

# Kinetics of Nitrogen Oxide Reduction by Means of Ammonia on a Polish Carbon Sorbent

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## Abstract

This paper studies nitrogen oxide reduction by means of ammonia in a flow reactor with a fixed bed of the Polish carbon sorbent AKP-5. The kinetic curves  $\beta(t)$ , showing the dependence of the degree of reduction of nitrogen oxide on time have been determined for four inlet NO concentrations. On the basis of the degree of NO reduction determined for the steady state conditions, a simplified model of the kinetic equation has been developed and verified. The results obtained are very important for environmental protection.

**Keywords:** nitrogen oxides, carbon sorbent, selective catalytic reduction, kinetics of reaction

## Introduction

The process based on the use of specially prepared carbon sorbents (so-called active cokes) is an interesting modification of the selective catalytic reduction (SCR) method. In this process the sorbent plays a double role: it is both an adsorbent of nitrogen oxides and a classical catalyst of NO<sub>x</sub> reduction. An advantage of this method is the low temperature of the process (100 ÷ 170°C). Moreover, a combined desulfurization of the combustion gases and the removal of other harmful components like heavy metals, dioxins, furans and polycyclic aromatic hydrocarbons are possible in this process [1-6].

The reduction of NO<sub>x</sub> by ammonia on the surface of a carbon sorbent in the presence of oxygen and steam is a complex multistaged process. There are two fundamental difficulties in describing this process. It is a heterogeneous process, taking place on the porous surface of the carbonic material. It consists of successively – parallel steps, viz., the transport phenomena (external and internal diffusion

of reactants), the physical adsorption and chemisorption of the substrates on the surface, and a series of catalytic surface reactions. Moreover, the process occurs according to a complex chemical mechanism [7]. In the case of the SCR process, the reduction of NO<sub>x</sub> by ammonia is most often described by the following overall equation:



The reaction of higher nitrogen oxides (NO<sub>2</sub>) is neglected, because their share in combustion gases is rather small (below 5 % vol. of the total amount of nitrogen oxides).

The present paper provides results of a study on the kinetics of the reduction of nitrogen oxides by ammonia on the Polish carbon sorbent AKP.

## Materials and Methods

The study was carried out on the Polish carbon sorbent AKP-5, meant to be used for industrial purification of combustion gases [8, 9]. This is a carbon sorbent which

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sorbent which has been produced by Gryfskand in Hajnwka, Poland, since 1990 under the trade name ‘‘active coke AKP’’. The raw material is coal dust as well as an aqueous solution of a starch binder. The granulated product is dried at 350C and then carbonised at a temperature of up to 900C and activated by steam at 800C. The obtained product is characterised by high mechanical strength, a high ignition temperature, and a small surface area. Therefore, it may qualify as a carbon carbonisate. The product is in the form of grains of 5 or 10 mm. Active coke AKP-5 is widely used in the Bergbau-Forschung process. The fundamental physico-chemical properties of this sorbent have been collected in Table 1.

The process of reducing nitrogen oxides was investigated in a system of four reactors connected in a series with a fixed bed of carbon sorbent AKP – Fig 1. Each reactor had a diameter of 0.038 m and a height of 0.3 m. Total height of the sorbent was 1.2 m and total weight of the sorbent was 0.88 kg. The set of reactors was thermostated by polyethylene glycol. All the measurements were carried out at a temperature of 120C. A model gas mixture containing nitrogen, nitrogen oxide NO, ammonia and steam, was passed through this reaction system. The flow rate of the gas was determined by means of flow mass controllers. Steam was conducted to gas flow by evaporation of water in a special mixer-vaporizer. The composition of the applied gas mixture was approximately the same as that of the average composition of combustion gases: i.e. 6% by vol. of oxygen and 10% by vol. of steam. In the experiments, the concentrations of nitrogen oxide ( $x_{01}$ ) and ammonia ( $x_{02}$ ) varied but volumetric ratio of both these gases was constant ( $n = x_{01}/x_{02} = 1$ ). The assumed ratio  $n = 1$  warranted a stoichiometric amount of ammonia in relation to nitrogen oxide (NO) resulting from reaction (1). The total gas flow rate was  $F_{OV} = 0.45 \text{ nm}^3/\text{h}$ , which corresponded to the linear flow rate of the gas through the reactor  $u = 0.11 \text{ m/s}$ . This corresponds to the industrial and testing sorbent conditions [4,6,8,11].

In investigation of flow processes with different heights of the sorbent bed a favourable independent variable is the contact time of the gas with the sorbent bed. The applied

set of reactors and flow of  $F_{OV} = 0.450 \text{ nm}^3/\text{h}$  allowed measurements for various contact times  $\tau$  from 2.7 to 10.9s.

The concentrations of nitrogen oxide at the inlet to the system  $x_{01}$  and at the outlet of each reactor  $x_1$  were determined ‘‘on line’’ by URAS 10E analyser connected with a computer system. The process was monitored until the steady state of the whole system was established. In practice, this was achieved after the NO concentrations at each reactor outlet had been stabilised.

For practical reasons, a dimensionless degree of reduction of nitrogen oxide  $\beta$  was assumed to be:

$$\beta = 1 - \frac{x_1}{x_{01}} \quad (2)$$

where:  $x_1$  – mole fraction of NO at the outlet of reactor,  $x_{01}$  – initial mole fraction of the NO determining that part of nitrogen oxide which has been reduced by means of ammonia in the sorbent bed with a given height.

## Results and Discussion

The reduction of nitrogen oxides was investigated for four different inlet concentrations of NO in the model gas, viz. 500, 1000, 2500 and 5000 ppm. The following parameters were constant: the concentration ratio of ammonia to nitrogen oxide  $n = 1$ , composition of the gas mixture: 84% by vol.  $N_2$ , 6% by vol.  $O_2$ , 10% by vol.  $H_2O$  process temperature 120C. Each experiment took at least 15 hours.

The system of four reactors arranged in a series enabled to determine the effect of the contact time of the gases with the sorbent bed on the process of the reduction of  $NO_x$ . The independent variables were the contact time  $\tau$  and the inlet NO-concentration  $x_{01}$ . The resulting quantity was the degree of reduction  $\beta$ . The exemplary dependencies  $\beta(t, \tau)$  obtained at inlet NO-concentrations  $x_{01} = 500 \text{ ppm}$  NO are presented in Fig.2.

As expected, with increasing contact time of model gases with the sorbent bed, the degree of the reduction of NO increases. The curves  $\beta(t)$  under various contact times and constant inlet concentration of NO, look similar. Any change of the contact time results only in a parallel shift of a curve. A stabilisation of the degree of reduction can be observed (that means the outlet NO-concentrations are constant). This enables an approximate determination of the time of the non-stationary operation of the reactor. This time is rather long (from 5 to 10 hours), according to the inlet NO-concentration. This long time of the non-stationary process proves the complex character of the reduction of NO in a reactor with a carbon sorbent bed.

On the basis of the data presented the average values of the degree of reduction under steady state conditions were determined. The results are shown in Fig. 3 as a function  $\beta = f(x_{01}, \tau)$ . The degree of reduction  $\beta$  increases with the contact time and increasing NO-concentration in the gas phase. The obtained curves tend to the limit value,

Table 1. Properties of the carbon sorbent AKP-5 [10].

Grain diameter	5.2 mm
Bulk density	680 kg/m <sup>3</sup>
Moisture	2.0 %
Content of ash	7.9 %
Mechanical strength	99.9 %
Grindability (0.5 h)	2.0 %
Ignition temperature	425C
Absorbability of water	0.424 cm <sup>3</sup> /g
Standardized sorption capacity [11]	35.2 g SO <sub>2</sub> /kg
Specific surface	192 m <sup>2</sup> /g

irrespective of the NO-concentration. Maximum values of the reduction degree ( $\beta = 0.75$ ) was achieved at contact time  $\tau = 10.7$  s. Hence, the essential practical conclusion may be drawn, in order to get a high efficiency in the removal of nitrogen oxide the contact time of the purified gases with the sorbent bed should be at least 10 seconds. At a flow rate of  $u = 0.11$  m/s, the height of the sorbent bed should be at least 1.2 meters.

The results presented in Fig. 3 refer to the steady state and can be used for the kinetic interpretation of the process. Therefore, it has been assumed that the reduction of nitrogen oxide by ammonia on a carbon sorbent may be expressed by the following overall stoichiometric equation (1).

The above reaction is a contact one, in which the surface phenomena of catalysis and adsorption are important. The rate of such a process can be generally described by the Watson-Hougen's model. Because the reaction is irreversible and the oxygen concentration (6% by vol.) is high compared to those of NO and  $\text{NH}_3$ , being therefore practically invariable, a simplified model of the kinetic equation can be applied:

$$r_1 = \frac{kc_1c_2}{1 + Ac_1 + Bc_2} \quad (3)$$

where:  $r_1$  – rate of the process in relation to nitrogen oxide;  $k$  – reaction rate constant,  $A$ ,  $B$  – adsorption constants;  $c_i$  – molar concentration of the reactant  $i$ .

The stoichiometric balance equation, assuming that the density of the reaction mixture is constant, is as follows:

$$c_i = c_{0i} + \frac{v_i}{|v_1|} c_{01} \beta \quad (4)$$

where:  $v_i$  – stoichiometric index (coefficient) of the reagent  $i$ ,  $c_{0i}$  – initial molar concentration of the reactant  $i$ .

Because the inlet concentrations of the nitrogen oxygen and ammonia were the same  $c_{01} = c_{02}$ , and taking into account equation (4) the following equation can be obtained:

$$c_1 = c_{01}(1 - \beta) \text{ and } c_2 = c_{02} - c_{01}\beta = c_{01}(1 - \beta) \quad (5)$$

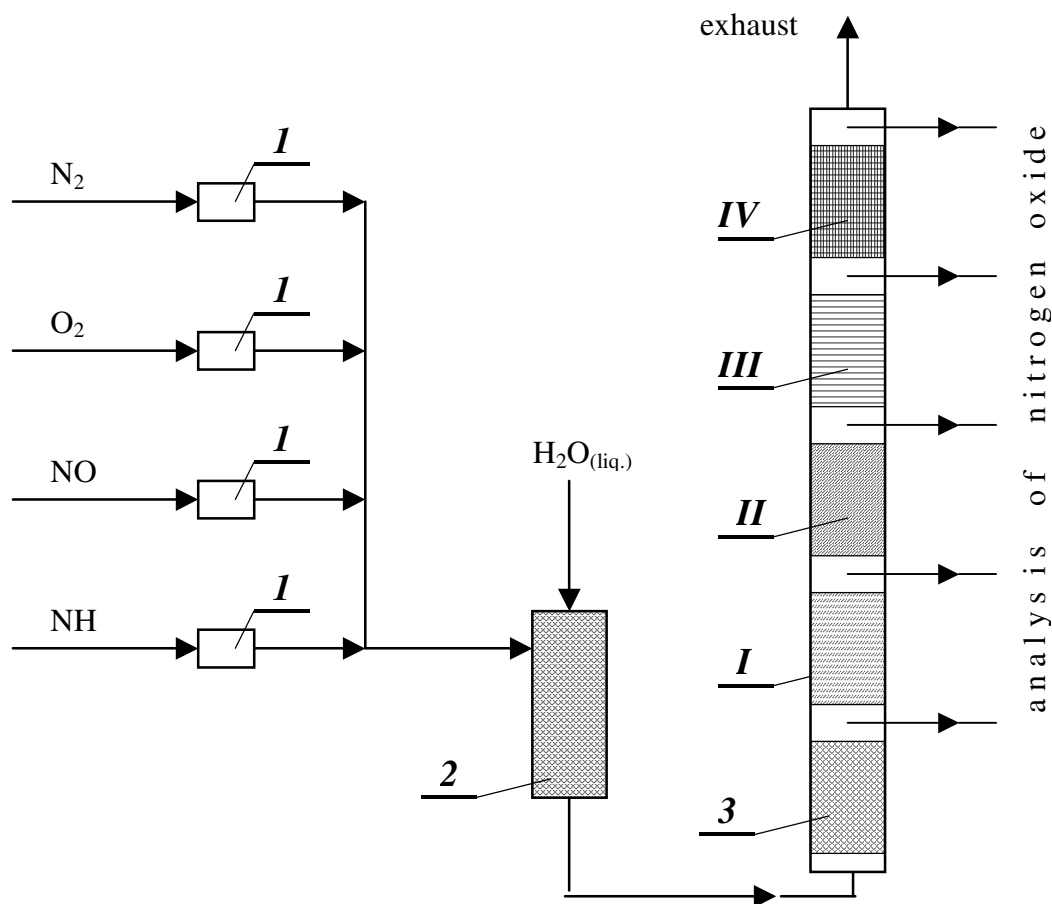


Fig. 1. The schematic diagram of the apparatus. 1 – mass flow controllers, 2 – mixer-vaporizer, 3 – heating coil, I-IV – reactors with sorbent.

Then the kinetic equation is in the following form:

$$r_1 = \frac{kc_{01}^2(1-\beta)^2}{1+Dc_{01}(1-\beta)} \quad (6)$$

where:  $D = A + B$ . Taking into account the definition of the reaction rate of the flow process:

$$r_1 = -\frac{dc_1}{d\tau} = c_{01} \frac{d\beta}{d\tau} \quad (7)$$

the differential form of the assumed kinetic equation was obtained:

$$\frac{d\beta}{d\tau} = \frac{kc_{01}(1-\beta)^2}{1+Dc_{01}(1-\beta)} \quad (8)$$

Solving this differential equation for the initial conditions  $\tau = 0$  and  $\beta = 0$ , we got the integral form of this equation:

$$k\tau = \frac{1}{c_{01}} \frac{\beta}{1-\beta} - D \ln|1-\beta| \quad (9)$$

Equation (9) was used for interpretation of the kinetic data. The initial concentration of nitrogen oxide ( $c_{01}$ ) should be expressed in molar concentration under normal conditions: (e.g. 1000 ppm NO = 0.0454 mole/nm<sup>3</sup>). Then the kinetic equation was transformed to

$$\tau = \frac{1}{kc_{01}} \frac{\beta}{1-\beta} - \frac{D}{k} \ln|1-\beta| = \Phi(\beta, x_{01}) \quad (10)$$

By using the method of non-linear regression [12, 13], coefficient  $k$  and coefficient  $D$  were determined:

$$k = 17.22 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \text{ and}$$

$$D = 100.7 \text{ m}^3 \cdot \text{mol}^{-1} \text{ (} R^2 = 0.962; \text{ RMS} = 710; \text{ SSE} = 11.4)$$

where:  $k$ ,  $D$  – coefficients of the regression equation,  $R^2$  – coefficient of determination; RMS – ratio of the sum of squares of the model and error; SSE – sum of the squares of error.

The obtained statistical coefficients indicate good agreement between the kinetic model and the empirical data. A comparison of the experimental data with the results of the calculations based on the derived equation is presented in Fig. 4. Some small deviations between experimental and calculated data are observed for the higher investigated NO-concentrations and long contact times, due to changes of the concentration of oxygen at high degrees of transformation and high NO-concentrations. Oxygen concentration is not introduced to the kinetic model of the process. In spite of that, a good agreement between the experimental and calculated data is observed, particularly in the low range of NO concentrations (up to 1000 ppm NO). The model developed is very simple

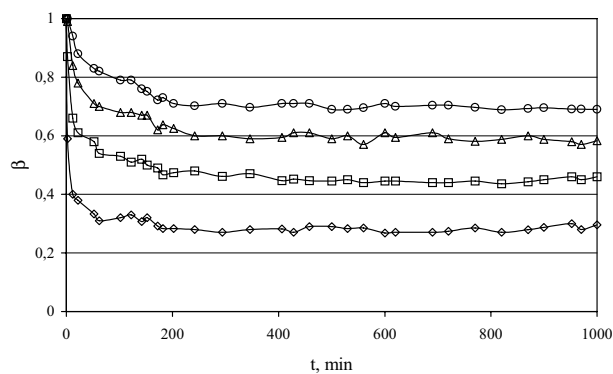


Fig. 2. Dependence of the degree of NO reduction after each reactor on time. Inlet NO concentration is 500 ppm. Contact time:  $\diamond$  - 2.7 s,  $\square$  - 5.4 s,  $\Delta$  - 8.2 s,  $\circ$  - 10.9 s.

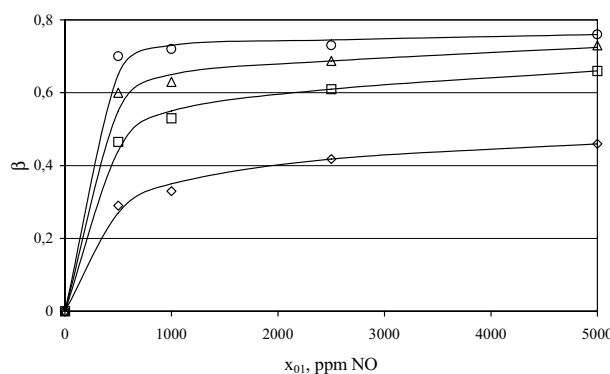


Fig. 3. Dependence of the degree of NO reduction on the inlet NO concentration and contact time, symbols as in Fig. 2.

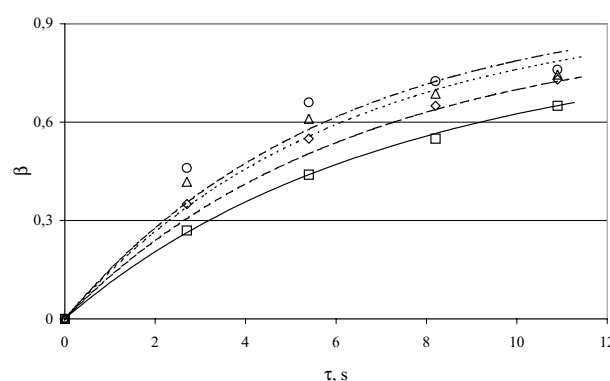


Fig. 4. Comparison of experimental and calculated data ( $\square$  - 500 ppm NO,  $\diamond$  - 1000 ppm NO,  $\Delta$  - 2500 ppm NO,  $\circ$  - 5000 ppm NO) and calculated data (— 500 ppm, — 1000 ppm, - - - 2500 ppm, - - - 5000 ppm).

because it consists of only two parameters. In order to develop a better kinetic model, further investigation is required, in which the concentrations of oxygen and ammonia should be taken into account.

## Conclusions

It has been shown in this paper that the reduction of NO by ammonia on the carbon sorbent AKP represents a process characterised by a very long time of non-steady state. The determined limits of the non-steady state are of great importance from the point of view of research and application. It has also been shown that within the investigated range of parameters, the time of non steady state operation of the reactor does not depend on the contact time, but increases with increasing NO-concentration in gases. In the range of concentrations from 500 to 5000 ppm NO, the time of achieving the steady state is between 5 and 10 hours. A practical conclusion resulting from the study is that the degree of reduction of NO increase with contact time. Maximum value of the reduction degree  $\beta = 0.75$  was achieved at contact time  $\tau = 10.7$  s for all the investigated NO concentrations. Hence, the optimal height of the sorbent bed is 1.2 m, at which the degree of the removal of nitrogen oxides is sufficiently high (about 75%).

On the basis of the results obtained, the kinetic model of reduction of nitrogen oxides by ammonia is proposed. There is good agreement between the experimental and calculated data. Therefore, the obtained kinetic equation can be used to describe the kinetics of reduction process of NO for lower NO concentrations in combustion gases.

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