Dilute TCE Decomposition by the Nonthermal Plasma Combined with MnO₂-supported Alumina

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1. Introduction

As the nonthermal plasma has very strong chemical activity, many researchers have reported the decomposition of various toxic gasses in the air or in the combustion flue gas. The back ground of this research is pretty old. Late Prof. Masuda would like to enhance the electron beam irradiation process by using the electric field of DC or pulse. Indeed, the energy consumption for that was very large because the electron irradiation to the air induced the conductivity of air which is a very good insulator without any electron or ions. Finally he succeeded in decomposing NOx in the flue gas by the high voltage pulse induced plasma[1]. As the same back ground, Mizuno also reported DeSOx by using the pulse plasma in Florida[2]. That possibility is reviewed by Chang et al[3] and many successive reports were done[4-6].

At the same time, Yamamoto et al at RTI (Research Triangle Institute) reported the decomposition of VOCs (volatile organic compounds) including 1,000 ppm CFC-113 in the air which was very difficult to decompose by the conventional flowing system and only the batch system with the pulse plasma could decompose 70 % of 1,000 ppm CFC-113[7]. The authors succeeded in decomposing more than 99% 1,000 ppm CFC-113 in the air[8] by using the ceramic surface discharge reactor. In this field, there are many reports also by many authors[9,10,11]. For VOCs decomposition by the nonthermal plasma, key words (most important performance requested for the plasma reactor and the system) are energy efficiency of the plasma reactor and toxic byproducts processing. Recently the authors are focused on the dilute TCE (trichloroethylene; CCl$_2$=CClH) decomposition to compare the all data observed by the authors each other. Main byproducts are TCAA (trichloro-acetaldehyde: CCl$_3$COH), DCAC (dichloroacetylchloride: CCl$_2$HCOCl), carbon oxide (CO and CO$_2$), COCl$_2$ Cl$_2$ and water. If the plasma energy is sufficient, DCAC and TCAA are fully decomposed. To improve the energy efficiency of the nonthermal plasma system, many researchers tried to combine the plasma reactor with catalysts. The authors also tried to test some catalysts, such as vanadium oxide (V$_2$O$_5$), titania (TiO$_2$), Na-doped zeorite, Cu-doped zeorite, alumina, tungsten oxide (W$_2$O$_5$), and so on[12]. The improvement of the decomposition efficiency by those catalysts is not so apparent without additives[13]. At the same time, the nonthermal plasma in air generates much amount of the toxic ozone which must be removed in the living room. The author found that the thermal decomposition of the ozone at the inlet of the GCMS (Gas Chromato Mass Spectrometry device) can decompose TCE very well[14]. When the TCE-contaminated air is mixed with pure plasma-processed air which contains much amount of the ozone and is introduced into GCMS, some part of the TCE is decomposed at the GCMS inlet of 250 ºC. That phenomenon is also reported by Einaga et al[15] by using the manganese-dioxide. The authors tried to use that manganese-dioxide and found that decompose TCE very well.

In this research, the authors reconstructed the plasma reactor with smaller discharge gap. As the catalyst, manganese-dioxide supported alumina spheres were fabricated and tested. Those experimental results are described. As the authors proposed Direct and Indirect Processes[13], that comparison is also examined.

2. Experimental

2.1 Experimental System The total experimental system is roughly the same as the previously reported one[14] and
is shown in Fig.1. The balance gas is the synthesized air (N<sub>2</sub>:O<sub>2</sub>=4:1 and no other contaminants, dry) and TCE concentration is controlled by using ultra slow liquid pomp through the fine syringe (liquid injection with heating). The gas flow rate is from 0.5 L/min to 2.0 L/min. Concerning with the gas flow, there are two modes. One is named as the Direct Method or Direct Process where the TCE-contaminated air passes through the plasma reactor directly and passes through the catalyst-filled area if necessary. Another method is named as the Indirect Method or Indirect Process where the plasma processed clean air is mixed with the TCE-contaminated air after the plasma reactor. If necessary, that mixed gas passes through the catalyst-filled area which can be temperature-controlled but kept at the room temperature in this case. Typical TCE concentration is 250 ppm. For Indirect Process, TCE concentration at the TCE injection (TCE in the Fig.2) is 500 ppm at some time to adjust the final concentration of 250 ppm where TCE concentration is only 250 ppm. For Indirect Process, TCE concentration at the TCE reactor. If necessary, that mixed gas passes through the catalyst-filled area if necessary. Another method is named as the Indirect Method or Indirect Process where the plasma processed clean air is mixed with the TCE-contaminated air after the plasma reactor. If necessary, that mixed gas passes through the catalyst-filled area which can be temperature-controlled but kept at the room temperature in this case. Typical TCE concentration is 250 ppm. For Indirect Process, TCE concentration at the TCE injection (TCE in the Fig.2) is 500 ppm at some time to adjust the final concentration of 250 ppm where TCE concentration is only calculated value from the gas flow and injected volume of TCE.

The decomposition byproducts and residual components are analyzed by the GCMS (Shimadzu Co. GCMS-QP5050A used to detect TCE, Cl<sub>2</sub>, COCl<sub>2</sub>, TCAA, DCAC etc) or FTIR (Fourier-Transform Infra Red Spectrometer; Shimadzu Prestage 21 used to detect TCE, CO, CO<sub>2</sub>, O<sub>3</sub>, NO, N<sub>2</sub>O etc). The ozone concentration is also observed by the ozone meter (Okitronics, QZM-700G) or the ultra violet spectrometer. NOx concentration is also checked by the chemical luminescence (Shimadzu Co. NOA7000A). The non-thermal plasma is excited by AC (50 Hz) high voltage boosted by the neon transformer. The electric discharge power is observed by Lissajous’ method. At the same time, current and voltage are also monitored by the digital oscilloscope. Final exhausted gas is cleaned by passing through the activated coal or bubbling through alkali solutions.

### 2.2 Plasma Reactor

Plasma reactors were newly constructed barrier type reactors assembled with good geometrical accuracy. The basic construction is the same as the former reactors. The reactor is made of 250 or 300 mm long glass tube whose inner diameter is 16.8 mm and outer diameter is 19.2 mm. The grounded thin copper film is wound around the tube where the total film winding width determines the plasma length of the reactor. The real plasma length is from 100 to 255 mm long. The discharge power is proportional to the plasma length, if the applied peak voltage is the same. In this energy range, the ozone production capability is also proportional to the input energy and following experiments were done for 200 mm long reactors.

Four different sizes of the bolt type discharge electrodes (made of the stainless steel) were tested which located at the center of the glass tube. Those sizes are 16.0 mm, 12.0 mm, 10.0 mm, and 6.0 mm in diameter meaning the discharge gap distances are 0.4 mm, 2.4 mm, 3.4 mm, and 5.4 mm long, respectively where the discharge bolt length is 255 mm long mostly. The plasma volumes are 5.25 cm<sup>3</sup>, 27.6 cm<sup>3</sup>, 36.4 cm<sup>3</sup>, and 49.2 cm<sup>3</sup>, respectively. The typical gas flow rate is 1.0 L/min indicating corresponding residence times are 0.35 s, 1.66 s, 2.18 s, or 2.95 s. The onset voltages of the reactor are 6 kV, 15 kV, 18 kV and 26 kV, respectively. However, the discharge power increases greatly with a slight increase of the voltage for a large gap reactor.

### 2.3 Manganese-dioxide Supported Alumina Spheres

As the plasma processed air contains much amount of the ozone, typically 100 ppm ~ 2,000 ppm which is strongly dependent on the discharge power, humidity and the reactor itself, the exhausted ozone in the living room must be very small (usually less than 0.1 ppm) by the regulation. Therefore the plasma processed air should pass through the ozone removal process. Moreover, the former experiments suggested that TCE can be decomposed by mixing TCE-contaminated air with the plasma processed air (12). At that time, high temperature was very effective in decomposing TCE which suggested that the decomposition of the ozone by heating is very important factor to decompose TCE. If GCMS does not use high temperature gasification at the inlet of the GCMS, no TCE decomposition was observed. As the ozone decomposition catalyst, the manganese-dioxide is well-known. When we use manganese-dioxide as the ozone remover, dilute TCE in the air with the ozone is also decomposed very well. However, the manganese-dioxide adsorbs TCE well and the separation of the TCE adsorption effect and real TCE decomposition is very difficult. For those reasons, new type catalysts are manufactured. The manganese-dioxide is supported on the other ceramic spheres. Several kinds of ceramic spheres are examined and alumina spheres with 3 mm diameter (neobeed made by Mizusawa Co.) are found to be the best as the host material of the manganese-dioxide. The manganese-dioxide supporting process is followings. Acetic manganese with water (Mn(CH<sub>3</sub>COO)<sub>2</sub>2H<sub>2</sub>O) is weighed and water solution of that is absorbed on/in the alumina spheres and oxidized for some time. Three different manganese-dioxide concentration (0.5 weight %, 1.0 weight % and 5 weight %) alumina spheres were fabricated by normal BET method or 1 point method recorded by the Gemini (Shimadzu Co.). Other alumina supplied as SSA has much smaller specific surface area and is not used any more because the TCE decomposition is not detected. As shown in the Table, bulk manganese-dioxide has very little surface area and very large volume (roughly 600 times large) compared with the neo-beed with MnO<sub>2</sub>. As the pure neo-beed cannot decompose TCE, the manganese-dioxide effect to decompose the ozone is very apparent. Bulk manganese-dioxide can also decompose the ozone but the volume of that bulk is very large and that adsorbs TCE so much which requests long time experiments to obtain the exact experimental data. As shown in Fig.2, the ozone decomposition performance is very well for 5 weight % manganese-dioxide and following experiments were done only.
Experimental

3.1 Ozone Generation

The ozone generation performance of the plasma reactor is shown in Fig. 3 where the horizontal axis is the discharge energy and the vertical indicates the generated ozone concentration. As described in the former chapter, the electric discharge power is rather small for high voltage application. In other word, the electric field in the discharge area is larger in the short gap than that in the wide gap when the electric discharge power is the same. Figure 3 suggests that the shortest gap (16 mm discharge electrode) is the most suitable for the ozone generation and maybe the chemical reaction should be the largest among 4 reactors. Following experiments were done by using the plasma reactor with the shortest gap of 0.4 mm. As the aim of this work is not the ozone generation but VOCs decomposition, the ozone generation study was not done so much. If the air contains 100 ~ 1,000 ppm level TCE, the ozone generation is much suppressed (15). However, details of such phenomenon have not been examined because the author’s aim is different.

3.2 Optimization of the Manganese-dioxide Supported Alumina

As shown in Table 1, the authors used plenty of the bulk manganese-dioxide (typically 1000 mg ~ 3000 mg) which is pulverized by the hammer-crashing. The specific surface area of the powder is not so large but it takes much time to realize the equilibrium (more than 1 hour typically). The author would like to identify the TCE adsorption effect of the new catalyst and TCE concentration change after passing through the manganese-dioxide supported alumina spheres and TCE concentration change with time are observed for different amounts of the catalyst as shown in Fig. 4. The adsorption time constant is from 8 minutes to about 60 minutes. From those data, the authors determined to use 1,000 mg manganese-dioxide supported alumina because small amount of catalyst cannot decompose the all ozone as shown in Fig.3 (50 mg alumina cannot decompose all ozone) but a large amount of catalyst needs a lot of time to understand the ozone and plasma effect, separately. The final ozone concentration should be 0.1 ppm for the living area in Japan. From Fig.4, the saturation time of the TCE adsorption for 1,000 mg alumina is about 45 minutes and usually data are recorded after about 1 hour operation. Heating process can remove the adsorbed TCE and refresh the catalyst which was also confirmed experimentally.

3.3 Degradation and Refreshment of the Catalyst

Not only the adsorption of TCE but also the ozone decomposition by the new catalyst is also degraded as shown in Fig. 2. If the catalyst is heated at 70 °C, the ozone decomposition capability is refreshed. Figure 5 is FTIR spectra of the gas (fresh non-plasma-processed air) passing through the catalyst area at 70°C, which process is refreshment, indicating the desorption of nitric oxide. The plasma-processed air contains nitric oxide (N2O and N2O3) as similar to Fig.5 and a large amount of ozone. Those nitric oxide and ozone are not shown in FTIR after passing.
the catalyst at the room temperature.

3.4 Direct Process of 250 ppm TCE Decomposition

When 250 ppm TCE contaminated air passes through the plasma reactor without any catalyst, the residual TCE concentration is shown in Fig. 6 where the different signals in the Figure mean the different reactor length. In practice, we cannot identify the difference. The horizontal axis is SED which is specific energy density. SED is defined as the discharge power / flow rate and the unit is Joule/Litter. As the original TCE concentration is 250 ppm in this case, the TCE decomposition efficiency is about 90 % at the SED of 40 ~ 50 J/L which value is pretty good without the catalyst. In this case, typical medium byproduct is DCAC.

3.5 Indirect Process of TCE Decomposition

The gas flow in the case of the Indirect Process is shown in Fig. 7. The synthesized air (N₂:O₂ = 4:1) is divided into two parts (50:50). One passes through the nonthermal plasma region. Another half gas passes the TCE injection area and TCE concentration is adjusted to 500 ppm. Both TCE-injected air and plasma processed air are mixed. After mixing, the gas passes through the catalyst-filled area where the catalyst is the manganese-dioxide supported alumina sphere (3 mm in diameter and total weight is 1,000 mg) and the temperature is the room temperature. The residual TCE and byproducts of carbon oxides (CO and CO₂) are shown in Fig. 8. As the original concentration of TCE is 500 ppm, the average concentration is half of the original, 250 ppm. If the mixed air does not pass the 1,000 mg manganese-dioxide supported alumina spheres, the ozone cannot be decomposed and TCE concentration is 250 ppm. At the SED of 20 J/L, TCE decomposition efficiency is more than 95 %. However, the carbon balance from TCE to COₓ is very poor. If 250 ppm TCE is perfectly oxidized, total CO and CO₂ should be 500 ppm but the figure suggested almost 50 % at the SED of 90 J/L. At SED of 40 J/L, almost TCE is decomposed but the concentration of the carbon-dioxide increases even at the higher SED but the concentration of carbon-monoxide is rather constant (saturated) to about 40 ppm. One possible idea is that CO is generated by the direct oxidation of TCE but the carbon-dioxide is generated by the further oxidation from the carbon monoxide TCAA and other byproducts. In this Indirect Process, no DCAC is detected as the byproduct indicating that the nonthermal plasma process oxidizes TCE to DCAC with the aid of the electron and ion impaction but the oxidation by the atomic oxygen radical generated by the decomposition of the ozone on the manganese-dioxide surface cannot produce DCAC but only TCAA. DCAC and TCAA have the same molecular weight and chemical compositions of them are also the same. Only the connecting position of the chlorine is different.

3.6 Direct Process with Catalyst

There are several methods to combined with the catalyst. One is that the plasma reactor filled with the catalyst. In that case, the catalyst affects the discharge mode. The original nonthermal plasma is standard barrier discharge mode but the catalyst in the discharge space causes surface discharge on the catalyst and also induces many point contact discharges between catalyst pellets. The author already reoprted the position effect of the catalyst(12) but still now the exact solution is not yet obtained. In this experiment, the alumina catalyst is filled in the separate teflon tube and the plasma processed TCE-contaminated air passes through that catalyst filled tube where the temperature is the room temperature. Figure 9 shows the residual TCE concentration after passing through the plasma reactor and the catalyst tube for different discharge energy plotted as the SED. Only at the SED of 10 J/L, TCE...
decomposition efficiency is already about 95 % which is much better than all other data for Direct Process without the catalyst or Indirect Process with the catalyst. The increase of carbon oxide (COx) versus the increase of SED in Fig. 9 is also the same tendency in Fig. 8 but the absolute value is much different. The maximum concentration of carbon-monoxide in Fig.9 is about 150 ppm which is much higher than the maximum carbon monoxide concentration of 50 ppm in Fig.8. The same tendency is also observed for carbon-dioxide. The maximum concentration of carbon-dioxide is about 350 ppm which is much larger than the maximum value of 200 ppm in Fig. 8. The carbon-dioxide curve is also saturating at SED of 90 J/L which is easily explained. The total concentration of CO and CO2 is roughly 500 ppm. At the SED of 90 J/L, almost byproducts should be carbon oxide (COx), water and chlorine. Other toxic byproduct is phosgene which still exists at the SED of 90 J/L. To remove the phosgene, other chemical process (bubbling through some basic liquid, for example) is necessary. From Fig. 9, TCE decomposition efficiency and carbon balance to COx are shown in Fig. 10 where the TCE decomposition efficiency is already 70 % at the SED of 7 J/L and is about 95 % at the SED of 10 J/L which is very small. At the SED of 90 J/L, carbon mass balance from TCE to COx is roughly close to 98 % and TCE decomposition efficiency is more than 99 %, close to 100 %.

3.7 Decomposition of Other VOCs As TCE is one of the easily decomposed materials by the nonthermal plasma, decomposition performance for other VOCs must be examined.

One example is shown in Fig. 11 where VOC is isopropylalcohol with the residual isopropylalcohol and carbon oxide concentrations are plotted. When the isopropylalcohol is oxidized, main byproduct is the acetone and acetone is also oxidized with the increase of the discharge power (or SED). Production of the carbon oxide is roughly the same tendency of the oxidation of TCE. Carbon balance from TCE to carbon oxide is only 50 or 60 %. The decomposition of the acetone is rather difficult and the acetone decomposition is about 80 % at the SED of 90 J/L.

4. Conclusions

The improvement of the nonthermal plasma reactor is realized with rather narrow discharge gap (0.4 mm) with an exact scaling. That TCE decomposition efficiency is about 90 % at the SED of 50 J/L which is better than the former results without the aid of the catalyst.

The manganese-dioxide is very good catalyst to decompose the ozone generated by the plasma process of the air and TCE is also decomposed at the decomposition of the ozone on the manganese-dioxide surface. The decomposition of the ozone would generate atomic oxygen which has very strong oxidation capability and TCE is oxidized very well. The new catalyst, where the manganese-dioxide is supported on the alumina sphere, can decompose TCE very well.

There are two methods where the manganese-dioxide works well. In the case of the Indirect Process where the plasma processed pure air is mixed with the TCE contaminated air and then passes through the manganese-dioxide catalyst, TCE decomposition efficiency is 95 % at the SED of 20 J/L but the carbon balance from TCE to the carbon oxide is about 50 % at the SED of 90 J/L.

Direct process cannot decompose TCE so well without any catalyst, but Direct Process with the new manganese-dioxide catalyst, realizes the TCE decomposition efficiency of 95 % at the SED of 10 J/L. At the SED of 90 J/L, more than 99 % TCE is decomposed and the carbon balance from TCE to carbon oxide is also more than 98 %, where SED of 90J/L and 100 % TCE decomposition means TCE decomposition efficiency is 60g/kWh. If that value is realized at the SED of 10 ~ 20 J/L, this system will
be soon in practice.

The degradation life time of the catalyst is not yet fixed in this experiment and must be done as the further work.

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