Effect of zeolite in surface discharge plasma on the decomposition of toluene

Seung-Min Oh[a], Hyun-Ha Kim[a], Atsushi Ogata[a,*], Hisahiro Einaga[a], Shigeru Futamura[a] and Dong-Wha Park[b]

[a]*Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba West, 16–1 Onogawa, Tsukuba 305–8569, Japan*

[b]*Department of Chemical Engineering, Inha University, 253 Yonghyundong, Namgu 402-751, Korea*

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Toluene was decomposed in a surface discharge plasma reactor packed with various zeolites. The positioning effect of the zeolite bed was also investigated Reactor-B, in which the zeolite bed was located upstream, performed much better than Reactor-A, in which the zeolite bed was located downstream. Furthermore, the decomposition efficiency in Reactor-B increased with the capacity for toluene adsorption on zeolite, while that in Reactor-A did not. The toluene adsorbed in micropores was not decomposed effectively by direct electron impact, but was decomposed by active oxygen species generated in the plasma zone on the zeolite surface. A good correlation was also observed between toluene decomposition and ozone consumption in the downward-type reactor.

KEY WORDS: surface discharge; toluene decomposition; zeolite; active oxygen.

1. Introduction

Toluene (C_7H_8) is a toxic volatile organic compound (VOC) that is found in gasoline, paints, glues, rubber, and varnishes. Many people encounter toxic gases in daily life, and occupational exposure in the workplace can lead to serious health problems. There has been recent interest in the non-thermal plasma process as a new environmental technology for the decomposition of VOCs [1–3] because of its unique advantages, such as high chemical activity and rapid reaction, in addition to its low operating costs, which are below the costs of conventional thermal decomposition, catalytic oxidation, and adsorption methods [2]. The feasibility of plasma processes is limited by energy efficiency and the formation of toxic by-products. Processes have been developed using various plasma reactors, including surface discharge [4,5], dielectric barrier discharge [6–8], pulsed corona discharge [2,3,9], and microwave plasma [10] reactors. To improve the efficiency of the process, recent research has been directed toward the combination of catalysts or adsorbents with a non-thermal plasma reactor [11–15].

The effects of process parameters for the surface discharge plasma on the decomposition efficiency of toluene were investigated with various zeolites under different conditions to examine the design of a non-thermal plasma system for improved VOC treatment. We demonstrated that the inclusion of zeolite in a non-thermal plasma reactor improves the decomposition efficiency and that the placement of zeolite downstream is effective in increasing the reaction efficiency. Moreover, the synergistic effect depends on the reactor configuration.

* To whom correspondence should be addressed.
E-mail: atsushi-ogata@aist.go.jp

2. Experimental

Figure 1 shows the experimental setup of the surface plasma reactor used for the decomposition of toluene. As a high-voltage electrode, a platinum wire (diameter: 0.4 mm) was inserted into a quartz tube (i.d.: 10 mm, thickness: 1.5 mm). Copper foil was wrapped around the outside of the quartz tube as a ground electrode. Plasma energy was supplied with an AC high-voltage neon transformer (50 Hz, NEON M-5, LECIP Co., Japan) and the input energy (plug-in power) was measured using a digital power meter (WT110, Yokogawa Electric Co., Japan). Various zeolites (Tosoh Co., Japan; Nikky-Universal Co. Ltd., Japan) were placed at the bottom of the quartz tube. The zeolites were heated to, and held at, 500 °C for 1 h under synthetic air (80% N_2 and 20% O_2) to remove some of the chemical impurities before the experiment. A fiber-optic thermometer (AMOTH FX8500, Anritsu Meter Co. Ltd., Japan) was inserted in the top of the reactor to measure the temperature of the effluent gas.

The composition of the raw material was adjusted to 200 ppm C_7H_8 and 0.5% H_2O by mixing in synthetic air (80% N_2 and 20% O_2). The mixed gas could be introduced from either the bottom or top of the reactor at a total flow rate of 500 mL/min. Depending on the flow method, the zeolite bed was located upstream, in

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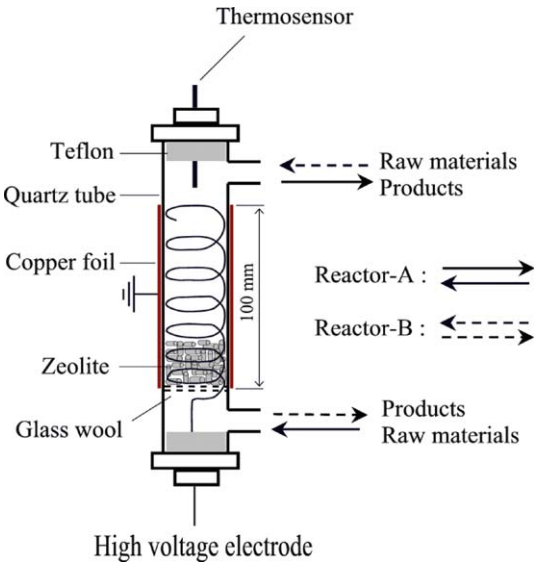

Figure 1. Zeolite-combined surface plasma reactor for decomposition of C_7H_8.

Reactor-A, or downstream, in Reactor-B. The product gases were analyzed using a Fourier-transform infrared spectrometer (FT-IR, FTS135, Bio–Rad Laboratories, USA) equipped with a gas cell (2.4 m long-path, 125 cm^3 volume, Infrared Analysis Inc., USA). The plasma was turned on and off periodically four times for a total of 160 min (off for 30 min → on for 10 min → off for 30 min → etc.), because previous research [16] demonstrated that cyclic operation improves the energy efficiency, i.e., adsorption followed by plasma decomposition. The effluent gas was measured continuously during the 160-min cyclic operation using the FT-IR analyzer. The total amounts of product species were calculated from the integrated spectra for each compound.

The total amount of CO_x produced, the sum of CO and CO_2, was used to evaluate the decomposition efficiency and compared with the amount produced in a normal plasma reactor without zeolite. CO_x adsorbed on the zeolite under plasma reaction was added to the total CO_x after a temperature-programmed desorption (TPD) process. In the TPD process, the zeolites were heated to 500 °C at a rate of 10 °C/min and held at that temperature under a N_2 atmosphere. Finally, the residual solid carbon in the zeolite derived from toluene decomposition was oxidized to CO and CO_2 at 600 °C under synthetic air. CO_2 selectivity was calculated from the CO_2 to CO_x ratio. The removal efficiency is due not only to decomposition but also to adsorption on the zeolite, and was calculated using the following equation:

$$C_7H_8 \text{ removal efficiency } [\%] = \frac{[C_0] - [C_i]}{[C_0]} \times 100 \qquad (1)$$

where C_0 is the total amount of toluene fed into the reactor and C_i is the total amount of toluene in the effluent gas during cyclic operation. In a normal plasma reactor, the removal efficiency is the same as the decomposition efficiency.

3. Results and discussion

Before examining the effects of zeolite, we investigated the process variables that affect the decomposition of toluene in a surface plasma reactor without zeolite. Toluene decomposed into mainly CO and CO_2, and the decomposition efficiency depended on the input energy and the total flow rate of mixed gas. In addition, intermediate HCOOH species due to partial oxidation and O_3 species were detected. Figure 2 shows the decomposition efficiency with the conventional plasma reactor when the mixed gas was introduced at a total flow rate of 500 mL/min with 200 ppm C_7H_8. Increasing the input energy increased the decomposition efficiency, which reached 60% at 5 W and 90% at 10 W. Carbon balance, including HCOOH, was obtained at ca. 90% at 5 W and it increased with the input energy due to the enhanced oxidation of C_7H_8. The introduction of a small amount of water vapor did not significantly affect the decomposition efficiency, but did suppress O_3 formation. In other words, there was no direct correlation between the vapor phase O_3 concentration and the decomposition efficiency. In the subsequent experiments, we set the concentration of water vapor at 0.5 wt% and the input energy (plug-in power) at 5 W.

To improve the decomposition efficiency of toluene, 1 g of various zeolites was packed in the plasma reactor.

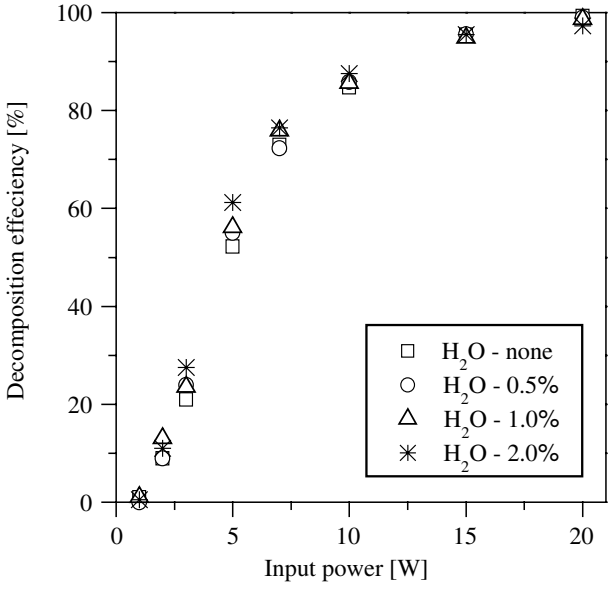

Figure 2. Effect of input energy and additive water vapor on the decomposition of C_7H_8.

Table 1
Experimental results for various zeolites

Reactor	Zeolites				Effluent gas analysis			
	Type	Surface area [m^2/g]	Channels [Å]	Adsorption capacity [10^{-4} mol]	CO_x amount [R]	CO_2 selectivity [%]	C_7H_8 removal [%]	O_3 amount [R]
Normal	–	–	–	–	5.7×10^{-4} mol	57	16	1.3×10^{-3} mol
A	Na-Y	750	7.4	6.5	1.2	55	73	1.0
A	H-Y	650	7.4	6.8	1.1	44	77	1.1
A	H-Y	520	7.4	6.6	1.0	38	83	1.1
A	H-Mordenite	460	6.7*7.0	3.7	1.3	50	43	1.0
A	Ferrierite	270	4.3*5.5	0.4	1.4	57	24	0.9
B	Na-Y	750	7.4	6.5	3.4	60	78	0.2
B	H-Y	650	7.4	6.8	3.3	38	82	0.3
B	H-Y	520	7.4	6.6	3.6	38	87	0.3
B	H-Mordenite	460	6.7*7.0	3.7	2.5	52	42	0.4
B	Ferrierite	270	4.3*5.5	0.4	1.8	67	22	0.6

[R]:relative amount compared with that produced under normal condition.

Table 1 summarizes the experimental results. To compare the results with the data for the plasma reactor without zeolite, the relative quantities of chemical species produced under various conditions were calculated. The adsorption capacity corresponds to the amount of toluene that can be adsorbed on the zeolite for 160 min without plasma discharge. The removal efficiency of toluene increased with the surface area of zeolite, which was related to the amount of C_7H_8 adsorption. The total amounts of CO_x and O_3 changed more noticeably in Reactor-B than in Reactor-A. In Reactor-B, the amount CO_x increased with the adsorption capacity, reducing the amount of O_3. The CO_2 selectivity seemed to be better with Reactor-B.

Figure 3 shows the relative amounts of CO_x for the two types of reactor with various zeolites. In Reactor-A, ferrierite performed best and the decomposition efficiency was 1.4 times higher than that in the normal plasma reactor without zeolites, although the amount of CO_x did not change significantly regardless of the adsorption capacity. From the TPD reactor, it was observed that the toluene adsorbed on the zeolite did not decompose effectively. Changing the reactor configuration to that of Reactor-B improved the decomposition efficiency. As the reactor configuration did not influence the adsorption behavior, the enhanced oxidation was likely due to the active species generated in the plasma zone. The total amount of CO_x increased

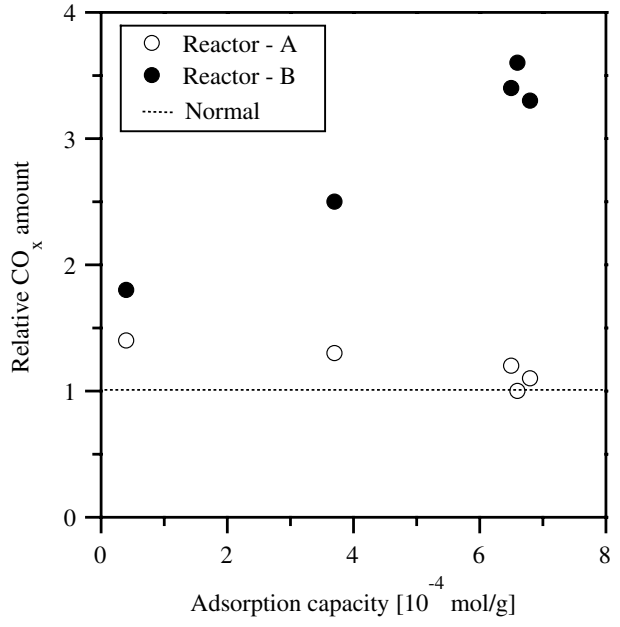

Figure 3. Relative amounts of CO_x produced using various zeolites with different adsorption capacity.

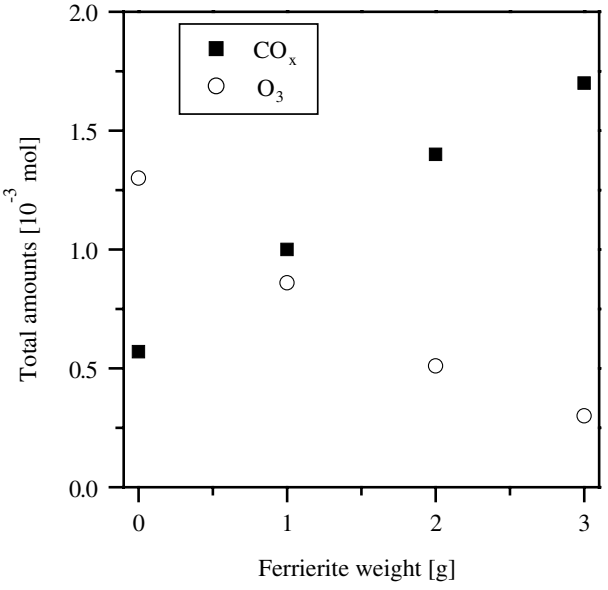

Figure 4. The correlation between the amount of CO_x and O_3 for different weight of zeolite.

significantly with the capacity for C_7H_8 adsorption. Note that the amount of O_3 decreased with increasing total CO_x, as shown in table 1, and the effect of thermal catalysis may be negligible because the maximum temperature of the effluent gas was below 60 °C. These results lead us to believe that the zeolite acts mainly as an adsorbent, and that internally adsorbed toluene does not decompose effectively via catalysis in the plasma reactor; rather, active oxygen generated in the plasma region promotes the oxidation of the adsorbed toluene.

Figure 4 shows the total amounts of CO_x and O_3 produced during a 160-min cyclic operation, with the zeolite bed located downstream. The amount of CO_x increased with the weight of zeolite (ferrierite), while the amount of O_3 decreased linearly. This suggests that the decomposition of C_7H_8 is due to active oxygen species derived from the decomposition of O_3 on the zeolite surface. The correlation between O_3 and active oxygen atoms was mentioned previously [11], where O_3 decomposed to give O_2 and active oxygen atoms on the surface of a metal oxide. Figure 4 shows that one mole of O_3 can produce more than one mole of CO_x, and the correlation between the amounts of CO_x and O_3 indicate that the oxidation of toluene is also attributed to other oxygen species.

We performed an additional experiment using a serial reactor, which combined a surface plasma reactor (1st reactor) with a catalysis reactor (2nd reactor) packed with H-Y zeolite. The amount of CO_x produced in the serial reactor was similar to that produced in Reactor-B. In addition, the oxygen balance showed that the oxidation of toluene was affected by both ozone and other oxygen species. These results suggest that the active oxygen derived from O_3 decompose toluene adsorbed on the zeolites and unknown oxygen species also attribute to the toluene oxidation. The detailed information on the unknown compounds will be obtained from further research.

4. Conclusions

Toluene was decomposed into CO and CO_2 using a zeolite-combined plasma reactor. The decomposition efficiency depended on the position of the zeolite bed and the capacity for toluene adsorption. The zeolite acted mainly as an adsorbent, and internally adsorbed toluene did not react directly in the upstream plasma region. The amount of O_3 in the product gas was reduced with the increase of the amount of CO_x because of the enhanced toluene oxidation on the zeolite surface. The oxygen balance indicated that the oxidation of toluene was also attributed to other oxygen species in the plasma reactor. To improve the decomposition efficiency of toluene, a zeolite bed with a high capacity for toluene adsorption should be placed downstream from the plasma zone, because the active oxygen species generated in the plasma region enhance the oxidation of adsorbed toluene.

References

[1] T. Oda, J. Electrostatics 57 (2003) 293.
[2] C.M. Nunez, G.H. Ramsey, W.H. Ponder, J.H. Abbott, L.E. Hamel and P.H. Kariher, Air & Waste 43 (1993) 242.
[3] T. Yamamoto and S. Futamura, Combust. Sci. Technol. 133 (1998) 117.
[4] T. Oda, R. Yamashita, I. Haga, T. Takahashi and S. Masuda, IEEE Trans. Ind. Appl. 32 (1996) 118.
[5] H.-C. Kang, J. Ind. Eng. Chem. 8 (2002) 488.
[6] U. Kogelschatz, Plasma Chem. Plasma Process. 23 (2003) 1.
[7] D.-W. Park, S.-H. Yoon, G.-J. Kim and H. Sekiguchi, J. Ind. Eng. Chem. 8 (2002) 393.
[8] A. Ogata, D. Ito, K. Mizuno, S. Kushiyama, A. Gal and T. Yamamoto, App. Catal. A:Gen. 236 (2002) 9.
[9] M.G. Sobacchi, A.V. Saveliev, A.A. Fridman, A.F. Gutsol and L.A. Kennedy, Plasma Chem. Plasma Process. 23 (2003) 347.
[10] Y.S. Mok, H.-C. Kang, M.H. Cho and I.-S. Nam, Korean J. Chem. Eng. 20 (2003) 239.
[11] S. Futamura, H. Einaga, H. Kabashima and L.Y. Hwan, Catal. Today 89 (2004) 89.
[12] A. Ogata, H. Einaga, H. Kabashima, S. Futamura, S. Kushiyama and H.-H. Kim, Appl. Catal. B:Environ. 46 (2003) 87.
[13] H.-H. Kim, Y.-H. Lee, A. Ogata and S. Futamura, Catal. Commun. 4 (2003) 347.
[14] Y.H. Song, M.S. Cha, Y. Kim, K.T. Kim, S.J. Kim, S.Y. Han and K.I. Choi, J. Adv. Oxid. Technol. 6 (2003) 11.
[15] H.-H. Kim, S.-M. Oh, A. Ogata and S. Futamura, Catal. Lett. 96 (2004) 189.
[16] A. Ogata, D. Ito, K. Mizuno, S. Kushiyama and T. Yamamoto, IEEE Trans. Ind. Appl. 37 (2001) 959.