Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 89 (2004) 103–107
CATALYSIS TODAY
www.elsevier.com/locate/cattod

# Basic study for gas cleaning using discharge and electrophoresis

Zhen-Zhou Su, Jun Sawada, Kazunori Takashima, Shinji Katsura, Akira Mizuno*

*Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan*

## Abstract

A $NO_x$ removal method using discharge plasma and electrophoresis for exhaust control was studied. The 65–50% of NO was oxidized to $NO_2$ or $HNO_3$ by the discharge plasma with specific input energy of 45 J/l. The electrophoresis was carried out to concentrate the $NO_2$ or $HNO_3$ adsorbed on the adsorbents. As a result, 80% of the adsorbed nitrate ions were found in the anode region. A combination of molecular sieve pellets of 13X and glass fiber cloth was tested for the collection of nitrate ions. The ability of simultaneous concentration of nitrate ions and sulfate ions using electrophoresis was examined.

*Keywords:* Specific input energy; $NO_x$ storage reduction; Electrophoresis

## 1. Introduction

$NO_x$ (NO and $NO_2$) from diesel engine causes air pollutions and health problems. Several effective catalytic processes for $NO_x$ removal have been under development. For gasoline engines, three-way catalyst and $NO_x$ storage reduction (NSR) catalyst have been widely used [1,2]. These catalytic processes, however, require high temperature and low oxygen concentration, and are not effective for diesel exhaust containing more than 10% of oxygen. At the present stage, the reductive removal of $NO_x$ from the diesel engine is still very difficult because of the following reasons: (1) high concentration of oxygen results in the oxidative reaction; (2) the activity of the catalysts is easily hampered by fine particle and $SO_2$.

The discharge plasma promotes oxidation even at room temperature and has a high efficiency for collection of carbon soot. Recently, NO oxidation without noble metals and the simultaneous removal of $NO_x$ and DEP have been under investigation [3–6]. Furthermore, the combination of discharge plasma and catalysts or adsorbents has been developed for reductive removal of $NO_x$ [7–11]. Reduction of $NO_x$ in the presence of excessive oxygen, however, is still difficult. Some researchers reported that the reduction of $NO_x$ by N radical is negligible when the oxygen concentration is larger than 3.6% [12].

If the adsorbed $NO_x$ is separated and concentrated in a low oxygen region, the reduction of $NO_x$ would be easier. In our previous study, a $NO_x$ removal method using discharge plasma and electrophoresis was proposed for diesel exhaust [13]. Using electrophoresis, the initial adsorbing capacity of the adsorbents was recovered by separating and concentrating the adsorbed nitrate ions in anode region. The concentrated nitrate ions can further be decomposed, e.g. by discharge with reductive agent such as ammonia, etc. In this work, the concept of concentrating nitrate ions outside the adsorbing section for reduction has been investigated. For this purpose, combination of molecular sieves' 13X for $NO_x$ adsorption and glass fiber cloth for the concentration of ionic species was tested.

$SO_2$ in diesel exhaust hampers the performance of the conventional catalyst. If $SO_2$ is oxidized on the catalyst and removed from the adsorbing section, activity of catalysts can be maintained. In this work, the ability of simultaneous concentration of nitrate ions and sulfate ions using electrophoresis has been studied.

## 2. Experimental

### 2.1. Reactor

The experimental setup is schematically depicted in Fig. 1. Detail of the reactor is shown in Fig. 2. The reactor consists of the following two parts:

(1) *Discharge reactor*. The discharge reactor was employed to oxidize NO to $NO_2$ by dielectric barrier discharge plasma. It consisted of a tungsten needle of 0.5 mm

---

* Corresponding author.

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.11.035

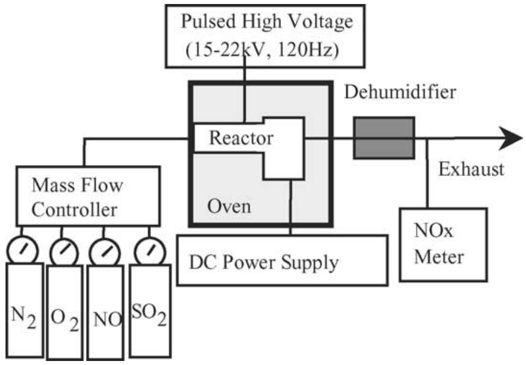

Fig. 1. Schematic diagram of the experimental setup.

in diameter serving as the high voltage electrode and an aluminum sheet of 150 mm length wrapped around a 12 mm diameter quartz glass tube as the ground electrode.

(2) *Adsorption cell for electrophoresis*. The adsorption cell was used for the adsorption of $NO_2$ and the separation of the nitrate ion. The cell was made of a quartz glass tube of 26 mm in diameter. $\gamma$-$Al_2O_3$ pellets of 2–3 mm diameter (Sumitomo Chemical Co.) were used in this experiment. A combination of molecular sieves' pellets of 1–2 mm diameter (13X-$Na_2O$, Union Showa) and glass fiber cloth (I&I Material Co.) was used as adsorbent materials for the comparison with $\gamma$-$Al_2O_3$. The glass fiber cloth is mainly composed of $Al_2O_3$ (47.1%) and $SiO_2$ (52.3%). A plate type platinum electrode and a plate type copper electrode were used as an anode and a cathode, respectively, and set on the ends of the cell. Separation of the adsorbed nitrate ions was made using a dc voltage applied to the electrodes.

### 2.2. Experimental conditions

The gas mixture of NO, $O_2$ and $N_2$ was adjusted using the mass flow controllers (Kofloc Co.). The reactor was driven by a square wave high voltage (peak voltage 20 kV, frequency 120 Hz) to generate a non-thermal pulsed discharge plasma. The electrical circuit of high voltage power supply is shown in Fig. 3. The specific input energy (SIE) was 45 J/l in this experiment. The input power was measured using a digital power-meter (Yokogawa, 2534).

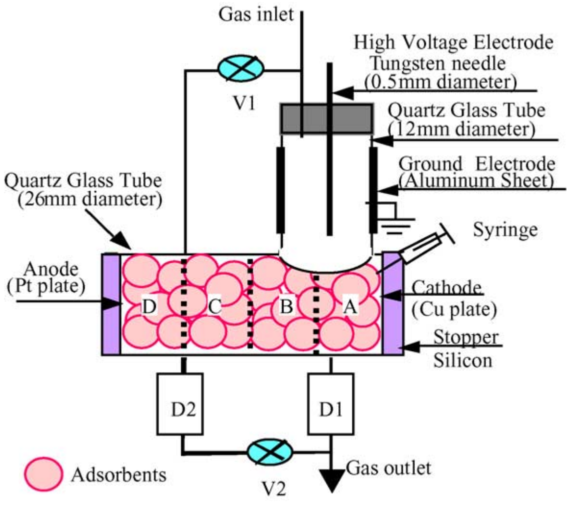

Fig. 2. The reactor.

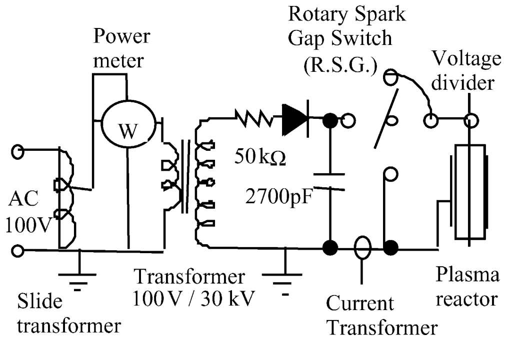

Fig. 3. Electrical circuit of the high voltage power supply.

The sequence of $NO_x$ oxidation, adsorption, and electrophoretic separation are as follows: 30 min after starting the gas flow and plasma application in the discharge reactor, the pulsed plasma was turned off and the gas flow was stopped. Eighteen millilitres of NaOH solution (0.2N) was injected to the adsorption cell using a syringe to increase the conductivity. Subsequently, the electrophoresis was carried out for 40 min. Temperature of the adsorption cell was measured using an infrared thermometer during the electrophoresis and remained within 70–90 °C. After 15 min of electrophoresis, the valves V1 and V2 were opened and the adsorbents were dried out for 25 min by feeding the nitrogen gas with 2 l/min at 150 °C. During this drying process, the nitrate ions concentrated in the adsorption cell were released and as nitric acid in the outlet gas collected by two dehumidifiers D1 and D2. Temperature of the gas and the adsorbent during the sequence was controlled using a ribbon heater. The sequence was repeated three times. To start the electrophoresis with equal amount of solution in the adsorption cell, 16 and 13 ml of pure $H_2O$ were injected into the adsorption cell instead of NaOH solution in the second and the third cycle. The variations of the injected $H_2O$ amounts were caused by the residual water of the former injection. NO and $NO_x$ concentrations were monitored by a $NO_x$ meter (Horiba, PG250) during the whole experiment.

The reactor used in this experiment was divided equally into four sections (A–D from cathode to anode) and pellets in each section were analyzed separately. They were washed with 100 ml of de-ionized water for 20 min using an ultrasonic cleaner to extract the ions adsorbed on the pellets. The extraction process was repeated to wash out the nitrate ions completely. The solution extracted as well as the solutions collected by D1 and D2 dehumidifiers were analyzed by an ion chromatography (Dionex DX-120).

## 3. Results and discussion

### 3.1. Reactivation of the adsorbents

The recovery of adsorbing capacity was confirmed by the monitoring the gas phase NO and NO$_x$ concentrations. The sample gas contained 350 ppm NO and 10% of $O_2$ in $N_2$. Gas flow rate was 2 l/min. The adsorbing cell was packed with the γ-$Al_2O_3$ pellets of 2–3 mm diameter in this experiment. The time-lapse change of NO and NO$_x$ concentrations during the experiment is shown in Fig. 4. During the first 30 min, 65–50% of NO was oxidized to $NO_2$, and more than 95% of $NO_2$ was adsorbed by the γ-$Al_2O_3$ adsorbents. Eighteen millilitres of the 0.2N NaOH water solution was injected into the adsorption cell in the 30th minute and electrophoresis started. After 15 min of electrophoresis $N_2$ gas was fed into the reactor to dry the catalyst pellets. NO and NO$_x$ in the gas phase were not detected, which suggests that desorption of NO$_x$ was negligible. After the drying procedure, the second cycle of the sequence was started. The concentrations of NO and NO$_x$ in the second cycle of the plasma oxidation were lower than that in the first cycle. The lower concentration of NO$_x$ can be ascribed to a chemical reaction between NO$_x$ and NaOH in addition to the physical adsorption.

The NO and NO$_x$ concentrations in the third cycle were similar to those in the second cycle, despite only 13 ml of the de-ionized water was injected into the adsorption cell. This result indicates that the initial adsorbing characteristics were recovered by the electrophoresis. The nitrate ions were swept to the anode side of the adsorption cell, and the sodium ions were concentrated near the cathode by the electrophoresis. The adsorption of $NO_2$ mainly takes place near the cathode side because the main gas flow passes the cathode region in this experiment. Therefore, the activity of the adsorbents can be kept high using this method.

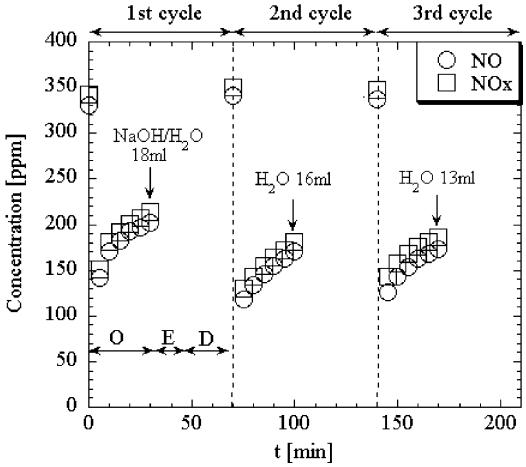

Fig. 4. The time-lapse of NO and NO$_x$ concentrations during the experiment (O: process of NO oxidation using discharge plasma, E: movement of nitrate ions using electrophoresis, D: drying of the adsorbents and collection of adsorbed ions. Electrophoretic voltage: 100 V).

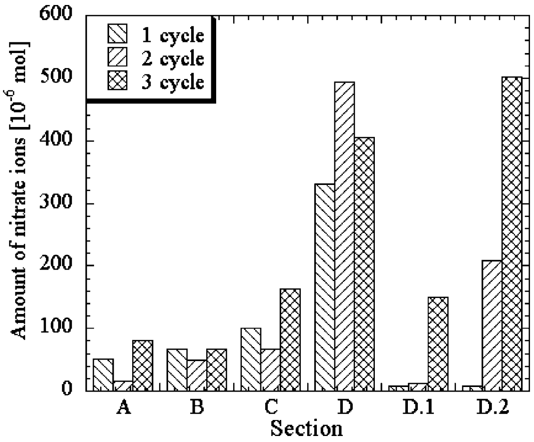

Fig. 5. The distribution of nitrate ions after each cycle.

### 3.2. Adsorption and desorption of nitrate ions

For the ion distribution analysis, a cycle consisting of (a) 30 min for oxidation of NO and adsorption using discharge plasma, (b) 15 min for electrophoresis to move the nitrate ions, and (c) 25 min for drying of the adsorbents was repeated three times. The amount of nitrate ions ($NO_3^-$, $NO_2^-$) contained in each section of the cell (A–D) and the dehumidifiers (D1 and D2) were measured after each cycle. The distribution of nitrate ions is expressed as a ratio of nitrate ions in a given section to the total amount of nitrate ions in all sections. It is obvious that most of the nitrate ions were concentrated in the area D and the dehumidifier D2 in each cycle, as shown in Fig. 5. This result indicates that the adsorbed nitrate ions were driven from the cathode side to the anode side by the electrophoresis and stored as $HNO_3$ or $HNO_2$. The acids are evaporated during the drying process, and collected by the dehumidifier.

Furthermore, the amount of nitrate ions in D2 increased with the number of cycles, but decreased in the section D. For example, only about 0.01 mmol of nitrate ions was collected by D2 in the first cycle, compared with 0.21 and 0.5 mmol in the second and the third cycle, respectively. The result indicates that the adsorbents in the section D, where most of the nitrate ions are concentrated, cannot store more nitrate ions when the concentration exceeds a certain limit. In such case the excess amount of the nitrate ions can be easily desorbed from the adsorbent and collected by the dehumidifier during the drying process. In contrast to the removal of the nitrate ions from the reactor, more than 90% of the injected sodium ions still remained in the adsorption cell until the experiment finished.

### 3.3. Comparison of γ-$Al_2O_3$ with combination of molecular sieves' 13X and glass fiber cloth (combined absorbents)

The section A and B of adsorbing cell were packed with 13X pellets, and the sections C and D were packed with glass fiber cloth. The results were compared with those of a reactor

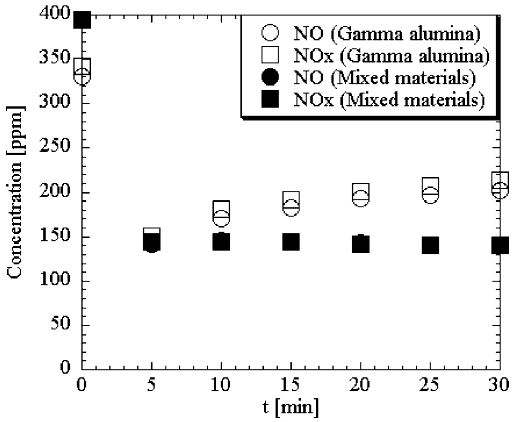

Fig. 6. The $NO_x$ adsorption by $\gamma$-$Al_2O_3$ and mixed materials. (Electrophoretic voltage: 100 V).

uniformly packed with $\gamma$-$Al_2O_3$. The molecular sieves 13X were used due to their better efficiency for $NO_x$ adsorption and electrophoresis compared with $\gamma$-$Al_2O_3$, reported by our previous study [13]. The reason for packing the other two sections (C and D) with the glass fiber cloth was the possibility of easier retrieval of the concentrated nitrate ions from the glass fiber cloth compared to the porous materials of 13X and $\gamma$-$Al_2O_3$.

Fig. 6 shows the $NO_x$ adsorption characteristics in time. The result indicates that the $NO_x$ adsorption is better with the combined absorbents. The electrical resistance of the adsorption cell during the electrophoresis and the drying process was evaluated for both cases: $\gamma$-$Al_2O_3$ and the combined absorbents (in the latter case pure water was used instead of NaOH solution). The results are shown in Fig. 7. Using the combined absorbents, the resistance decreased to about one third. In this case the energy efficiency of the electrophoresis can be improved.

The efficiency of the collection of nitrate ions depended on the absorbent material. Comparison of the distribution of nitrate ions for the $\gamma$-$Al_2O_3$ and the mixed materials is shown in Fig. 8. About 0.038 mmol of nitrate ions were collected by D2 when the mixed adsorbents were used, higher than in case of the $\gamma$-$Al_2O_3$. It indicates that the glass fiber cloth has a lower adsorption ability of nitrate ions, compared to porous $\gamma$-$Al_2O_3$.

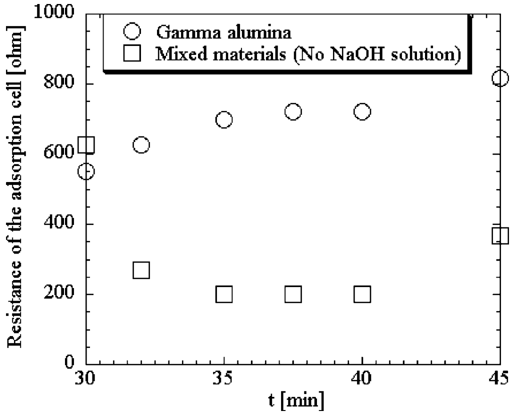

Fig. 7. The time-lapse of resistance of the adsorption cell. (Electrophoretic voltage: 100 V).

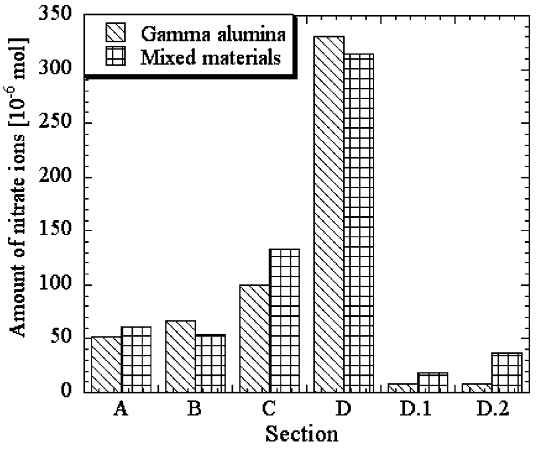

Fig. 8. The $NO_x$ adsorption characteristics for $\gamma$-$Al_2O_3$ and mixed materials. (Electrophoretic voltage: 100 V).

### 3.4. Separate concentration of nitrate ions and sulfate ions

The ability of simultaneous concentration of nitrate ions and sulfate ions was examined by monitoring the time change of the concentration of gas phase $NO/NO_x$ and $SO_2$. The sample gas contained 360 ppm NO, 200 ppm $SO_2$ and 10% of $O_2$ in $N_2$. Gas flow rate was 2 l min. The molecular sieves 13X was used in this experiment. The time-lapse change of $NO/NO_x$ and $SO_2$ concentrations during the experiment are shown in Fig. 9. Almost 100% of $SO_2$ was adsorbed on the 13X. The amount of nitrate ions and sulfate ions were measured after 15 min of the electrophoresis, and the distributions are shown in Fig. 10. The result shows that almost 50% of $SO_4{}^{2-}$ was concentrated in the section C, and 70% of $NO_3{}^{-}$ was concentrated in the section D. This result indicates that the nitrate ions and the sulfate ions can be separated and concentrated in different section.

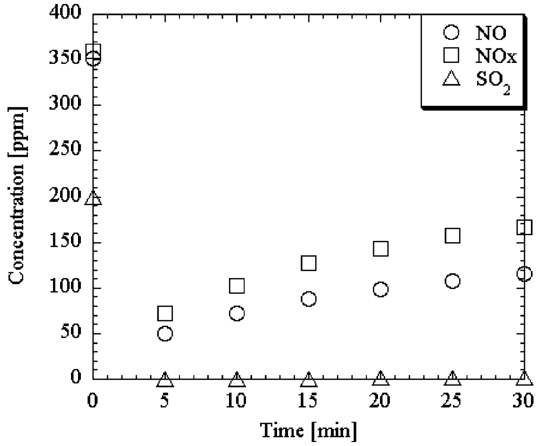

Fig. 9. $NO/NO_x$ and $SO_2$ adsorption characteristics.

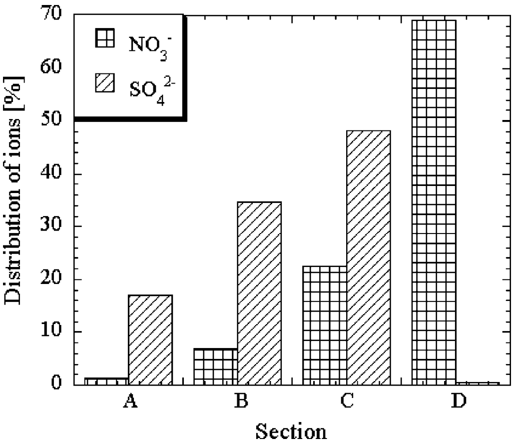

Fig. 10. Distribution of nitrate ions and sulfate ions.

## 4. Conclusion

The removal of $NO_x$ and $SO_2$ using the pulsed discharge plasma and the electrophoresis has been experimentally investigated using the simulated gas. The following conclusions were obtained:

(1) Activity of the adsorbents can be restored by the electrophoresis.
(2) The adsorbed nitrate ions can be concentrated near the anode. The concentrated nitrate ions can be retrieved from the adsorbents during the drying process and collected by dehumidifier.
(3) The efficiencies of $NO_x$ adsorption, electrophoresis and collection by dehumidifier by using the combination of the molecular sieves 13X and glass fiber cloth were higher than those of the $\gamma$-$Al_2O_3$.
(4) Nitrate ions and sulfate ions can be concentrated at different section of adsorption cell. This result suggests that the selective removal of nitrate ions and sulfate ions is possible.

## Acknowledgements

This research was partially supported by the 21st Century COE Program ‘Ecological Engineering for Homeostatic Human Activities’ from the ministry of Education, Culture, Sports, Science and Technology.

## References

[1] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamaxaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, Catal. Today 27 (1996) 63.
[2] S. Matsumoto, CAT TECH 4 (2000) 102.
[3] H. Miessner, K.-P. Francke, R. Rudolph, T. Hammer, Catal. Today 75 (2002) 325.
[4] J. Hoard, R.L. Bretz, Y. Ehara, SAE 2003-011184, 2003, p. 97.
[5] G. Sathiamoorthy, S. Kalyana, W.C. Finney, R.J. Clark, B.R. Locke, Ind. Eng. Chem. Res. 38 (1999) 1844.
[6] Y. Matsui, M. Hashimoto, A. Sakaguchi, K. Takashima, S. Katusra, A. Mizuno, in: Proceedings of the Eighth International Conference on Electrostatic Precipitation, vol. 2, 2001.
[7] H. Miessner, K.-P. Francke, R. Rudolph, Appl. Catal. B: Environ. 36 (2002) 53.
[8] S. Yoon, A.G. Panov, R.G. Tonkyn, A.C. Ebeling, S.E. Barlow, M.L. Balmer, Catal. Today 72 (2002) 243.
[9] S. Yoon, A.G. Panov, R.G. Tonkyn, A.C. Ebeling, S.E. Barlow, M.L. Balmer, Catal. Today 72 (2002) 251.
[10] C.L. Aardahl, K.G. Rappe, P.W. Park, C.S. Ragle, C.L. Boyer, S.A. Faulkner, SAE 2003-01-1186, 2003, p. 121.
[11] S. Broer, T. Hammer, Appl. Catal. B: Environ. 28 (2000) 101.
[12] K. Yan, S. Kanazawa, T. Ohkubo, Y. Nomoto, ICESPVII, Kyongju, Korea, 1998, p. 257.
[13] Z.-Z. Su, J. Sawada, Y. Matsui, K. Takashima, S. Katsura, A. Mizuno, SAE 2003-01-1188, 2003, p. 139.