

Influences of H₂ and O₂ and in situ Ca(OH)₂ absorption on nonthermal plasma decomposition of trichloroethylene in N₂

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Abstract

The decomposition of trichloroethylene (TCE) with a wire-in-tube pulsed corona reactor was experimentally investigated. It was found that the decomposition of TCE was higher in N₂ gas, compared to the decomposition in the gas stream containing H₂ or O₂ gas. The main gaseous products were HCl and Cl₂ for TCE decomposition in N₂ gas. With the existence of 2% H₂ in gas stream, the yield of HCl was three times higher than that in N₂ gas. When O₂ gas was added into N₂ gas stream, the main decomposition products were COCl₂, CO₂ and DCAC. In order to prevent the production of unwanted byproducts from TCE decomposition, a combination of plasma decomposition and in situ absorption was proposed by coating a layer of Ca(OH)₂ on the surface of the grounding electrode. It was demonstrated that the Ca(OH)₂ sorbent in the plasma reactor played an effective role as a scavenger participating in the TCE decomposition by in situ capturing of the unwanted products like HCl, therefore resulting in the increase of TCE decomposition.

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1. Introduction

Trichloroethylene (TCE) is widely used in industrial processes as an effective detergent and solvent for metals degreasing and dry cleaning. Since it has been recognized as a carcinogenic compound, strict regulations have been issued for TCE discharges [1]. Most of TCE is discharged as a gaseous compound into air. But, due to its heavy density compared to water, once dissolved in water, it will accumulate under the water and therefore contaminating soils and underground water by permeation [2].

However, to control the emission of large volume and low concentration of TCE in an economical and effective manner is still a challenging work. Fortunately, many novel technologies have been developed in recent years, and among them nonthermal plasma is regarded as a prospective means for removing multifarious air pollutants [3,4].

A variety of nonthermal plasma techniques, such as electron beam [5,6], pulsed corona [7–9], dielectric packed bed/silence discharge [10–13], and hybrid plasma-catalyst methods [14] have been employed for the treatment of volatile organic compounds (VOCs). The decompositions of VOCs by nonthermal plasmas undergo the steps of initiation, propagation, and termination of the concerned reactions. The dissociation and/or excitation of the targeted VOC molecules by direct electron impacts, and the production of active reaction radicals and ions by electron dissociation and ionization of background gas molecules represent the initial step. The subsequent chain reactions between the produced radicals and VOC molecules propagate until stable products are formed.

Nevertheless, a problem associated with this technology is that unwanted byproducts and some toxic compounds are inevitably produced by the decomposition of some VOCs, especially for halogenated VOCs, as reported in the above-cited studies. In other words, the plasma-induced chemical reaction seems inherently difficult to control in terms of the generation of unfavorable products. Therefore, it is essential to prevent the production of secondary pollutants for this technology to be used in practical applications.

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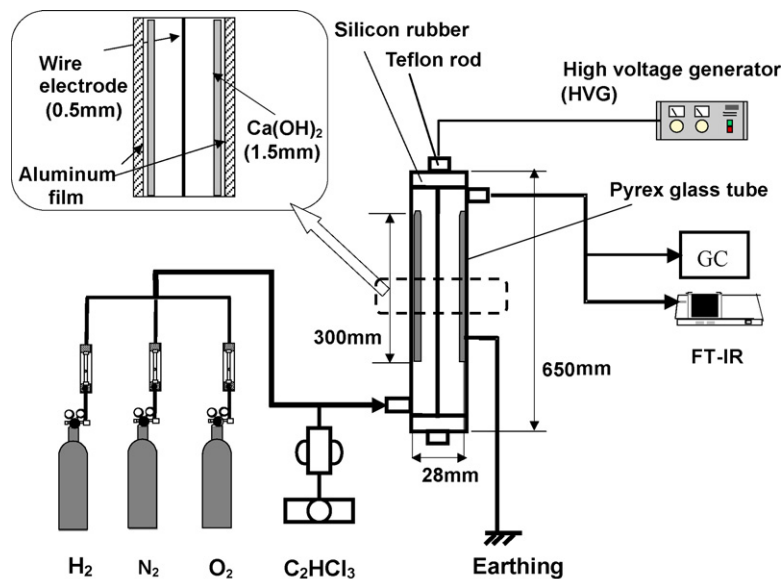


Fig. 1. Schematic diagram of experimental system.

In this study, we investigated the decomposition of Trichloroethylene (C_2HCl_3) by a wire-in-tube pulsed corona reactor, as a successive study to work on pulsed corona plasma for halogenated VOCs decomposition [9]. We investigated the effects of H_2 and O_2 on the decomposition behaviors of trichloroethylene. With the aim of preventing the production of harmful byproducts from the plasma decomposition of trichloroethylene, a technique of plasma decomposition combined with in situ gas absorption by an alkaline sorbent of $Ca(OH)_2$ was examined to capture the undesirable species from the plasma decomposition reaction.

2. Experimental

A schematic diagram of the experimental system is shown in Fig. 1. The system consists of a sample gas feeding system, a corona reactor, a high pulse voltage generator, and a gas sampling and analysis system. The sample gases were prepared by mixing cylindered N_2 and H_2 or O_2 gas at a predetermined proportion. The concentration of C_2HCl_3 in sample gas was adjusted to a constant concentration of 200 ± 2 ppm by injecting liquid TCE with a micro-syringe system before feeding into the reactor. In order to stabilize the TCE concentration in the sample gas, a buffer tank of 0.1 m^3 was installed in the sample gas flowing line. The total flow rate of gas was fixed at a constant value of $500 \text{ cm}^3/\text{min}$ for all experiments.

A wire-tube combination was adopted as the corona reactor for the experiment. It consists of a Pyrex glass tube with an aluminum film (0.3 mm thick) attached to the inner wall as the grounding electrode and a coaxial stainless steel wire of 0.5 mm in diameter as the positive electrode connected to high pulse voltage. The inner diameter of the tube is 28 mm, and the effective height of corona discharge is 300 mm. For the corona reactor combined with in situ absorption, a $Ca(OH)_2$ layer of about 1.5 mm thickness was coated on the grounding electrode, the surface of the aluminum film. To make the $Ca(OH)_2$ coated

electrode, a $Ca(OH)_2$ slurry, prepared by mixing 60% water and 40% $Ca(OH)_2$ powder, was evenly painted on the aluminum film of the grounding electrode. After the $Ca(OH)_2$ layer was naturally dried in air for about 1 h, the whole reactor was placed in an electric stove for heating at 110°C in air for 3 h to form the electrode. The mass of $Ca(OH)_2$ layer was about 40 g (corresponding to $0.15 \text{ g}/\text{cm}^2$).

A typical pulse-forming circuit, using a rotating spark gap (RSG) system, was adopted to produce the pulsed voltage [15]. It was measured that the width of the voltage pulse was less than 300 ns, and that the rising time was within 50 ns. The pulse repetition rate was set at 50 pulses/s. The power input into the reactor was adjusted by changing the voltage of power source. The onset voltage is about 18–20 kV and the voltage applied to reactor changing from 20 to 26 kV. The energy injected into the reactor was calculated by measuring the voltage and current waveforms by a high voltage probe. The influences of the $Ca(OH)_2$ layer on the discharge characteristics were also measured. We did not find obvious changes in current and voltage waveform with the coating except that the onset discharge voltage increased a little.

Analyses of the sample gas, before and after reaction, were carried out by both an on-line FT-IR spectrometer (Shimadzu, FTIR-8900) and a gas chromatograph (Shimadzu, GC-14B). The decomposition of C_2HCl_3 is defined as

$$\eta = \frac{c_{in} - c_{out}}{c_{in}} \times 100\% \quad (1)$$

where c_{in} and c_{out} are the inlet and outlet concentrations of C_2HCl_3 , respectively. All experiments were implemented at atmospheric pressure and ambient temperature of about 20°C .

In this study, only the concentrations of C_2HCl_3 and HCl yielded from TCE decomposition were quantitatively analyzed. The calibration of the FT-IR instrument was performed by a series of certified concentrations of C_2HCl_3 between 0 and 300 ppm. The same method was also used to get the calibration

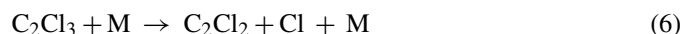
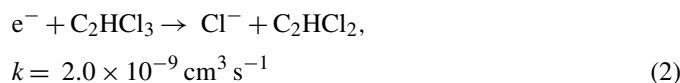
curve for HCl measurement. The accuracy of the measured concentration can be estimated to be within 2% of the true value. To ensure reproducibility, the concentration of C_2HCl_3 under certain operation conditions was measured several times until the difference between the nearest three times was within 2 ppm.

3. Results and discussion

3.1. TCE decomposition in N_2 gas

As the first step, the experiment was implemented by the reactor without $Ca(OH)_2$ coated on the inner wall of the reactor. Fig. 2 shows the decomposition of C_2HCl_3 in pure N_2 gas as a function of the input power into the reactor. The initial concentration of C_2HCl_3 is 200 ppm and the mass flow rate is $500\text{ cm}^3/\text{min}$. It was found that the decomposition of C_2HCl_3 increased from 35% removal to 99.5% with the increase of input power from about 6.5–27 W. Meanwhile, the production of HCl also increased with the increase of energy injected into the reactor as shown in Fig. 2.

In N_2 gas, the plasma decomposition of C_2HCl_3 is most likely initialized by a dissociative electron attachment reaction (2) to the generation of Cl radicals [3], and then followed by a chain of radical reactions to form the final products. Some reactions concerned are given below [5,12,16,17]:



It was calculated by material balance that over 90% hydrogen derived from C_2HCl_3 molecule in sample gas finally existed in the form of HCl after reaction. The Cl atoms produced will

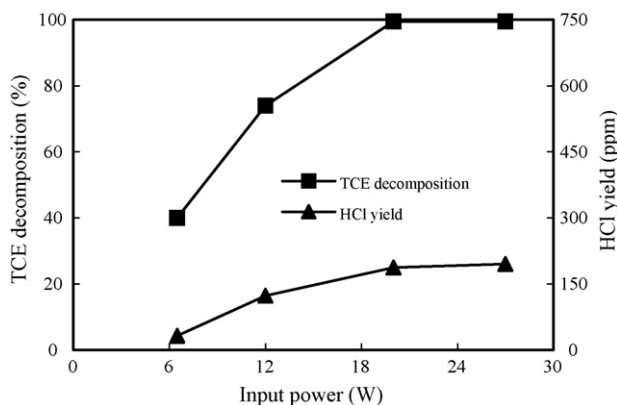
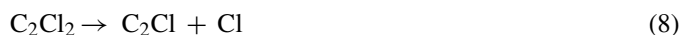


Fig. 2. Decomposition of TCE and HCl yield as a function of input power (in N_2).

finally recombine together to form molecular Cl_2 by reaction (7) (symbol M in equations represents neutral molecule, such as N_2) [10]. On the other hand, the compound of C_2Cl_2 might be the main intermediate product according to C_2HCl_3 decomposition path. But, we did not detect the production of any organic compound to a significant degree by infrared spectroscopy as shown in Fig. 3. It was indicated that the intermediate of C_2Cl_2 might participate in reactions further, such as



Because there are no additional reactants like O_2 in gas stream, the carbon atom derived from C_2HCl_3 molecule might be exist in the form of solid product (such as C_n) [18]. In fact, some tar-like product was found depositing on the electrodes in the reactor after the reaction.

3.2. TCE decomposition in gas mixture of H_2 and N_2

With the adding of 2% H_2 into N_2 gas, the decomposition of C_2HCl_3 exhibited some difference with that in pure N_2 gas. Compared with C_2HCl_3 decomposition in N_2 gas (Fig. 3), the decomposition of C_2HCl_3 in 2% $H_2/98\%$ N_2 gas mixture (Fig. 4) was a little lower. But, the yield of HCl was almost three times of that produced in N_2 gas. It was quantified that the production of HCl in 2% $H_2/98\%$ N_2 gas mixture accounts for the most liberated chlorine from C_2HCl_3 decomposition, which indicated that the hydrogen in gas stream participated in the C_2HCl_3 decomposition reaction to form the final product of HCl. Reactions (10)–(13) are the possible reactions to the yield of HCl. Fig. 5 shows the FT-IR pattern of the products from C_2HCl_3 decomposition in gas mixture of H_2 and N_2 . There might be some hydrocarbons produced as byproducts with the presence of H_2

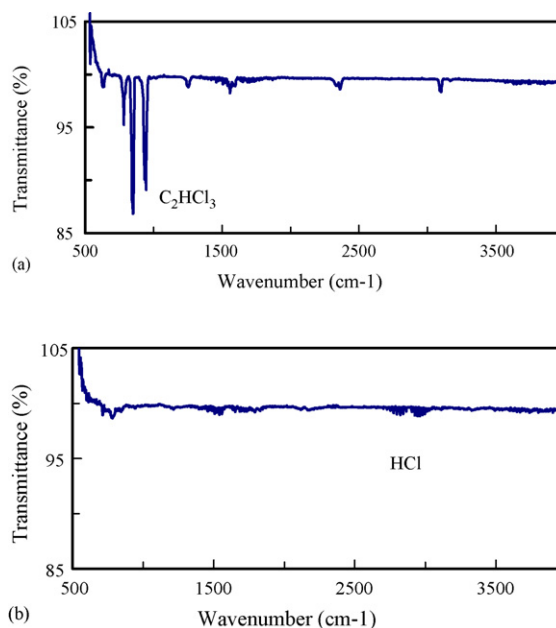


Fig. 3. FT-IR pattern of the products from TCE decomposition in nitrogen gas. (a) Without power injection; (b) with power injection of 20 W.

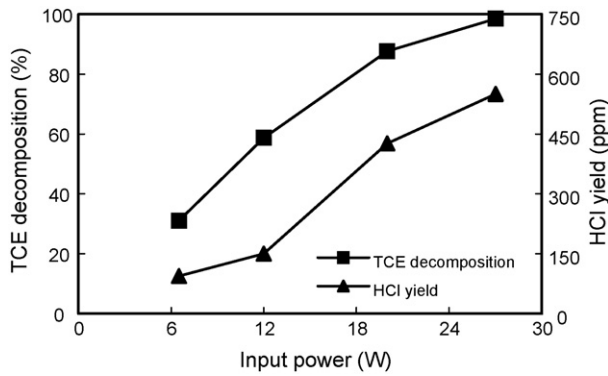
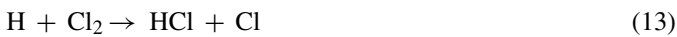


Fig. 4. Decomposition of TCE and HCl yield as a function of input power (in 2% H₂/98% N₂).

in gas stream [19]:



3.3. TCE decomposition in gas mixture of O₂ and N₂

In most practical cases, TCE should be removed from gas stream containing oxygen. Therefore, the influence of O₂ concentration in gas stream on TCE decomposition was investigated in present experiment. Fig. 6 shows the decompositions of TCE with 2%, 10% and 20% O₂ in N₂ gas.

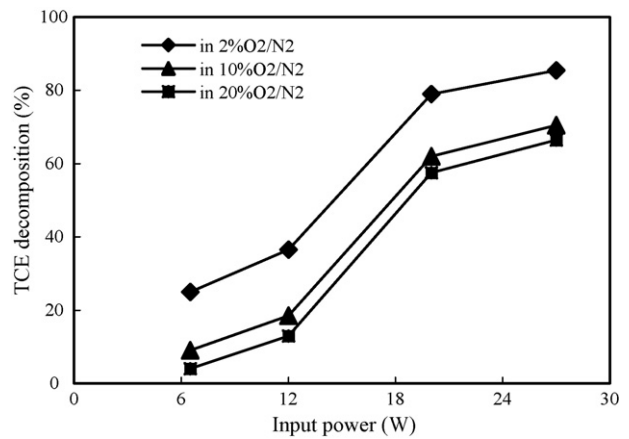
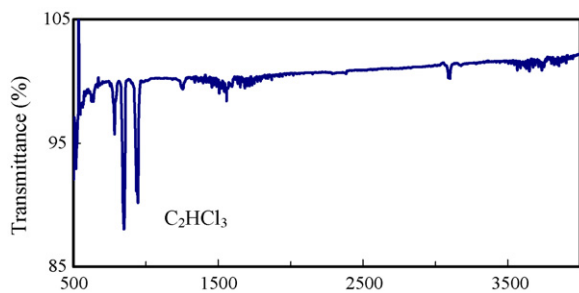
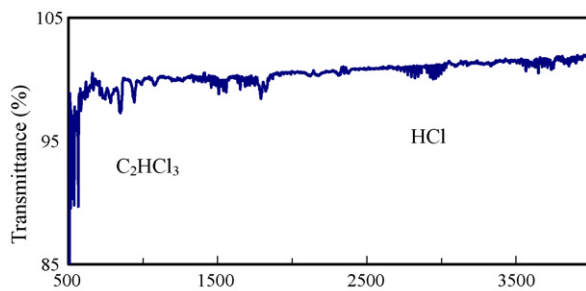


Fig. 6. Decomposition of TCE as a function of input power (in gas mixture of O₂ and N₂).

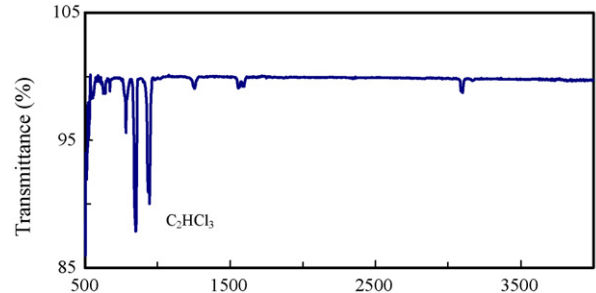
With the presence of O₂ in sample gas, the ideal products from C₂HCl₃ destruction are expected to be HCl, CO₂ and H₂O. From the FT-IR spectra of the sample gas after reactions (Fig. 7), we detected an amount of CO₂ produced. But, only a limited amount of HCl was detected when O₂ was contained in the sample gas. Moreover, the HCl yield largely decreased with the increase of O₂ concentration in the gas stream, as shown in Fig. 8. Also, we did not detect a distinct H₂O production, which means that H₂O was not the main final product of the H atom derived from C₂HCl₃ molecular after reaction. As shown in Fig. 7, the identified products were COCl₂, CO₂ and C₂HCl₃O (DCAC). The existence of DCAC as an intermediate product from TCE decomposition was also confirmed by previous researchers [20]. It is thought that with the presence of O₂ in the gas stream, both Cl chain reaction and O chain reaction contributed to the



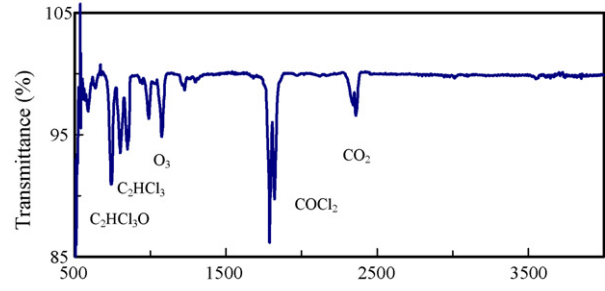
(a) Wavenumber (cm-1)



(b) Wavenumber (cm-1)



(a) Wavenumber (cm-1)



(b) Wavenumber (cm-1)

Fig. 5. FT-IR pattern of the products from TCE decomposition (in 2% H₂/98% N₂) (a) without power injection; (b) with power injection of 20 W.

Fig. 7. FT-IR pattern of the products from TCE decomposition (in 10% O₂/90% N₂) (a) without power injection; (b) with power injection of 20 W.

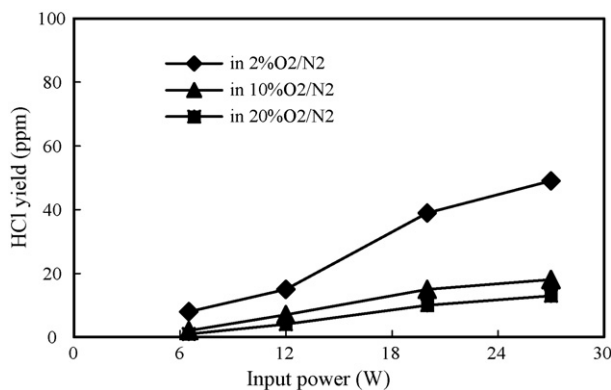
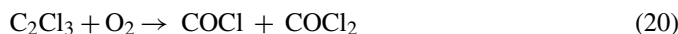
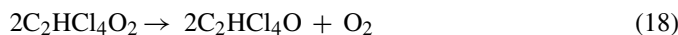
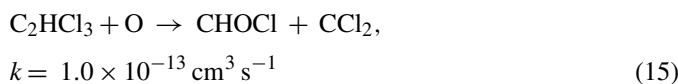


Fig. 8. HCl yield as a function of input power from TCE decomposition in gas mixture of O₂ and N₂.

decomposition of C₂HCl₃. The O atom in reaction (15) is most possibly produced by electron-impact dissociation of molecular oxygen (14). Reactions (15)–(24) are the main reactions for the decomposition of C₂HCl₃ with the presence of O₂ [5,6,20]. The intermediate product of C₂HCl₃O might finally convert to COCl₂ after experiencing a complex chain reaction:



As shown in Fig. 6, the decomposition of C₂HCl₃ decreased with the increase of O₂ concentration. This deterioration of C₂HCl₃ decomposition by O₂ coexisted in the gas was considered that excitement and dissociation of O₂ molecules consumed a certain amount of energy that might contribute to the destruction of C₂HCl₃. The initiation step of C₂HCl₃ decomposition, direct dissociation or excitation of C₂HCl₃ and production of active Cl radicals by electron attachment reaction might be restrained to some degree. Furthermore, O₂ is easy to dissociate under corona discharge to produce active O atoms and O ions due to its low dissociation energy, but the rate coefficient of O atom with C₂HCl₃ is much lower, compared with the rate coefficient of C₂HCl₃ dissociative electron attachment reaction (2). With the increase of O₂ concentration up to 10% in the sample gas, we detected the higher concentration of ozone production

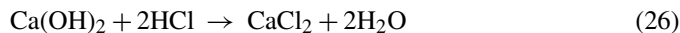
via reaction (19) in the off-gas, which was regarded to have slow rate coefficients with VOCs [10,20,21]:



3.4. TCE decomposition by nonthermal plasma combined with in situ absorption

The prevention of production of unwanted species can be achieved by removing the reaction intermediates such as dissociated chlorine from C₂HCl₃ decomposition. We employed Ca(OH)₂ as the sorbent of reaction intermediates, which was introduced into the corona reactor as described in Section 2. It was observed that the onset corona voltage increased a little with the layer of Ca(OH)₂ coated on the electrode. The Ca(OH)₂ layer functioned as a dielectric barrier between the two electrodes, which caused the increase of the onset voltage. However, it was not observed the obvious change in the aspect of current and voltage waveform of the pulsed power injected into the corona reactor.

The experimental results from TCE decomposition with this modified reactor are presented in Fig. 9, representing the FT-IR patterns of C₂HCl₃ decompositions in N₂ (a), in 2% H₂/98% N₂ (b), and 10% O₂/10% N₂ (c), respectively. By a comparison of Fig. 9(a) and Fig. 3, it was observed that the decomposition product of HCl almost disappeared in the FT-IR pattern with the new reactor combined with Ca(OH)₂ absorption. Instead, we detected the products of CO₂ as shown in Fig. 9(a). The similar result was also obtained when the C₂HCl₃ was processed in 2% H₂/98% N₂ gas mixture as shown in Fig. 9(b). It was found that TCE decomposition in 2% H₂/98% N₂ increased from 87% to almost 100% with an input power of 20 W when Ca(OH)₂ sorbent was coated on the inner wall of the reactor. It is considered that the Ca(OH)₂ layer on the electrode participated in the C₂HCl₃ decomposition reaction by removing the reaction intermediates and products like HCl via reactions (26), thereby promoting the decomposition reaction. The O atom in the product of CO₂ was provided by H₂O molecular produced from reaction (26). Reactions (27)–(30) might be the possible reactions for CO₂ formation [3,17]:



The most interesting result was observed when TCE was processed in the gas mixture composed of 10% O₂ and 90% N₂ with the reactor combined with in situ Ca(OH)₂ absorption. Comparing Fig. 9(c) with Fig. 7, it was found that only CO₂ and O₃ was detected in the FT-IR pattern of decomposition products, and all unwanted products such as COCl₂ and intermediates like DCAC disappeared. Furthermore, the C₂HCl₃ decomposition was greatly increased as shown in Fig. 10, which represents valuable results for practical applications.

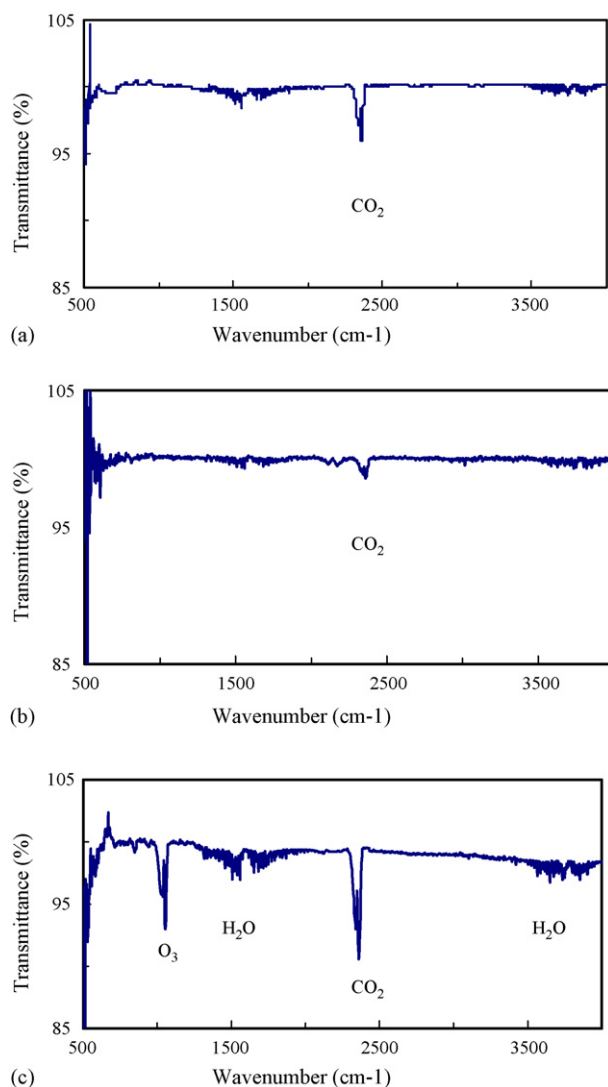


Fig. 9. FT-IR pattern of the products from TCE decomposition with the corona reactor combined with in situ $\text{Ca}(\text{OH})_2$ absorption (with power injection 20 W) (a) in N_2 ; (b) in 2% $\text{H}_2/98\% \text{N}_2$; (c) in 10% $\text{O}_2/90\% \text{N}_2$.

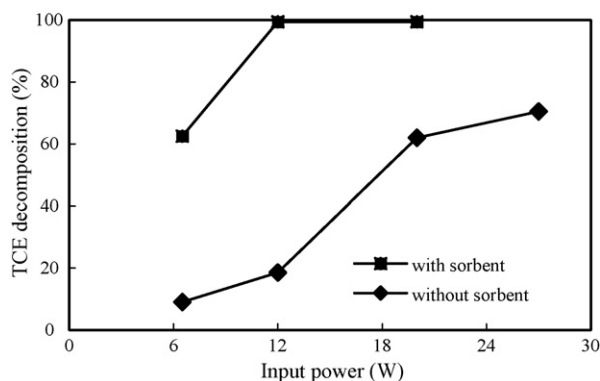


Fig. 10. A comparison of TCE decompositions with and without $\text{Ca}(\text{OH})_2$ absorption (in 10% $\text{O}_2/90\% \text{N}_2$).

To confirm the solid products of $\text{Ca}(\text{OH})_2$ participated in the C_2HCl_3 decomposition, an ion chromatograph was used to analyze the water solution of the surface layer after the decomposition experiment. As the result, we detected the existence of Cl^- ion in the water solution. It was found that the total amount of dissolved chlorine ion in water was almost equal to all the derived chlorine from C_2HCl_3 decomposition, which means that the chlorine derived from C_2HCl_3 decomposition was finally captured by the surface layer of $\text{Ca}(\text{OH})_2$ in the reactor.

4. Conclusions

Experimental results show that the plasma decomposition of TCE was higher in N_2 gas, compared to the decomposition in the gas stream containing H_2 or O_2 gas. The main gaseous products were Cl_2 and HCl for TCE decomposition in N_2 gas. With the adding of 2% H_2 into N_2 gas stream, the yield of HCl was three times higher than that in N_2 gas atmosphere. With the existence of O_2 in N_2 gas stream, the main decomposition products were COCl_2 , CO_2 and DCAC. It was demonstrated that nonthermal plasma combined with in situ $\text{Ca}(\text{OH})_2$ absorption is an effective way to prevent the production of unwanted byproducts such as COCl_2 and HCl from TCE decomposition, and meanwhile significantly promotes the decomposition of TCE. TCE decomposition of 100% was achieved by the reactor combined with in situ $\text{Ca}(\text{OH})_2$ absorption for 200 ppm TCE in a gas mixture of 10% O_2 and 90% N_2 with an input power of 20 W.

Acknowledgements

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