Decomposition of Toluene by Atmospheric Pressure Microwave Plasma Generated Using Metal Salt-impregnated Carbon Felt Pieces

Hideki Kurihara*[1] and Tatuhiko Yajima[2]
[1]*Saitama Industrial Technology Center, 3-12-18 Kamiaoki, Kawaguchi 333-0844*
[2]*Department of Applied Chemistry, Faculty of Engineering, Saitama Institute of Technology, 1690 Fusaiji, Fukaya 369-0293*

(Received January 5, 2007; CL-070013; E-mail: kuri@saitec.pref.saitama.jp)

Atmospheric pressure microwave plasma (APMP) could be easily generated even in air by using carbon felt pieces impregnated with a metal salt such as alkali metal chlorides, alkali earth metal chlorides, and so on (CF/metal salt). As one of applications, the decomposition and complete removal of toluene, one of volatile organic compounds (VOCs) as environmental air pollutants, with APMP assisted by CF/NaCl and CF/$CaCl_2$ was examined. Consequently, we succeeded in decomposing and removing it completely without carbon monoxide formation and CF consumption.

Industrial exhaust gases containing VOCs exhausted from industrial processes are highly toxic to human health. Therefore, it needs to establish a useful method to remove VOCs. Microwave plasma is usually in low pressure and in high electron and ion densities.[1] Argon and nitrogen are often used as ion source gases for the microwave plasma.[2–8] Recently, various methods to generate microwave plasma at atmospheric pressure have been developed, and some of these has been applied to the removal of VOCs.[4–11] Our previous study revealed that CF pieces arranged properly in a reactor tube worked effectively to generate APMP between CF pieces and sustain it steadily.[12] In this study, we examined the decomposition reaction of toluene as a typical VOC gas in air with the APMP. We succeeded in decomposing toluene completely without carbon monoxide formation and CF consumption by using CF pieces containing a metal salt (CF/metal salt), which could generate APMP more easily than pure CF pieces.

A microwave power generator (Shimada Rika Kogyo Co., Ltd.) was used as a microwave source, whose output power can be modulated from 100 to 1500 W at 2.45 GHz. CF/metal salt pieces were prepared by impregnating CF pieces, which were made of rayon fibers calcined at 2500 °C, with 2% aqueous solution of a metal salt and then drying them. Sodium chloride, potassium chloride, magnesium chloride and calcium chloride were used as a metal salt. Two pieces of CF ($5 \times 5 \times 10$ mm) were set lengthwise in a quartz glass tube (16-mm inner diameter), which was located in a cavity chamber. The distance between CF pieces was 1 mm. Air containing 200-ppm toluene was used as a standard VOC gas sample, and the flow rate was 200 $cm^3\,min^{-1}$. The temperature of the gas passing through the cavity chamber was usually between 25 and 53 °C. The outlet gas was cooled down to 25 °C and analyzed by gas chromatography and mass-spectroscopy (Shimazu Co., Ltd., type GC12A and type QP5050). The APMP emission spectra were measured and analyzed by a photonic multi-channel analyzer (Hamamatsu Photonics Co., Ltd., type PMA 11).

The APMP emission spectra measured in airflow were shown in Figure 1. When CF pieces were used alone, no emission spectral peak was observed as shown in Figure 1A. In the case of CF/NaCl pieces, only one spectral peak appeared at 589 nm as shown in Figure 1B, which may consist of sodium D lines attributed to the following electron transitions: $3^2P_{1/2} \rightarrow 3^2S_{1/2}$ (589.6 nm) and $3^2P_{3/2} \rightarrow 3^2S_{1/2}$ (589.0 nm). The APMP emission spectrum from CF/KCl pieces was found to have two spectral peaks at 766 and 770 nm as shown in Figure 1C, which may be attributed to the following electron transitions in K atoms: $3^2D_{3/2} \rightarrow 4^2S_{1/2}$ and $3^2D_{5/2} \rightarrow 4^2S_{1/2}$, respectively. On the other hand, in both cases of CF/$MgCl_2$ pieces and CF/$CaCl_2$ pieces, their emission spectra had their own characteristic broadband structure as shown in Figures 1D and 1E, respectively, besides extremely week peaks attributed to Mg atoms at 383 nm[13] in Figure 1D and Ca atoms at 422 nm[13] in Figure 1E. Speaking to CF/$CaCl_2$, it gave broadband emission spectra at 560 nm and in the region from 590 to 650 nm as shown in Figure 1E. The former may be attributed to $Ca(OH)_2$,[13] and the latter to CaO.[13] These data indicate that alkali metal salts are hardly oxidized, whereas alkali earth metal salts tend to be oxidized in our reaction system.

The decomposition behaviors of toluene in the APMP assisted with CF/NaCl pieces and CF/$CaCl_2$ pieces were examined. Especially, the input power (P_{MW}) dependence of the decomposition of toluene was examined in detail, where, P_{MW} shows the net input power, i.e., the difference between the forward power and the reflected power which was usually less than 10% of

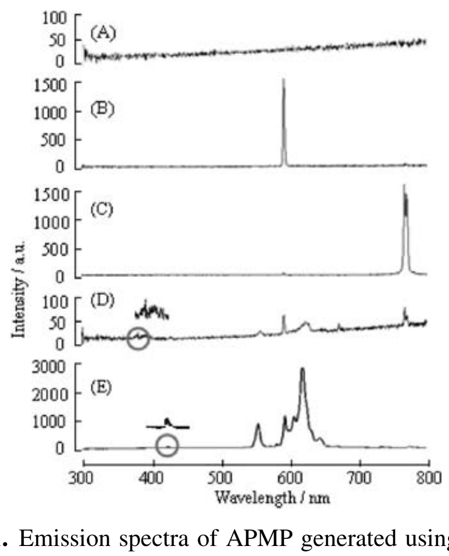

Figure 1. Emission spectra of APMP generated using CF (A), CF/NaCl (B), CF/KCl (C), CF/$MgCl_2$ (D), and CF/$CaCl_2$ (E) in air flow.

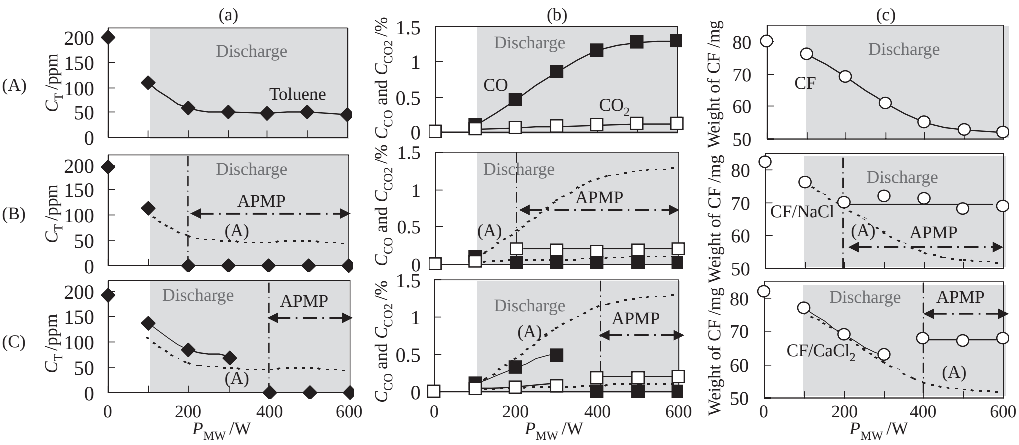

Figure 2. P_{MW} dependence of (a) the removal of toluene (□), (b) the generation of CO (■) and CO_2 (□), and (c) the weight loss of CF (○), when toluene vapor was exposed to APMP generated using CF pieces: CF (A), CF/NaCl (B), $CF/CaCl_2$ (C).

the former. After five-minute irradiation of the microwave, toluene and the products in the effluent gas were quantitatively analyzed. The weight of CF pieces was also measured. Figure 2 shows the P_{MW} dependence of (a) toluene concentration (C_T) and (b) the product concentration, i.e. CO (C_{CO}) and CO_2 (C_{CO2}), and (c) the weight of CF pieces. When CF pieces were used alone, small spark discharges were observed in the gap between CF pieces at more than 100 W of microwave power. However, plasma was not observed even at the higher P_{MW}. The thermographical measurement of the temperature of CF pieces revealed that it reached over 1000 °C at the gap between CF pieces and ca. 200 °C at the reactor wall.[12] Under such conditions, C_T decreased with the increase of P_{MW} to reach ca. 50 ppm at 200 W. CO was a main product in this system. C_{CO} in the effluent gas exponentially increased with increase in P_{MW} to reach the equilibrium of ca. 1.3% in the higher power region, which was the far larger than the concentration estimated from toluene consumed. CO_2 was also yielded, whose concentration reached ca. 0.1% in the higher power region, which corresponds to the value estimated from toluene consumed. CF pieces lost their weight, in the manner shown in Figure 2A(c), as the increase of P_{MW}. We think that the microwave discharge and heating in a limited space in the reactor tube, i.e., a gap between CF pieces may cause the decomposition of toluene. The microwave energy concentrated at the gap may be enough, and in large excess particularly in the higher power region, to decompose toluene molecules and the excess energy may be used in the oxidation of CF to generate CO gas. Some toluene molecules could manage to slip through the gap and escape decomposition. To elucidate the above discussion, further investigation is in progress. When CF/NaCl pieces were used, plasma was generated in the higher power region than 200 W. Under the plasma generation, toluene was decomposed completely, both the formation of CO and the weight loss of CF were drastically diminished, and CO_2 concentration increased in the equivalent amount to toluene consumption as shown in Figure 2B. When $CF/CaCl_2$ pieces were used, plasma was just generated in the higher power region than 400 W, Under the plasma generation, toluene was decomposed completely, both the formation of CO and the weight loss of CF were diminished, and CO_2 increased in the equivalent amount to toluene consumption as shown in Figure 2C. Under conditions without generation of APMP, even reactions using CF/metal salt apparently appeared to proceed in the same manner as CF alone. However, the noticeable decrease of CO concentration was measured when $CF/CaCl_2$ was used, as shown in Figure 2C(b). It is considered that the existence of the metal salt covering CF contributed to relieve CF from oxidation in some extent.

Conclusively, these results suggest that the plasma generation is important to decompose toluene completely to form CO_2 and prevent the incomplete oxidation of CF which produce the poisonous CO and the weight loss of CF. We think that plasma spreading out the whole reactor brought us good results for decomposing toluene effectively because of providing the longer contact time with gaseous toluene. Under these conditions, most of microwave energy might be used to generate and sustain plasma so that the oxidation of CF may be absolutely restricted not to produce CO. Furthermore, we found that plasma could be generated at the lower minimum microwave power by using CF/NaCl, CF/KCl, or $CF/MgCl_2$ than $CF/CaCl_2$. The fact may be explained empirically by the difference in the boiling point of these salts; 1461 °C for NaCl, 1420 °C for KCl, 1412 °C for $MgCl_2$, 1600 °C for $CaCl_2$. For this subject, further investigation is also in progress.

References

1 M. Moisan, J. Pelletier, *Microwave Excited Plasmas*, Elsevier, **1992**, p. 18.
2 H. Kabashima, H. Einaga, S. Futamura, *Chem. Lett.* **2001**, 1314.
3 M. Tezuka, M. Iwasaki, *Electrochem.* **1998**, *66*, 662.
4 L. Bardosh, Yu. A. Lebedev, *Tech. Lett.* **1998**, *43*, 1428.
5 Y. Shimizu, K. Ogawa, Y. Tanaka, M. Egashira, *Electrochem.* **1998**, *66*, 1018.
6 Y. Shimizu, H. Inada, T. Hyodo, M. Egashira, *Electrochem.* **2003**, *71*, 860.
7 M. Moisan, G. Sauve, Z. Zakrewski, J. Hubert, *Plasma Sources Sci. Technol.* **1994**, *3*, 584.
8 M. Moisan, Z. Zakrewski, J. C. Rostaing, *Plasma Sources Sci. Technol.* **2001**, *10*, 387.
9 S. Tanada, T. Nakamura, N. Kawasaki, A. Iwaki, Y. Torii, *Chem. Lett.* **1995**, 773.
10 T. Oda, T. Takahashi, *IEEE Trans. Ind. Appl.* **1999**, *35*, 373.
11 R. McAdams, *J. Phys. D: Appl. Phys.* **2001**, *34*, 2810.
12 H. Kurihara, T. Yajima, *Hyomen Gijutsu*, in press.
13 *M. I. T. Wavelength Table, Vol. 2*, ed. by Phelps, Frederick M. M. I. T. Press, **1982**.

Published on the web (Advance View) March 10, 2007; doi:10.1246/cl.2007.526