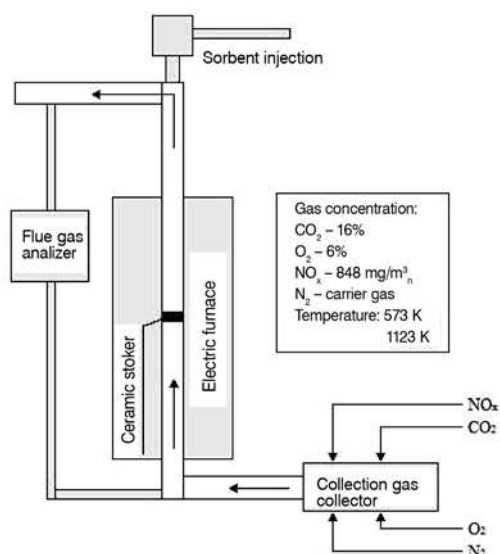

Fig. 1. The laboratory test bed to determine the sorption ability of the model gases

The main element of the test bed was electric furnace with a quartz column. The sorbent and a model gas in the flow of 1.2 m^3/h

containing nitrogen oxides at a concentration of 848 mg/m_n^3 (500 ppm), oxygen (6%), carbon dioxide (16%), and nitrogen as a carrier gas were introduced to the column. The studies were involved in the application of sorbents in parts of 6 g to the stream of model gases and were conducted in two temperature ranges in the reaction chamber: 300°C and 850°C. After injection the part of sorbent into the reaction zone the analyzer registered NO_x concentration in flue gases in every second and averaged it to the value in every 10 seconds. Nitrogen oxides were controlled by regulation system: the controller coupled with flow meter and volumetric flow controller. The flow of other gases was monitored and regulated by reducers and flow meters. The concentrations of the gaseous component were measured with flue gas analyzer GASMET DX-400, using FT-IR method (Fourier Transform Infrared Spectroscopy Fourier-transform infrared).

Experimental results

Sodium sorbents used for the studies were characterized by a very similar particle size distribution (Fig. 2), which confirms an average grain diameter and surface area obtained (Tab. 1).
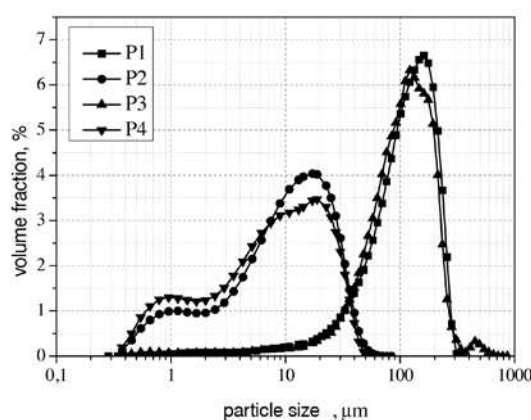

Fig. 2. The particle size distribution of sodium bicarbonate and raw bicarbonate before and after grinding

An unimodal size distribution of the grounded sorbents shifted towards the finer grains as a result of mechanical activation. Average grain of grounded sorbents decreased from 126 μm to 13.2 μm for the sodium bicarbonate and from 123.4 μm to 11.5 μm for the dried raw bicarbonate. The grain size analysis and BET surface area measurements showed small relationship between the grains size and the surface area of a material. Mechanical activation slightly affected the growth of surface area. A significant increase in surface area of tested sorbents was possible to achieve by thermal activation, which is used in industrial processes for the purification of flue gases, using sodium sorbents. The structural properties of sorbents are presented in Table 1.

Table 1

The structural properties of analyzed sorbents

Sample number	Material	Average grain, μm	Surface area, m^2/g	
			Lack of thermal activation	Thermal activation in 300°C
P1	Ungrounded sodium bicarbonate	126.0	0.07	3.99
P2	Sodium bicarbonate after impact milling	13.2	0.73	5.97
P3	Ungrounded raw bicarbonate	123.4	0.34	5.87
P4	Raw bicarbonate after impact milling	11.5	1.02	7.31

The influence of thermal activation on a surface area of sodium sorbents was tested at a temperature of 300°C. The own studies [14], as well as the literature [15] states, that above this temperature sintering and pore plugging occurs, which is caused by sodium bicarbonate decomposition. At a temperature above 450°C. there is return to original surface area. Using thermal activation at 300°C resulted in increasing the surface area of sorbents, as shown in Table 1. The largest surface area development was obtained for the raw bicarbonate, subjected to mechanical activation and its surface area increased from 1.02 m²/g to 7.31 m²/g

In studies of nitrogen oxides removal efficacy from model gases, sorbents without and after mechanical activation were used, as shown in Table 2, using the methodology described above.

Table 2

Samples of sorbents used for the studies

Sample number		Process temperature	Material
P1	a	300°C	Ungrounded sodium bicarbonate
	b	850°C	
P2	a	300°C	Sodium bicarbonate after impact milling
	b	850°C	
P3	a	300°C	Ungrounded raw bicarbonate
	b	850°C	
P4	a	300°C	Raw bicarbonate after impact milling
	b	850°C	

After injection of tested sorbents sample into gas flow model, a rapid short-term decrease in NO$_x$ concentration followed, which returned to baseline after a period from 200 to more than 600 seconds, depending on the type of sorbent used.

To assess the effectiveness of nitrogen oxides removal by sodium sorbents, two criteria were used: partial efficiency and overall efficiency of NO$_x$ removal. Partial NO$_x$ removal efficiency in the time interval of the experiment was determined by the following equation:

$$\varphi(t) = \frac{c_0 - c_t}{c_0} \cdot 100\% \tag{9}$$

where:
C_0 – inlet NO$_x$ concentration, ppm NO$_x$
C_t – outlet NO$_x$ concentration after time t, ppm NO$_x$
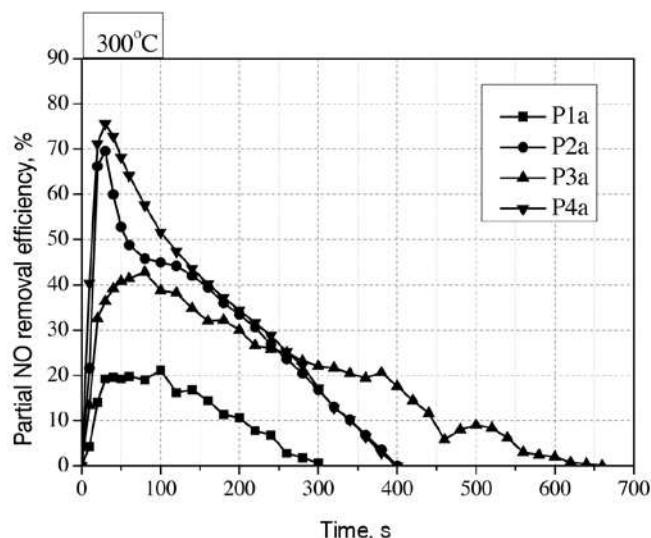

Fig. 3. The partial NO$_x$ removal efficiency at the temperature of 300°C

At the temperature 300°C in the first seconds of the experiment the effect of nitrogen oxides removal was observed, particularly for sorbents after mechanical activation (Fig. 3). For these sorbents was also achieved the highest partial NO$_x$ removal efficiency, about 75% in case of raw bicarbonate and almost 70% for sodium bicarbonate. For ungrounded sorbents NO$_x$ removal efficiency was lower, almost 43% for ungrounded raw bicarbonate, and only about 21% for ungrounded sodium bicarbonate.

Better effect of NO$_x$ removal was obtained for grounded sorbents at process temperature of 850°C (Fig. 4). Similarly as for the temperature of 300°C, maximum partial NO$_x$ removal efficiency was obtained for grounded sorbents, which in 40th second duration of experiment was 84–85%. Ungrounded sodium products also obtained much lower NO$_x$ removal efficiency, comparing with grounded materials.
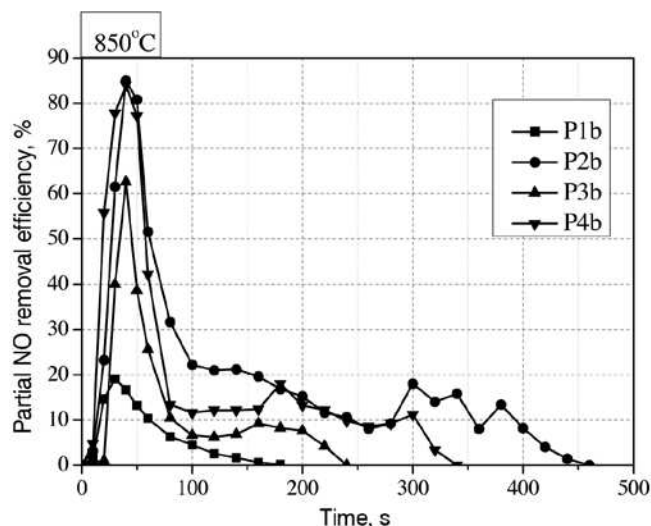

Fig. 4. The partial NO$_x$ removal efficiency at the temperature of 850°C

The results of measurements of NO$_x$ concentration were also used to determine the overall NO$_x$ removal efficiency from model gas, which was defined as the ratio of moles of NO$_x$ removed from gases to moles of NO$_x$ introduced, determined from the equation:

$$\varphi = \frac{\int_0^t (c_0 - c_t)dt}{c_0} \cdot 100\% \tag{10}$$

where: t – the reaction time, s

The overall NO$_x$ removal efficiency is the sum of the partial efficiency, determining the effect of sorption from the beginning to the specified time interval of the process. For sorption carried out at a temperature of 300°C, the highest overall removal efficiency of nitrogen oxides was obtained for grounded sorbents, the best result was observed in the case of raw bicarbonate – 60%, and for sodium bicarbonate – about 49% (Fig. 5). Grounded sorbents reacted faster, than ungrounded ones, it may be the result of better contact of smaller grains with NO$_x$ in the gas stream model. After obtaining the maximum value, NO$_x$ removal efficiency of these sorbents rapidly decreased, what can be a result of a partial entrainment of fine grounded material by gas stream. For sorbents without mechanical activation, the highest NO$_x$ removal efficiency was achieved only after 100–140 seconds and it was much lower. For raw bicarbonate it was about 36% and for sodium bicarbonate – only 17%.

At a temperature of 850°C overall NO$_x$ removal efficiency for all sorbents was lower than the values obtained at 300°C (Fig. 6). This is due to the lower process dynamics, grains reacted with a slight delay, thus they received smaller increase in efficiency. The overall efficiency was achieved after about 60 seconds and the highest value was observed for the sorbents after grinding, which ranged from 53% for raw bicarbonate to 47% for sodium bicarbonate. Sorbents without grinding showed much lower values of 12–26%.
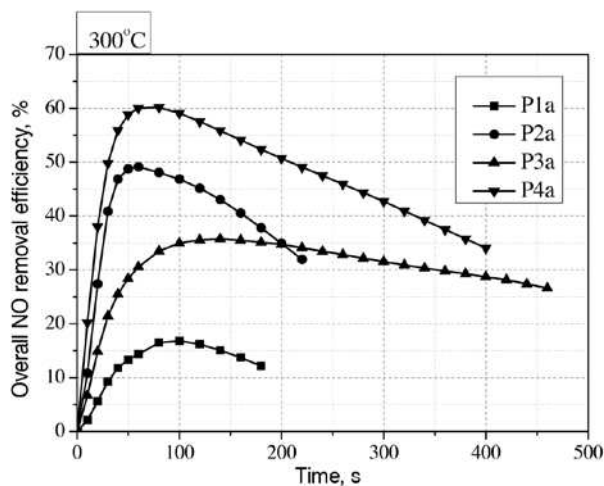
Fig. 5. The overall NO$_x$ removal efficiency in the flue gases at the temperature of 300°C
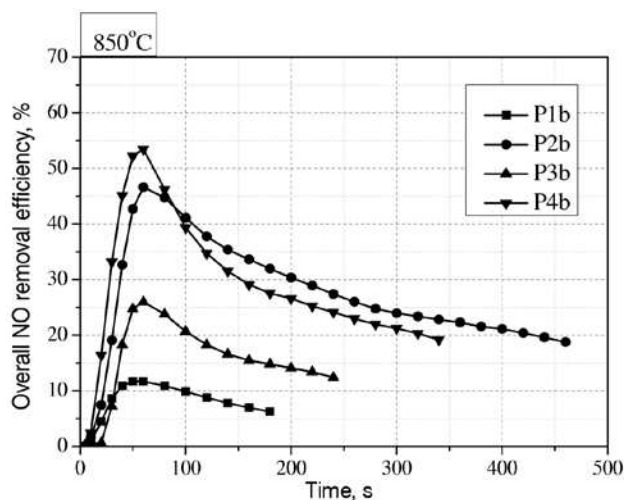

Fig. 6. The overall NO$_x$ removal efficiency in the flue gases at the temperature of 850°C

Table 3 shows the calculated values of criteria discussed above, which were set for the total time intervals of sorption process with parameters, that may have an impact on these values for all tested sorbents.

<div align="right">Table 3</div>

The results of NO$_x$ removal

Material	Sample number	Temperature, °C	Reaction time, s	Overall NO$_x$ removal efficiency, %	NO$_x$ removal efficiency, %
Sodium bicarbonate ungrounded	P1a	300°C	310	21,2	11,8
	P1b	850°C	180	21,6	6,2
Sodium bicarbonate after impact milling	P2a	300°C	400	69,6	31,9
	P2b	850°C	460	85,0	18,8
Raw bicarbonate ungrounded	P3a	300°C	650	42,8	20,1
	P3b	850°C	240	62,6	12,4
Raw bicarbonate after impact milling	P4a	300°C	400	75,6	34,0
	P4b	850°C	340	84,0	19,1

The results presented above suggest that grounded sodium sorbents exhibit a higher ability to remove nitrogen oxides, comparing with sorbents not subjected to mechanical activation at both temperatures of 300°C and 850°C. Aside from particle size,

also temperature is a factor affecting the process efficiency. As the temperature increased, the overall NO$_x$ removal efficiency of sorbents also increased. The exception was ungrounded sodium bicarbonate, which did not show such as tendency. A much better sorbent for NO$_x$ removal was dried raw bicarbonate in comparison with sodium bicarbonate, in both cases: before and after grinding.

The overall nitrogen oxides removal efficiency is related to time intervals of sorbents action, which was measured from the time of injection the sample into model gas stream to time of return of measured NO$_x$ concentration to the initial value. The obtained results for all sorbents show rapid but short – time reactivity towards NO$_x$. Better and more dynamic effects were observed for mechanically activated sorbents. In that case reaction followed after about 60 seconds. Carrying out sorption at 300°C. in most cases slightly longer reaction time intervals of sorbents, up to 650 seconds, were obtained. They were caused by the slower return of analyzed gas to the initial concentration. Increasing the process temperature to 850°C significantly reduced time interval of sorption.

The highest maximum effectiveness and maximum NO$_x$ removal efficiency was observed for grounded raw bicarbonate, while the shortest running times and the weakest reactivity was obtained for ungrounded sodium bicarbonate, for which the overall removal efficiency of nitrogen oxides was the lowest from all sodium sorbents used.

Conclusions

The studies of removing nitrogen oxides with sodium sorbents from model gases indicates their short-term exposure, regardless of the type and temperature sorption used. Time interval of sorption, i.e. the time, at which after sorbent injection, the NO$_x$ concentration in the flue gases returned to the initial value, for the studied sorbents was in the range of 240–650 seconds. The highest decrease in nitrogen oxides concentration occurred after about 30–50 seconds, regardless of the type of sorbent and sorption temperature, in contrast to achieved NO$_x$ removal efficiency. The highest NO$_x$ removal efficiency (84–85%) was obtained using the mechanical activation of sorbents: sodium bicarbonate and raw bicarbonate at sorption temperature of 850°C. For these sorbents after a sharp drop, a rapid increase in NO$_x$ concentration was followed. Slightly worse results were obtained for the temperature of 300°C, using the same sorbents, NO$_x$ removal efficiency: 70% and 75% were obtained, but at these temperatures sorbents exhibit longer time intervals of action. The worst result was obtained by using sodium bicarbonate without mechanical activation in both 300°C and 850°C, where overall NO$_x$ removal efficiency was only about 21%.

The obtained results show that high ability to remove nitrogen oxides by sodium sorbents is mainly due to the applied mechanical activation. Sorbents without mechanical activation were not achieved such a high nitrogen oxides removal efficiency. The form in which sodium bicarbonate is used, i.e. baking soda or raw bicarbonate has much less impact on the process.

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