Dilute Trichloroethylene Decomposition by Non-Thermal Plasma –Catalyst and Humidity Effect, and OH Radical Behavior-

Yusuke Nakagawa, Yuta Tomimura, Ryo Ono and Tetsuji Oda
The University of Tokyo
phone: (+81) 3-5841-6766
e-mail: nakagawa@streamer.t.u-tokyo.ac.jp

Abstract— **Dilute trichloroethylene (about 250 ppm TCE) in air was decomposed by the non-thermal plasma processing. Two factors were focused. One is the amount effect of the ozone decomposition catalyst. The authors reported already that the energy efficiency of dilute TCE decomposition was much improved if the catalyst is enough but the maximum efficiency was not yet realized. Moreover, the residual ozone concentration was still pretty high at high specific energy density of 100 J/L. Especially that concentration should be less than 0.1 ppm if the processed gas was exhausted in the living space. If the catalyst amount is enlarged for the same volume gas flow rate, higher decomposition efficiency is observed still more. Most TCE (more than 90%) is decomposed at SED of 10 J/L, if the 3g catalyst was used in this case but carbon balance was not so high. Moreover, the leakage of the ozone was pretty high if SED is more than 20J/L. The decomposition byproducts will be discussed at the meeting because the carbon balance is not so good at SED of more than 40J/L. As the second target, humidity effect for the decomposition efficiency was examined again and some new results are obtained. The former experiment was done at dry condition (no artificial humidifying) but the decomposition efficiency was improved at the humidity of 20 % (still pretty dry). That fact will be explained by the generation and behavior of OH radicals. OH radical is observed by using OPO laser fluorescence method now. That discussion will be done at the meeting.**

I. Introduction

Since air pollution is a serious problem today, it is desirable that decomposition technique of toxic gas with non-thermal plasma (NTP) be put to practical use[1,2]. Our group has been developed the NTP technique for decomposition of VOCs (volatile organic compounds), but we have to improve the energy efficiency and suppress byproducts[3]. Especially, catalyst and humidity effect are of great interest[4,5]. In this study, we tried to investigate the effect of catalyst amount and water vapor concentration on trichloroethylene decomposition by NTP.

First, we measured the dependence of decomposition efficiency and amount of by-

products on the amount of MnO_2/Al_2O_3 catalyst.

Second, we investigated the humidity effect by both approach of practical decomposition experiment and direct optical measurement of OH radicals.

II. EXPERIMENTS

A. Practical TCE decomposition

TCE decomposition rate and ozone (as a byproduct) concentration are measured in practical-type coaxial cylinder DBD reactor. Fig.1 shows the experimental system. In this experiment, humid or dry air (O_2 (20%)/N_2 mixture) with dilute TCE (250 ppm) flows in the plasma reactor at 1.0 L/min flow rate. The amplified alternative (50 Hz) voltage is applied to the reactor in order to provide DBD. The inner diameter of glass tube is 16.8 mm and central electrode is screw of 16 mm in diameter, therefore discharge gap is 0.4mm. The amount of ozone and residual TCE in output gas is detected by FTIR (IRPrstige21, SHIMAZU) or GCMS (GCMS-QP5050A, SHIMAZU). In the investigation of catalyst effect, MnO_2 (5 wt% in granular Al_2O_3) catalyst is placed after the reactor so that catalyst does not influence discharge. As for the humidity effect, the TCE decomposition efficiency is measured in various background humidities (controlled by mixing rate of dry and approximately 100% humid air). The discharge power is calculated by *V-Q* Lissajous method.
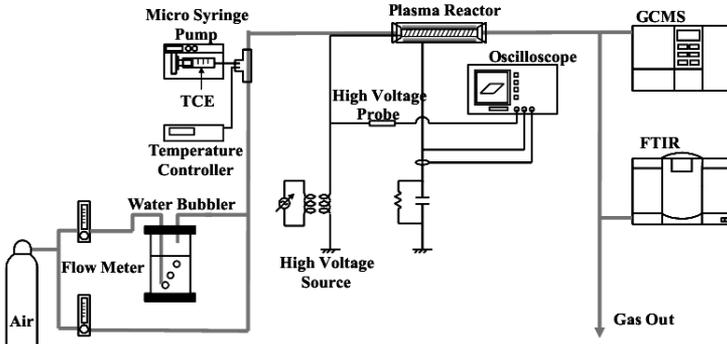
Fig. 1. Experimental setup for TCE decomposition

B. OH measurement

The density of OH radicals is measured in-situ by laser-induced fluorescence (LIF) method[6-8]. An optical parametric oscillator (OPO) is used to excite OH radicals in the $X^2\Pi$ (*v*=0) ground state to the $A^2\Sigma$ (*v*=1) excited state. We measure the fluorescence of direct relaxation $A^2\Sigma(v=1)$–$X^2\Pi(v=1)$ corresponding to 314 nm, and 309 nm $A^2\Sigma$ (*v*=0) – $X^2\Pi(v=0)$ relaxation after vibrational energy transfer (VET) in the $A^2\Sigma$ state. The fluorescence intensity I_{LIF} is proportional to the incident laser intensity I_L and ground state density n_0[9],

$$I_{LIF} = cBI_L n_0 \left(\frac{A_0 Q_v}{\Gamma_1 \Gamma_0} + \frac{A_1}{\Gamma_1} \right) \tag{1}$$

where A and B are Einstein's coefficients, Γ represents the decay rates of excited states, Q_v correspond to the rate of VET in $A^2\Sigma$ ($v=1$) to $A^2\Sigma$ ($v=0$), and the indices 0 and 1 under A and Γ are related to $A^2\Sigma$ ($v=0$) and $A^2\Sigma$ ($v=1$), respectively. With the coefficients of each state[10-13], we can determine the OH relative density from fluorescence intensity.

The trigger of the laser pulse is obtained from pulse generator and delayed τ [s] from the trigger of the discharge so that we can observe the time evolution of OH density by changing τ. The reactor for this OH measurement has relatively long discharge gap (5 mm) compared to the TCE decomposition experiment, because there must be enough space for incident laser beam.

III. RESULTS AND DISCUSSIONS

A. Catalyst effect on TCE decomposition

In this study, the TCE decomposition efficiencies are measured in dry air DBD. The catalyst amount is set to 0, 1 or 3 g. TCE decomposition efficiency η is defined as

$$\eta[\%] = \left(1 - \frac{[VOC]}{[VOC]_0}\right) \times 100. \tag{2}$$

Fig. 2 shows the obtained TCE decomposition efficiency against input power. Horizontal axis represents specific energy density (SED);

$$\text{SED [J/L]} = \frac{\text{Input Power [J/s]}}{\text{Flow rate [L/s]}}. \tag{3}$$

The results indicate that catalyst enhances the TCE decomposition efficiency. Moreover, increase of catalyst amount suppresses the energy required to decompose TCE completely. However the effect of 3 g catalyst does not seem to be triple of 1 g catalyst, therefore there should be the saturation of catalyst effect between 1 and 3 g of MnO_2/Al_2O_3.

The ozone productions with catalyst amount of 0, 1 and 3 g are represented in Fig. 3. The catalyst also suppresses the ozone production, almost under 20 ppm at 20 [J/L] when 3 g catalyst is set. This suppression of ozone is considered to be caused by ozone decomposition leading to atomic oxygen production on the catalyst surface.
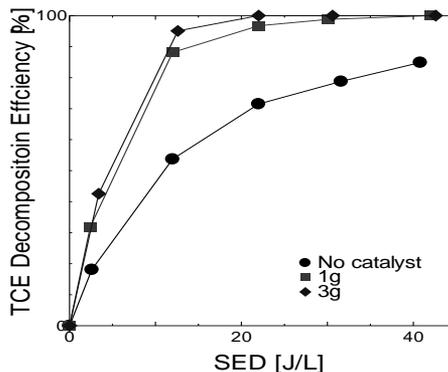
Fig. 2. Effect of catalyst amount on TCE decomposition efficiency.
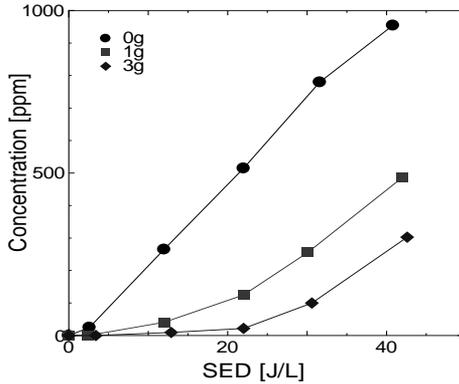
Fig. 3. Effect of catalyst amount on O_3 production.
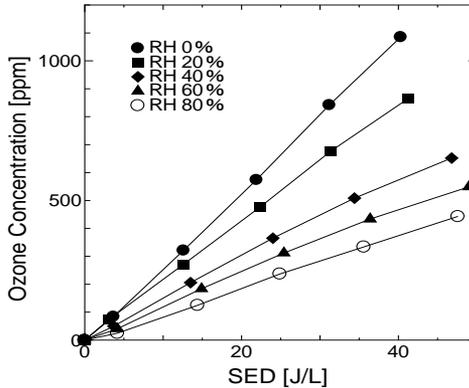
Fig. 4. Effect of humidity in background gas on residual O_3 concentration.

B. Humidity effect on TCE decomposition and ozone concentration

Effect of humidity on TCE decomposition is also investigated. Fig. 4 represents residual ozone concentration after the DBD reactor with various relative humidity (RH). The higher humidity leads to the lower ozone exhaust. It is explained by the decrease of atomic oxygen through the reactions below;

$$H_2O + O \rightarrow OH + OH \tag{11}$$
$$O + OH \rightarrow O_2 + H . \tag{12}$$

Ozone is mainly formed by combination of atomic oxygen and molecular oxygen, therefore decrease of atomic oxygen critically reduces eventual ozone concentration.

Besides, Fig. 5 shows the humidity effect on TCE decomposition efficiency. The decomposition efficiency against humidity has a complicated behavior. The efficiency at RH = 20% is almost the same as (rather higher at high SED than) that in dry air (RH = 0%), while the efficiency under RH = 40% or over monotonically decreases with increasing humidity.
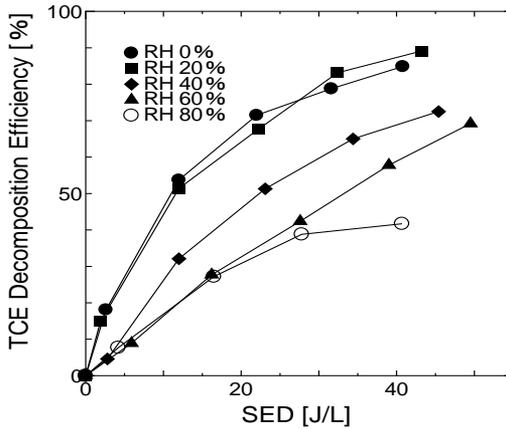
Fig. 4. Humidity effect on TCE decomposition efficiency.
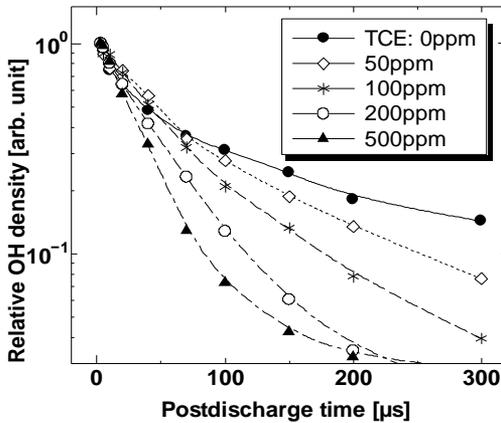
Fig. 6. Time evolution of OH radicals with various TCE concentration (RH =100%).

In order to understand these results, the chemical reaction processes inside NTP must be clarified. Especially, the humidity effect is significantly related to the reactions including OH radical. The suppression of TCE decomposition efficiency against increasing humidity may suggest that OH radicals do not decompose TCE. In order to clarify the OH influence upon TCE decomposition, we measured the time evolution of OH radicals with various TCE densities in the background gas in coaxial cylinder DBD. For pursuit of chemical reactions after the discharge, pulsed barrier discharge is used. The results are shown in Fig. 5. In the figure, the addition of TCE leads to quick OH decay, which implies that OH reacts with TCE.

With the results, the reason for humidity effect on TCE decomposition is estimated below;
(i) OH radicals decompose TCE.

(ii) However, OH radical strongly reacts with O radical (atomic oxygen) which significantly decompose TCE. As a consequence, O reduction by OH has considerable influence leading to suppression of decomposition efficiency.

With the consideration above and results in Fig. 5, it can be estimated that the effect of (i) and (ii) balances at 20% of RH. The effect of (i) should be larger than (ii) under 20% of RH, which leads to enhancement of decomposition with increasing efficiency, and vice versa.

IV. CONCLUSION

The catalyst and humidity effects on TCE decomposition are investigated in this study. The addition of MnO_2/Al_2O_3 catalyst after the DBD reactor improves the decomposition efficiency and suppresses ozone. However there seems the saturation of catalyst effect between 1 and 3 g of catalyst.

As for the humidity effect, increasing humidity suppresses ozone exhaust. The decomposition efficiency does not depend on humidity under 20%, while increasing humidity leads to decrease of TCE decomposition over 20% of RH. With the direct optical measurement of OH radicals reacting with TCE, this phenomenon can be explained by the magnitude of OH reactions with TCE and atomic oxygen.

REFERENCES

[1] H. H. Kim,"Nonthermal Plasma Processing for Air-Pollution Control: A Historical Review, Current Issues, and Future Prospects," *Plasma Process. Polym.*, Vol.1, 91-110 (2004)

[2] T. Oda, "Non-thermal plasma processing for environmental protection:decomposition of dilute VOCs in air," *J. Electrostat.*, Vol.57, 293–311 (2003)

[3] F. Holzer, U. Roland, F.-D. Kopinke, "Combination of non-thermal plasma and heterogeneous catalysis for oxidation of volatile organic compounds: Part 1. Accessibility of the intra-particle volumue," *Appl. Catalysis. B*, Vol. 38, 163-181 (2002)

[4] M. Magureanu, N. B. Mandache and V. I. Parvulescu: "Chlorinated organic compounds decomposition in a dielectric barrier discharge", *Plasma Chem. Plasma Process*, Vol. 27, 679 – 690 (2007)

[5] S. Futamura, A. H. Zhang and T. Yamamoto, "The dependence of nonthermal plasma behavior of VOCs on their chemical structures", *J. Electrostat.*, Vol. 42, 51–62 (1997)

[6] R. Ono and T. Oda, "Measurement of gas temperature and OH density in the afterglow of pulsed positive corona discharge," *J. Phys. D: Appl. Phys.*, Vol.41, 035204 (2008)

[7] S. Kanazawa, H. Tanaka, A. Kajiwara, T. Ohkubo, Y. Nomoto, M. Kocik, J. Mizeraczyk and J. S. Chang, "LIF imaging of OH radicals in DC positive streamer coronas," *Thin Solid Film*s, Vol.515, 4266–4271 (2007)

[8] A. Ershov and J. Borysow, "Dynamics of OH (X2Π,v=0) in high-energy atmospheric pressure electrical pulsed discharge," *J. Phys. D: Appl. Phys.*, Vol. 28, pp.68-74 (1995)

[9] Y. Nakagawa, R. Ono and T. Oda, "Density and temperature measurement of OH radicals in atmospheric-pressure pulsed corona discharge in humid air", *J. Appl. Phys.*, Vol. 110, 073304 (2011)

[10] J. Luque and D. R. Crosley, "LIFBASE, Database and spectral simulation for diatomic molecules," *SRI International Report*, MP-99-009 (1999)

[11] C. Y. Chan, R. J. O'Brlen, T. M. Hard, and T. B. Cook, "Laser-Excited Fluorescence of the Hydroxyl Radical: Relaxation Coefficients at Atmospheric Pressure," *J. Phys. Chem.*, Vol.87, pp.4966-4974 (1983)

[12] G. P. Smith and D. R. Crosley, "Vibrational energy transfer in A 2Σ+ OH in flames," *Applied Optics*, Vol.22, No.10, pp.1428-1430 (1983)

[13] L.R. Williams and D. R. Crosley, "Collisional vibrational energy transfer of OH (A 2Σ+, v'=1)," *J. Chem. Phys.*, Vol. 104, No 17, 1 (1996)