

# Oxidation of NO by ozone in the presence of TiO<sub>2</sub> catalyst

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Oxidation of NO by ozone in the presence of TiO<sub>2</sub> catalyst was studied at varying NO inlet concentrations and gas flow rates. Ozone produced by a coaxial DBD reactor was mixed with NO diluted with N<sub>2</sub> and directed to a reaction chamber. The experiments were carried out with and without the presence of TiO<sub>2</sub> catalyst. Independent of varied parameters of NO inlet concentration, gas flow rate, reactor temperature and presence of catalyst, NO was totally oxidized to NO<sub>2</sub> when the inlet O<sub>3</sub> concentration reached the value of the inlet NO concentration. Further oxidation of NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub> took place when the O<sub>3</sub> concentration exceeded 1.5 times the value of the inlet NO concentration. At higher reactor temperatures, the presence of TiO<sub>2</sub> catalyst increased the oxidation efficiency of NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub>. The effect of catalyst can be explained by additional oxidation of NO<sub>2</sub> on the catalyst surface by oxygen species created on the surface by catalytic decomposition of ozone.

## 1. Introduction

The removal of NO<sub>x</sub> (NO and NO<sub>2</sub>) from the flue gases can be carried out by a number of absorption and adsorption based methods [1]. However, all these methods suffer from poor absorption and adsorption of NO which is the dominant specimen in the flue gas. The efficiency of the removal process can be improved by oxidation of NO to NO<sub>2</sub> or N<sub>2</sub>O<sub>5</sub>. This oxidation can be efficiently carried out with ozone [1].

We have recently shown that the efficiency of NO<sub>x</sub> oxidation to N<sub>2</sub>O<sub>5</sub> by ozone can be further improved by the use of a catalyst (TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>) [2,3]. Present study describes a more detailed investigation of the effect of TiO<sub>2</sub> by varying the flow rate (residence time), inlet NO concentration and temperature.

## 2. Experimental set-up

The experimental setup consisted from two reactors (Fig. 1), one used for the production of ozone and the second as the reaction chamber with catalyst. The ozone generator was based on a coaxial dielectric barrier discharge reactor described in our earlier paper [2]. The length of the reaction chamber was 8.5 cm and the volume was 5.76 cm<sup>3</sup>.

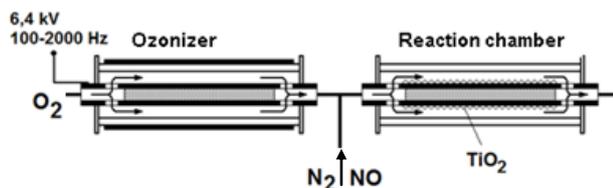


Figure 1. Experimental set-up with ozonizer and reaction chamber.

Sinusoidal voltage with the amplitude of 6.4 kV and frequency of 100-6000 Hz was applied to the inner electrode of the reactor. The specific input energy (SIE) was measured by the Manley method [4]. The ozone was produced from pure O<sub>2</sub>. The ozone output concentration of the DBD reactor was a linear function of SIE.

The produced ozone was mixed with N<sub>2</sub>-diluted NO. The NO concentration was varied in the range of 200-800 ppm. The flow rates of O<sub>2</sub> at the ozonizer inlet and N<sub>2</sub> at the reaction chamber inlet were always equal and the total flow rate was set to 0.5, 1 and 2 L/min. The mixed gas was directed to the reaction chamber which had the same dimensions with the ozone generator. The catalyst used in the reaction chamber was a commercial Degussa P25 powder (BET surface area of 50 m<sup>2</sup>/g). The powder with a total mass of 0.3 g was pressed on the inner electrode to form a thin coating layer.

The concentrations of NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> and O<sub>3</sub> were measured by optical absorption spectroscopy in the UV range [2].

## 3. Results and discussion

### 3.1. NO<sub>x</sub> and N<sub>2</sub>O<sub>5</sub> concentrations

Figure 2 shows a typical dependence of stable outlet concentrations of NO<sub>x</sub>, N<sub>2</sub>O<sub>5</sub> and O<sub>3</sub> on the inlet ozone concentration. The dependences had two characteristic parts. At lower O<sub>3</sub> inlet concentrations, the NO concentration decreased while NO<sub>2</sub> concentration increased. The oxidation of NO to NO<sub>2</sub> by O<sub>3</sub> was practically stoichiometric. When NO was totally removed, the NO<sub>2</sub> concentration reached its maximum value. At higher values of the inlet O<sub>3</sub> concentration N<sub>2</sub>O<sub>5</sub> and O<sub>3</sub> appeared while NO<sub>2</sub> concentration started to

decrease. The conversion of  $\text{NO}_2$  to  $\text{N}_2\text{O}_5$  was a sub-linear function of inlet  $\text{O}_3$  concentration.

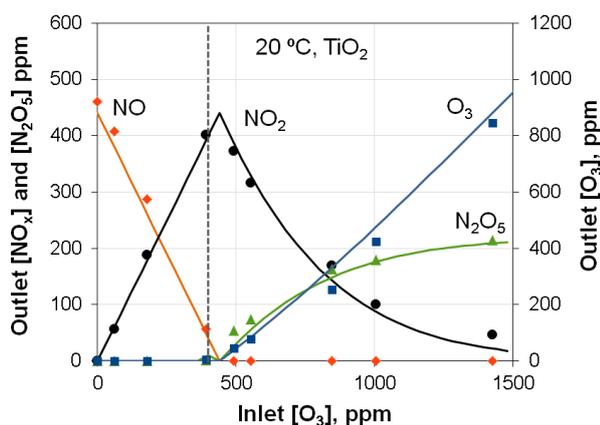


Figure 2. The outlet concentrations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$  and  $\text{O}_3$  as a function of inlet concentration of  $\text{O}_3$  after 10 minutes of reactor work with total flow of 1L/min and  $\text{NO}$  inlet concentration of 400 ppm. The lines present the calculated dependences.

The relationships between  $\text{NO}$  and  $\text{NO}_2$  in lower  $\text{O}_3$  concentration region as well as  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$  in high  $\text{O}_3$  concentration region were independent of inlet  $\text{NO}$  concentration and gas flow. This was the reason why in further figures only outlet concentrations of  $\text{NO}_2$  were used to compare the  $\text{NO}_x$  oxidation at various experimental conditions.

### 3.2. The effect of inlet $\text{NO}$ concentration and gas flow rate

The effect of inlet  $\text{NO}$  concentration on the outlet  $\text{NO}_2$  concentration as a function of inlet  $\text{O}_3$  concentration is shown in figure 3. Regardless of the experimental conditions, the outlet  $\text{NO}_2$  concentration grew linearly with the inlet ozone concentration until ozone concentration reached the value equal to the inlet  $\text{NO}$  concentration.

When inlet  $\text{O}_3$  concentration exceeded the value necessary for the total oxidation of  $\text{NO}$  to  $\text{NO}_2$ , the  $\text{NO}_2$  concentration started to decrease due to the oxidation of  $\text{NO}_2$  to  $\text{N}_2\text{O}_5$ . The relative decay was faster at higher inlet  $\text{NO}$  concentrations and at higher reactor temperatures. At room temperature, the  $\text{TiO}_2$  catalyst had practically no effect on the oxidation of  $\text{NO}$  (not shown in figures) while at 100°C the oxidation became more efficient when catalyst was used.

The effect of the gas flow on the outlet  $\text{NO}_2$  concentration as a function of ozone concentration is shown in figure 4 with and without the catalyst and at two different temperatures. Similarly to the results shown in figure 3, the outlet  $\text{NO}_2$  concentration always grew linearly with the inlet

ozone concentration until all  $\text{NO}$  was removed from the gas. Further oxidation of  $\text{NO}_2$  to  $\text{N}_2\text{O}_5$  was more efficient at smaller gas flow rates (longer residence times). Regardless of the used gas flow, the catalyst had no effect at room temperature (not shown). At higher temperatures the catalyst enhanced the  $\text{NO}_2$  oxidation. In addition, the outlet  $\text{NO}_2$  concentration did not depend on the gas flow rate in the presence of the catalyst.

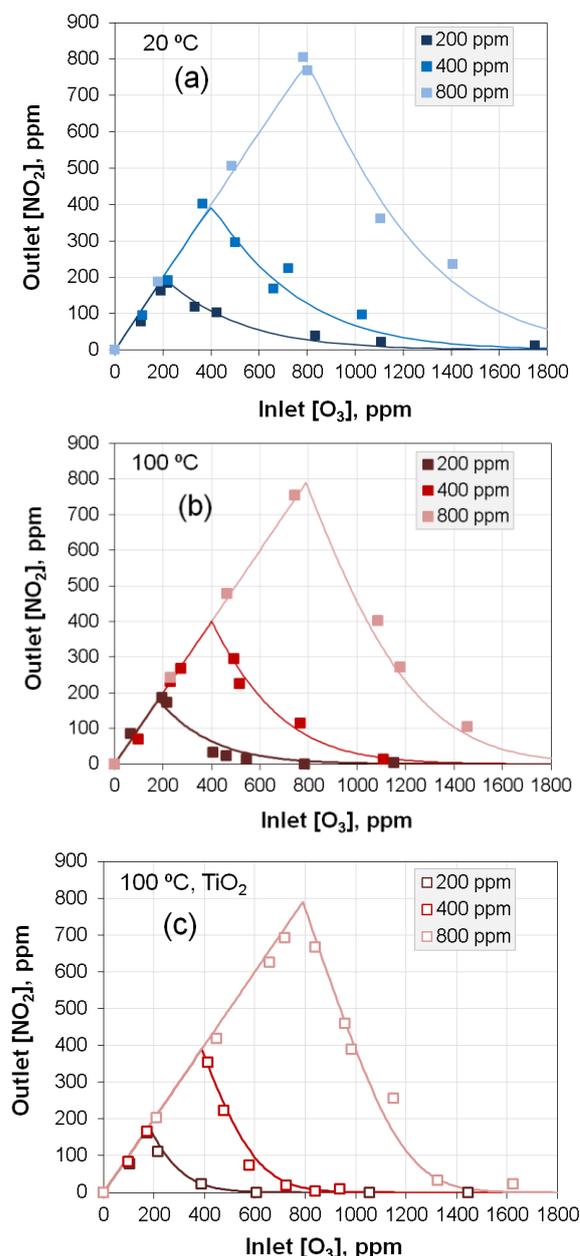


Figure 3. The outlet concentration of  $\text{NO}_2$  as a function of inlet  $\text{O}_3$  at varying inlet concentration of  $\text{NO}$  without catalyst at room temperature (a) and 100°C (b) and with  $\text{TiO}_2$  catalyst at 100°C (c). Flow rate was fixed at 1 L/min. The lines present theoretical dependences.

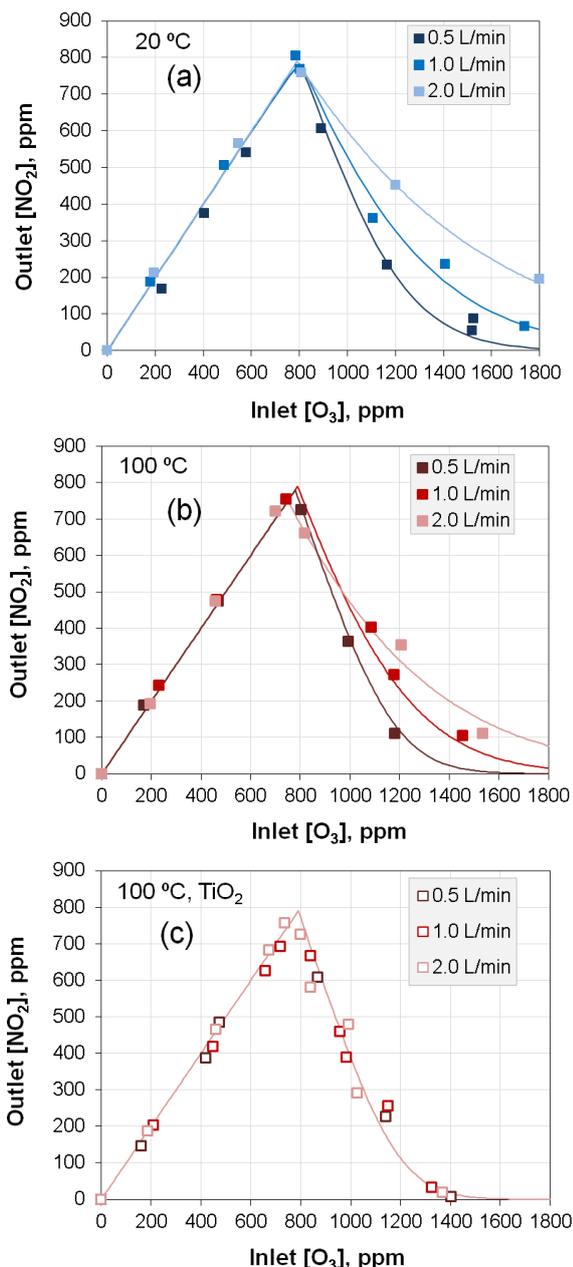


Figure 4. The outlet concentration of NO<sub>2</sub> as a function of inlet O<sub>3</sub> at varying flow rates without catalyst at room temperature (a) and 100°C (b) and with TiO<sub>2</sub> catalyst at 100°C (c). Inlet concentration of NO was fixed at 800 ppm. The lines present the theoretical dependences.

### 3.3. The destruction of O<sub>3</sub> by TiO<sub>2</sub> catalyst

The effect of TiO<sub>2</sub> on the destruction of ozone without the presence of NO was tested at varying temperatures. Figure 5 shows the relative change of outlet O<sub>3</sub> concentration with and without TiO<sub>2</sub> as a function of the reactor temperature. The inlet O<sub>3</sub> concentration was kept at 3000 ppm. The TiO<sub>2</sub> catalyst clearly increased the ozone destruction at

higher temperatures while at room temperature the effect was negligible.

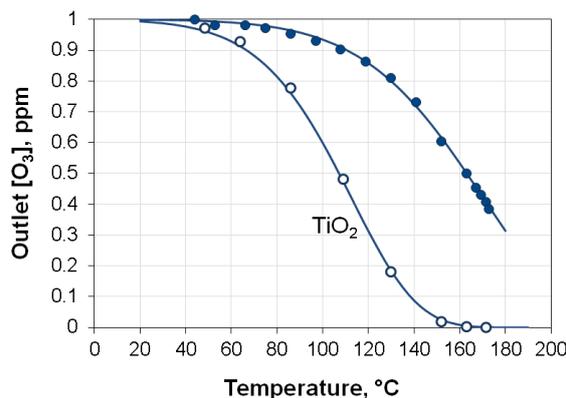
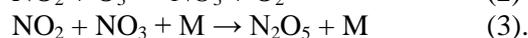
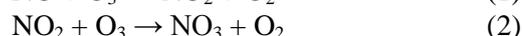


Figure 5. Temperature dependent destruction of O<sub>3</sub> in the reaction chamber with and without TiO<sub>2</sub> catalyst at constant inlet O<sub>3</sub> concentration of 3000 ppm. The O<sub>2</sub> flow was 1 L/min. The solid lines are used as a guide to the eye.

### 3.4. Analytical formula for oxidation of NO<sub>x</sub>

The oxidation of NO to NO<sub>2</sub> and subsequently N<sub>2</sub>O<sub>5</sub> could be described by three main reactions [5]:



The characteristic time of reaction 1 is in millisecond range while the residence time was 1-4 s. In our conditions, the characteristic time of reaction 2 is several seconds which is comparable to the residence time. The reaction 3 is much faster than reaction 2 and as a consequence, the reaction 2 is the limiting step in the oxidation of NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub>.

At lower values of inlet O<sub>3</sub> concentrations the reaction 1 dominates while at higher values of the inlet O<sub>3</sub> concentrations the reaction 2 governs the oxidation of NO<sub>2</sub>. The oxidation of NO to NO<sub>2</sub> can be calculated by using simple linear dependence e.g. the outlet concentration of NO<sub>2</sub> is equal to inlet concentration of O<sub>3</sub>. It is possible to show, that the oxidation of NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub> depends on the initial concentrations of O<sub>3</sub> and NO<sub>2</sub>:

$$[\text{NO}_2] = \frac{2[\text{O}_3]_0 - [\text{NO}_2]_0}{\frac{2[\text{O}_3]_0}{[\text{NO}_2]_0} (e^{(2[\text{O}_3]_0 - [\text{NO}_2]_0)kt} - 1)}$$

Where  $k$  is the reaction rate coefficient and  $t$  is residence time.

Theoretical curves shown in figures 2-4 were obtained by these analytical formulas by using

experimental inlet concentrations and residence times. In the case of calculations without the catalyst the  $k$  values were based on the data of NIST [5]. For the calculation of the outlet concentration of  $\text{NO}_2$  in the presence of  $\text{TiO}_2$ , the reaction rate coefficient  $k$  was adjusted to obtain good fit with the experimental results. The effective rate coefficient was up to 5 times larger in the presence of  $\text{TiO}_2$  catalyst when flow rate was 2 L/min.

### 3.5. Catalytic effect of $\text{TiO}_2$

In the gas phase, the limiting reaction in  $\text{N}_2\text{O}_5$  formation is the oxidation of  $\text{NO}_2$  to  $\text{NO}_3$  (2). We propose that the oxidation of  $\text{NO}_2$  to  $\text{NO}_3$  is more efficient on the catalyst surface. In this case, oxygen species causing the enhanced oxidation of  $\text{NO}_2$  should be formed by the ozone decomposition on the  $\text{TiO}_2$  surface. This mechanism is consistent with the fact that catalytic  $\text{NO}_2$  oxidation and  $\text{O}_3$  decomposition occur both at higher temperatures.

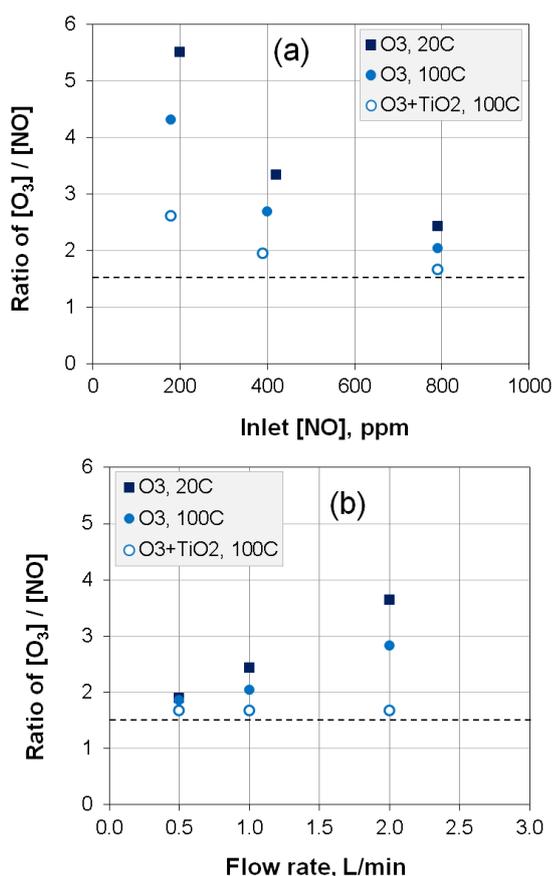


Figure 6. The ratio of inlet concentrations of  $\text{O}_3$  and  $\text{NO}$  required for the oxidation of 95% of  $\text{NO}$  to  $\text{N}_2\text{O}_5$  at various inlet  $\text{NO}$  concentrations (a) and flow rates (b). The stoichiometric ratio of 1.5 is shown by the dashed line.

### 3.6. Efficiency of $\text{NO}_x$ oxidation

A technologically important variable is the inlet  $\text{O}_3$  concentration where at least 95% of  $\text{NO}$  was oxidized to  $\text{N}_2\text{O}_5$ . The ratio of this inlet  $\text{O}_3$  to the inlet  $\text{NO}$  concentration is a convenient parameter for the comparison of the efficiency of ozone oxidation process at varying gas flow rates and inlet  $\text{NO}$  concentrations. The theoretical stoichiometric ratio of the total oxidation is 1.5.

Figure 6 shows this ratio as a function of inlet  $\text{NO}$  concentration and flow rate at two temperatures, with and without the catalyst. The ratio decreased considerably at increasing  $\text{NO}$  concentrations (Fig. 6a). Higher reactor temperatures decreased the ratio at all  $\text{NO}$  concentrations and the use of catalyst further improved the ratio at higher temperatures.

At increasing flow rates, the ratio increased almost linearly (Fig. 6b). This increase of the ratio was less pronounced at higher reactor temperatures. With the use of the catalyst, it was possible to keep the ratio close to the theoretical value of 1.5 in the whole range of the used flow rates.

## 4. Conclusions

Main results of the study were:

- The oxidation efficiency of  $\text{NO}$  to  $\text{N}_2\text{O}_5$  depended both on the flow rate and inlet  $\text{NO}$  concentration. The results were consistent with the model where the oxidation of  $\text{NO}_2$  to  $\text{NO}_3$  limited the efficiency.
- The presence of catalyst considerably improved the efficiency of ozone oxidation at 100°C while at room temperature the effect of catalyst was negligible.
- The effect of catalyst can be explained by the catalytic destruction of  $\text{O}_3$  which created surface bound oxidizing species responsible for improved oxidation of  $\text{NO}_2$  to  $\text{NO}_3$ .

## 5. References

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