Reaction Kinetics and Dependence of Energy Efficiency in the Dilute Trichloroethylene Removal by Non-thermal Plasma Process combined with Manganese Dioxide

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Abstract : In order to improve energy efficiency in the dilute trichloroethylene removal using the nonthermal plasma process, the barrier discharge treatment combined with manganese dioxide was experimentally studied. Reaction kinetics in this process was studied on the basis of final byproducts distribution. Decomposition efficiency was improved to about 99% at the specific energy 40J/L with passing through manganese dioxide. C=C π bond cleavage in TCE gave DCAC (single bond, C-C) through oxidation reaction during the barrier discharge plasma treatment. Those DCAC were broken easily in the subsequent catalytic reaction due to the weak bonding energy about 3 ~ 4 eV compared with the double bonding energy in TCE molecules. Oxidation byproducts of DCAC and TCAA from TCE decomposition are generated from the barrier discharge plasma treatment and catalytic surface chemical reaction, respectively. Complete oxidation of TCE into COx is required to about 400J/L.

Key Words : barrier discharge, trichloroethylene, manganese dioxide

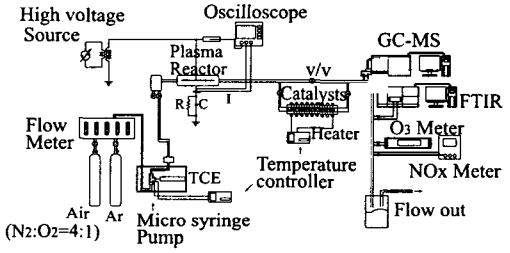
I. INTRODUCTION

Nonthermal plasma technologies in the treatment of gaseous pollutants have investigated by many researchers [1]-[3]. Recently, nonthermal plasma technologies in the environmental application showed a tendency to combine with catalysts for improving energy efficiency.

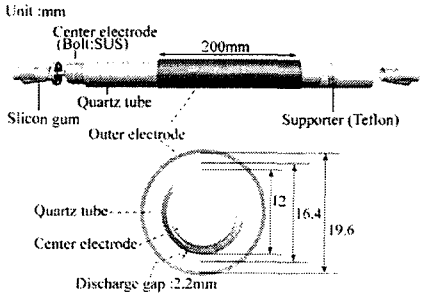
In this work, manganese dioxide (MnO_2) is used for its high ability on ozone decomposition. The objective of the present work is to improve energy efficiency combined with catalysts at the downstream of the barrier discharge reactor. Reaction kinetics in this process was studied on the basis of final byproducts distribution related with the specific energy density (SED).

II. EXPERIMENT

Concentration of TCE-contaminated synthesized air was adjusted by injecting liquid TCE with a micro-syringe pump. Catalysts of manganese dioxide (MnO_2 25g less than 3mm length) filled in teflon tube (I. D.: 8mm, filled zone: 250mm) is arranged at the downstream of the barrier discharge reactor. Specific surface area of manganese dioxide (Pyrolusite β-MnO_2) was 12.14 m^2/g. GCMS-QP5050A (Shimadzu Co.) with a wide-bore capillary column BTX-200 (length: 30m, inner diameter: 30㎛) is used to analyze chlorine contained-substances including TCE. FT-IR (Shimadzu Co.,) was to measure CO, CO_2, N_2O, and other byproducts using long-path gas cell (Infrared Analysis Inc., optical path: ca. 2.4m), which is possible to identify not only on-line byproducts variation, but also the calculation of absolute density using calibration curve of specified vibrational modes. Ozone meter (Okitronics, OZM-700G) and chemical luminescence NOx gas analyzer (Shimadzu Co., NOA-7000) were used for the analysis of byproducts distribution. The barrier discharge reactor is composed of a quartz tube and a stainless steel bolt as shown in Figure 1. The inner diameter of a quartz tube is 16.4mm with thickness 1.6 mm, and the diameter of the discharge electrode is 12mm. The discharge region is long about 200mm, and the discharge gap was 2.2mm.



(a) Experimental setup



(b) The barrier discharge reactor

Fig. 1 Schematics of experimental setup and the barrier discharge reactor

III. EXPERIMENTAL RESULTS

In Fig. 3, decomposition efficiency of TCE versus SED is improved to about 99% with passing through manganese dioxide at 40J/L. When plasma processed gas did not pass through manganese dioxide, decomposition efficiency about 99% was attained at 240J/L. From this result, the barrier discharge plasma treatment combined with manganese dioxide is an effective approach for decreasing the energy

consumption.

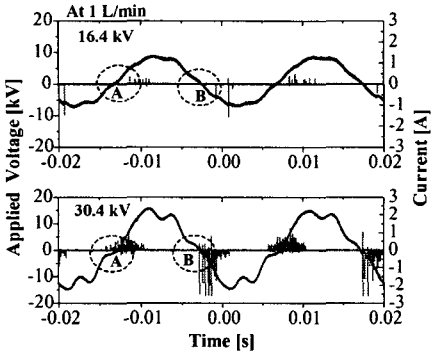


Fig. 2 Waveform of the applied voltage and discharge current (AC high-voltage source at 50Hz)

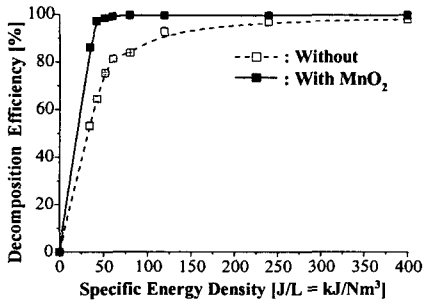


Fig. 3 Decomposition efficiency of TCE vs. SED

In Fig. 4, main chlorine contained-byproducts are DCAC (Dichloro-acetylchloride, $CHCl_2$-COCl), TCAA (Trichloro-acetaldehyde, CCl_3-CHO), and Cl_2, it showed using the value of relative peak areas on the TCE initial concentration. When the plasma processed gas did not pass with catalysts, DCAC increased about 0.55 at below 60J/L, but it decreased slightly with increasing SED. With passing through catalyst, DCAC decreased about a half upto 60J/L. It is ascribed that DCAC decomposed through catalytic surface chemical reactions.

At the same time, Cl_2 concentration and COx yield increased largely with passing through catalysts. Based on these results, oxygen species generated from ozone decomposition at catalysts enhanced the oxidative chemical reaction to increase Cl_2 and COx concentration. Oxidation byproducts of DCAC and TCAA are generated from the barrier discharge plasma treatment and catalytic surface chemical reaction, respectively. The subsequent chemical reaction at catalysts increased CO and CO_2 concentration by the oxidation reaction. In this result, ozone decomposition at catalysts is assumed to give oxygen species for enhancing energetic chemical reactions. The complete oxidation of TCE and discharge byproducts into COx was required to about 400J/L under this experimental conditions at 250ppm. (This did not show those data.)

In the plasma treatment, chlorine radical chain reaction is considered as a plausible decomposition mechanism of TCE. Chlorine radicals might be generated from collisions of electron or excited species with TCE and other chlorine contained-byproducts. The subsequent catalytic reactions after the barrier discharge plasma treatment could be expected from increasing COx and Cl_2 concentration, when plasma treated gases were passed through manganese dioxide. Oxygen radicals from the dissociation of the chemisorbed ozone might be generated at manganese dioxide, and reactive chlorine contained-intermediates such as Cl_2, ClO, ClO_2, and Cl radicals might be generated as well. Those reactive species might cause energetic chemical reactions to increase COx and Cl_2 concentration as the final byproducts. Briefly, these reactions are likely that C=C π bond cleavage in TCE gave DCAC (single bond, C-C) through oxidation reaction during the barrier discharge plasma treatment. those DCAC were broken easily in the subsequent catalytic reaction due to the weak bonding energy (Approx. 3 ~ 4 eV) compared with the double bonding of TCE (C=C). Since the slight oxidation of TCE into DCAC has a possibility to cause misunderstand as the increase of the decomposition efficiency. Authors are suggested that final byproducts distribution from TCE removal should be analyzed thoroughly in this plasma process.

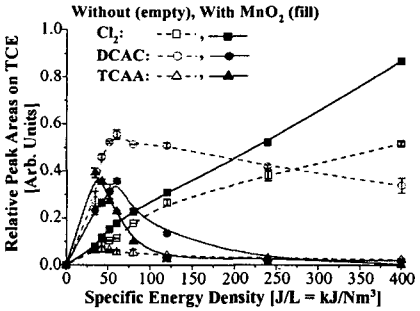


Fig. 4 Byproducts distribution on SED

IV. CONCLUSIONS

The barrier discharge plasma treatment combined with ozone decomposition catalysts was studied experimentally for decomposing dilute TCE, due to ozone generation in the barrier discharge plasma process under the aerated conditions. Experimental results are summarized as follows.

1) Decomposition efficiency was improved to about 99% at 40J/L with passing through manganese dioxide. The barrier discharge plasma treatment combined with manganese dioxide is likely to an effective approach for decreasing the energy consumption.

2) The required specific energy density for the highest oxidation of TCE into COx and Cl_2 was about 400J/L.

C=C π bond cleavage in TCE gave DCAC (single bond, C-C) through oxidation reaction during the barrier discharge plasma treatment. Those DCAC were broken easily in the subsequent catalytic reaction due to the weak bonding energy about 3 ~ 4 eV compared with the double bonding energy in TCE molecule.

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