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Decomposition of toluene using an atmospheric pressure plasma/TiO_2 catalytic system

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Abstract

Application of atmospheric pressure plasma as an alternative technology for the destruction of toluene is demonstrated in this study. Used TiO_2 colloidal solution was obtained by an improved sol–gel method, and coated on glass beads to prepare decomposition of toluene. The physical property of synthesized TiO_2 catalyst film was analyzed by XRD and SEM spectroscopy. From these results, it was identified that the catalyst film exhibited anatase structure with particle size of about 50–100 nm after calcination at 500 °C for 1 h. The decomposition of toluene in TiO_2/O_2 plasma system was investigated. Amounts of the catalyst and toluene concentration were fixed as 3 wt.% and 1000 ppm, respectively. The analyses for performance of toluene decomposition and intermediates in reaction were done by the in situ method using the mass spectroscopy and gas chromatography. The toluene of 40% was decomposed at pulse voltage of 13 kV in the only O_2 plasma condition without TiO_2 catalyst. Furthermore, the conversion enhanced remarkably in the TiO_2/O_2 plasma system, and it reached 70% at pulse voltage of 13 kV after 120 min. This result was very notable compared with that in photocatalytic system, with below 40% after 120 min reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Toluene decomposition; TiO_2 catalyst; Atmospheric pressure plasma; In situ method

1. Introduction

Control of volatile organic compounds (VOCs) in the atmosphere is a major environmental problem due to their great proliferation and to limitations of treatment methods. In particular, much research on chemical detoxification and pollution abatement has focused on the disposal of toxic and hazardous wastes containing benzene, toluene, ethyl benzene, xylene (BTEX) in recent years. Most of these aromatic compounds contained benzene ring(s), have distinct volatility, solubility, and very stability. These toxic compounds used as solvent in of organic chemistry and industry, were explosive without special restrictions. In case of pollution in underground water, the pollutants were generated from the explosion of storage tanks with various petroleum compounds used as fuel. In particular, the toluene in soil have affect potable and agricultural water, and also human life.

On the other hand, recently, a number of alternative technologies have been developed to destroy these organic wastes. Examples of these innovative processes include thermal, photocatalytic, chemical, physical (plasma-technology), and biological methods. In particular, photocatalytic process using UV-irradiation

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$$TiO_2 + \text{plasma} \rightarrow h^+ + e^-$$

$$h^+ + H_2O \rightarrow OH + H^+ : \text{Oxidation}$$

$$e^- + O_2 \rightarrow O_2^- : \text{Reduction}$$

$$O_2^- + H^+ \rightarrow HO_2$$

Scheme 1. The expected reaction mechanism on TiO_2 by the plasma.

has been studied by many researchers [1–5]. The highly reactive oxidant, which is generated during the photocatalytic process, is the HO radical. This strongly oxidized some hazardous VOCs. Although it is now receiving a great deal of attention in various application fields, however, it also has several limitations. For example, reactor geometry is limited by the problem of UV-irradiation, and the energy yield is lowered by recombination of photo-produced holes and electrons. In most recently years, it was reported that these problems could be overcome by using discharge plasma as a driving force of photocatalysts in many papers [6–8]. The reaction induced on the excited TiO_2 surface with plasma could be suggested as Scheme 1.

As shown in Scheme 1, the plasma, instead of the UV-irradiation excites the TiO_2 surface. However, it could be expected that the excited rate of the electron on surface of TiO_2 catalyst be more promoted by strong plasma power compared with UV-irradiation. Therefore, the VOC decomposition should be increased.

In this study, the TiO_2 catalyst was fixed stably on glass beads as using an inorganic binder containing silicon. The toluene decomposition was done under an atmospheric pressure plasma/TiO_2 catalyst system with O_2 flowing, and was compared the performance for toluene decomposition in a photocatalyst system.

2. Experimental

2.1. Catalyst preparation

Fig. 1 shows the preparation of solution containing TiO_2 and its fixation to produce a TiO_2 anatase film. Reagents for preparation of TiO_2 sol mixture were as follows: titanium tetra-isopropoxide (99.95%, TTIP, Junsei Chemical, Japan) and ethyl alcohol (Wako Pure Chemicals Ltd.) were used as a titanium precursor and a solvent, respectively.

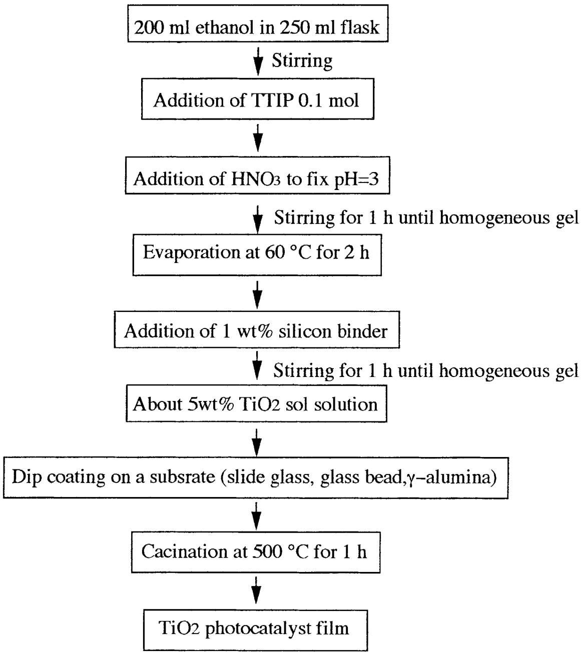


Fig. 1. Preparation of TiO_2 colloidal solution and its fixation on a substrate.

To promote the crystallization, HNO_3 was added in sol solution. Then, an inorganic binder of 1.0% prepared in our laboratory was added in the final solution for fixation on the substrate. To characterize, the sol solution was coated on a slide glass and it was also coated on glass beads (diameter: 2 mm, spherical type) or γ-alumina (diameter: 2 mm, granule type) to decompose toluene. Finally, the film was calcined at 500 °C for 1 h to transfer TiO_2 amorphous to anatase structure.

2.2. Characterizations of synthesized catalyst

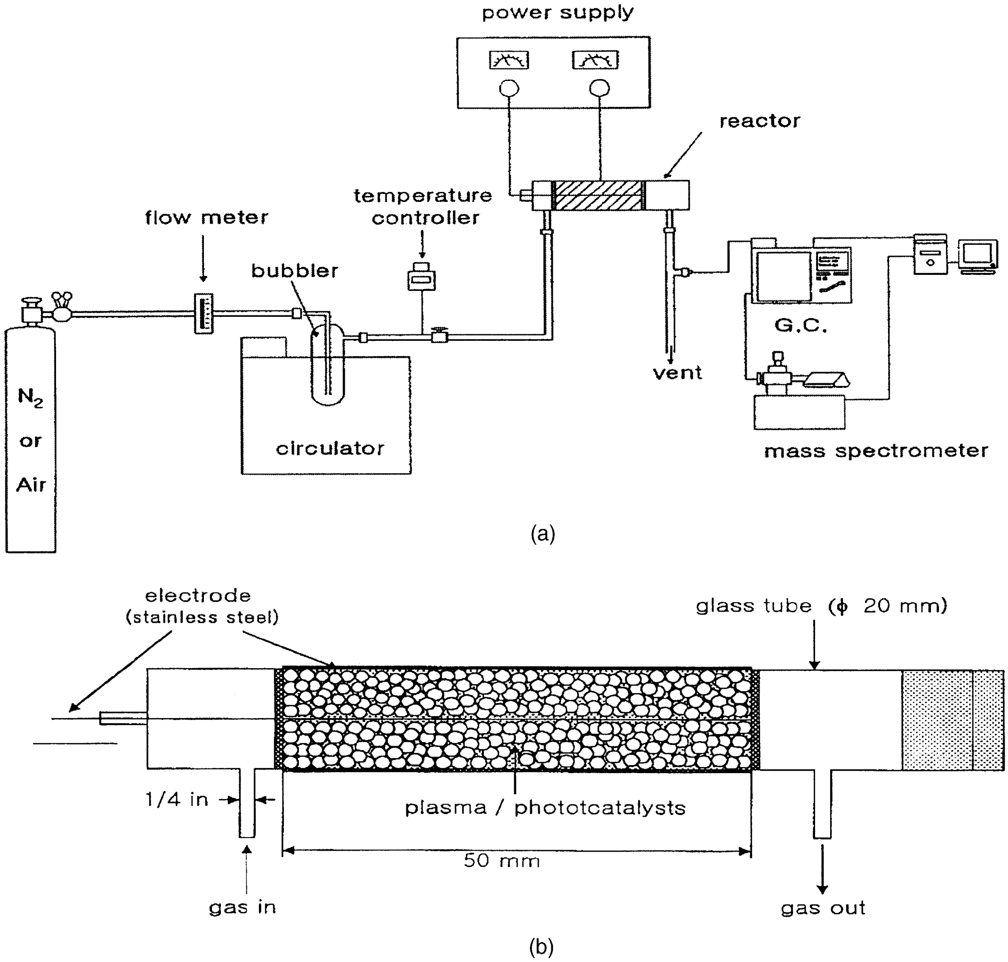
The crystallization of synthesized sample was identified by powder X-ray diffraction analysis (XRD, model PW 1830 from Philips) with nickel filtered Cu Kα radiation (30 kV, 30 mA) at an angle of 2θ ranges from 5 to 70 °C. The scan speed was 10°/min and time constant was 1 s.

The particle size, shape, and surface situation of TiO_2 catalyst film were observed by scanning electron microscope (SEM, model JEOL-JSM35CF).

The power and working distance were set to 15 kV and 3 cm, respectively.

2.3. Reaction method and analysis of product for toluene decomposition

The decomposition of toluene was carried out using atmospheric pressure plasma reactor as shown in Fig. 2. It could be catalytically activated by free radicals from the plasma. The reactor made from quartz glass is fixed with an i.d. 20 mm and a length of 50 mm. The catalyst, used in our experiment was obtained by coating TiO_2 solution on spherical glass beads. These glass beads coated with TiO_2 were packed in a quartz tube and the weight of the used catalyst with glass beads was 30.0 g. A stainless steel high-voltage electrode was held in the center of the tube. Test gas (O_2 10%, toluene 1000 ppm, N_2 balance) was prepared using gas cylinders. The initial toluene and O_2 concentration, and the gas flow rate (1000 ppm, 10%, and 4000 ml/min, respectively, at 16 °C and 1 atm) were kept constant throughout this study. To avoid condensation in the tube, a heating tape rolled tube and the temperature was kept at 30 °C. The reactor was installed in an oven to control temperature conditions.



(a)

(b)

Fig. 2. Atmospheric pressure plasma system for toluene decomposition. (a) apparatus of atmospheric pressure plasma/TiO_2 reactor; and (b) apparatus in reactor.

The waveform of the pulse voltage and current were measured using a digital oscilloscope with the voltage divider and current probe. The input power was measured with a digital power meter at the wall plug of the transformer. This value includes the discharge power as well as energy loss in the power source. The energy transferred from the power source to the plasma reactor was 20–30% in this study. Generated radiation powers were attained by regulation of the current and pulse voltage. The intensities of pulse voltages were 7, 9, 11, and 13 kV, and the intensities of currents were 60 and 100 MHz.

The toluene and intermediates in reaction were analyzed by in situ method using mass-spectroscopy (model M-QA 100F, BEL, Japan). The mass spectroscopy of toluene before and after reaction is shown in Fig. 3. It is seen that the molecular ion peak ($m/z = C_7H_8^{+\bullet}$) and other ion peaks, $m/z = 40(C_3H_4^{+\bullet})$, $m/z = 44(CO_2)$, $m/z = 53(C_4H_5^{+\bullet})$, and $m/z = 66(C_5H_6^{+\bullet})$ were formed. As shown in this Fig. 3, the almost peak intensity decreased after reaction and the decrease tendency was the same. In particular, with a reaction time, molecular ion peak decreased, but peak of $m/z = 40(CO_2)$ increased. The intensity of other peaks was not largely changed. From this result, it could be suggested that toluene was decomposed variously through many steps, and then, finally, carbon dioxide was formed. On the other hand, a gas chromatograph (model HP6890) with HP-624 column was used to analyze the amount of remained toluene.

3. Results

3.1. Physical property

Fig. 4 shows the XRD pattern of synthesized TiO_2 by the preparation in Fig. 1. In general, it was well-known that the TiO_2 photocatalyst with anatase structure exhibited more high performance for VOC decomposition than that of other types, like rutile, brookite, and amorphous. In Fig. 1, the TiO_2 sol solution was coated on a slide glass to make the film, and then it was thermal treated at 500 °C for 1 h to produce anatase structure. As the result, the structure of attained TiO_2 film was accorded to pure anatase structure as shown in Fig. 4b.

Fig. 5 shows the SEM photograph for surface situation (a) of TiO_2 fixed on a slide glass and the shape of TiO_2 (b) after thermal treatment at 500 °C for 1 h. The particle shape was spherical, but the particles were coagulated each other, and then, the size of single particle could not surely calculated. However, it was confirmed that the particle size was distributed around 50–100 nm from the result of particle size distribution (the particle size distributions of TiO_2 in colloidal solutions were analyzed by dynamic light scattering (DLS) spectrophotometer (model BI 9000AT) after ultrasonic wave treatment with 140 W in water for 2 min). On the other hand, the coating situation was stable and uniform as shown in (a), and it was not taken off the slide glass in spite of violently stirring.

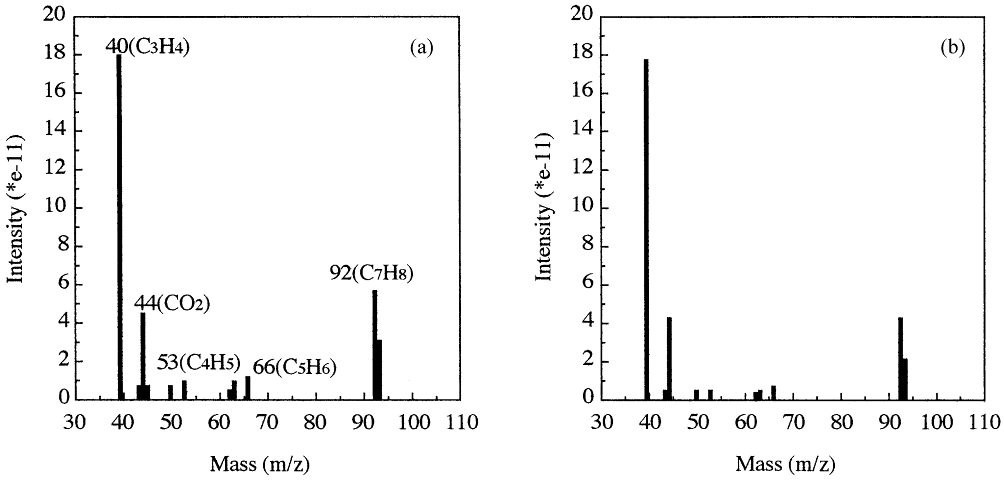


Fig. 3. Mass spectroscopy of toluene before and after reaction. (a) Before reaction; and (b) after reaction.

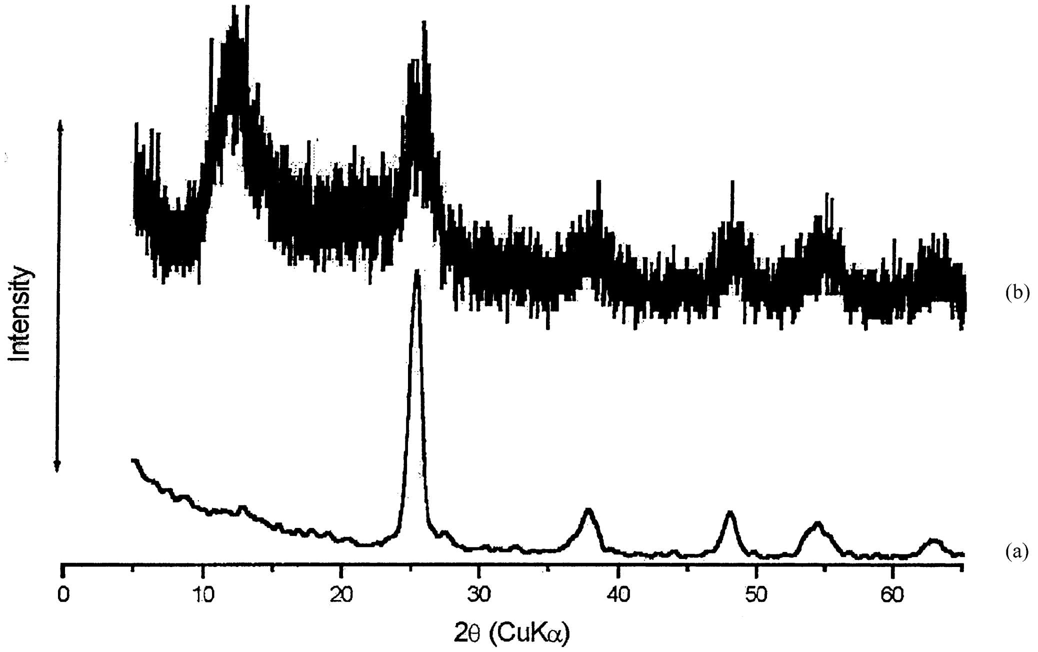
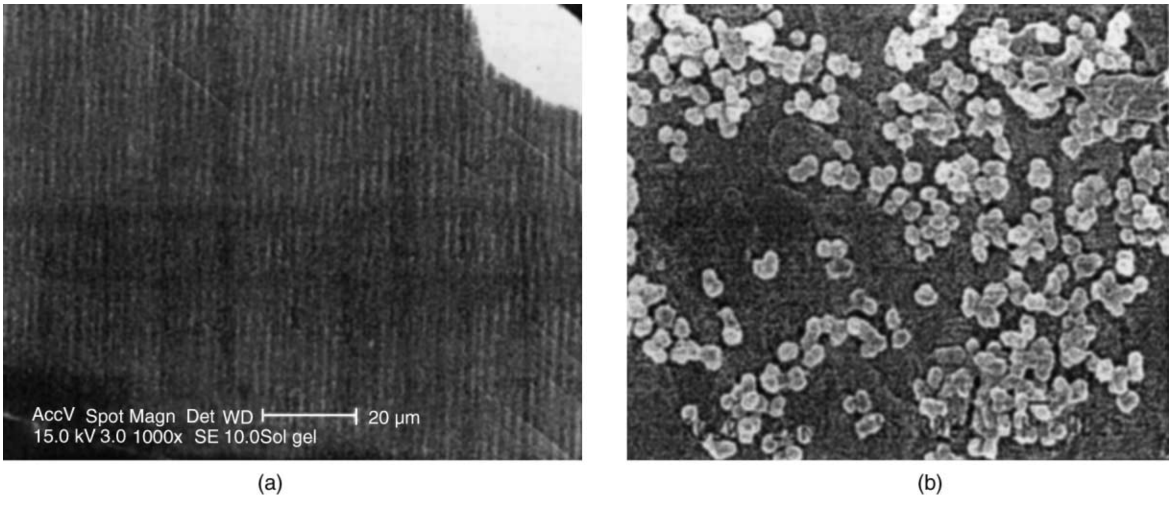


Fig. 4. XRD patterns of synthesized TiO_2 film. (a) Anatase structure; and (b) TiO_2 film synthesized.

3.2. Decomposition of toluene

3.2.1. Effects of O_2 flowing and pulse voltage intensity on decomposition of toluene

In Fig. 6, the conversion for toluene decomposition under only plasma with N_2 flowing without TiO_2 catalyst is shown. The pulse voltages were various, 7, 9, 11, and 13 kV, and the current was constant as 60 MHz. With an increase of the intensity of pulse voltage, the toluene decomposition increased. In particular, the conversion of toluene was 20% after 120 min in pulse voltage of 13 kV. This was remarkable result



(a)

(b)

Fig. 5. SEM photographs of the surface situation of TiO_2 film synthesized. (a) TiO_2 film surface; and (b) TiO_2 particle after dry of TiO_2 colloidal solution.

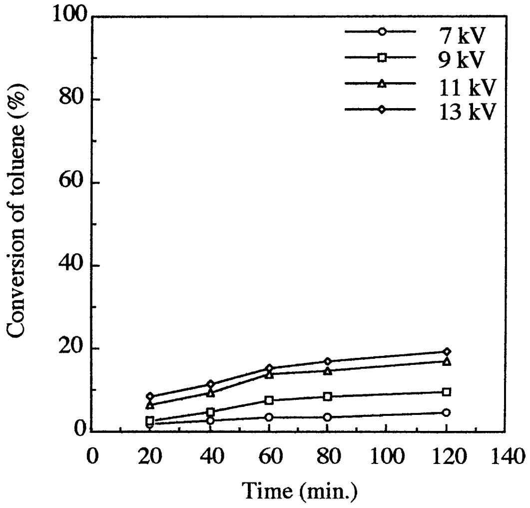


Fig. 6. Toluene decomposition under only N_2 plasma without TiO_2 catalyst.

compared with that in only UV-irradiation condition with non-decomposition of toluene.

Fig. 7 shows the conversion of toluene in O_2 plasma without TiO_2 catalyst. Other conditions were the same to Fig. 6. With an increase of the pulse voltage, the decomposition performance for toluene increased. The conversion was up to about 40% after 120 min at 13 kV. Otherwise, in UV-irradiation of 254 nm (24 W) per air bubbling, the toluene conversion exhibited 10% after 120 min. From results of Figs. 6 and 7, it was confirmed that the plasma system was very useful for decomposition of toluene.

3.2.2. Effects of TiO_2 catalyst and current intensity on decomposition of toluene

The performance for toluene decomposition under the TiO_2/O_2 plasma system is shown in Fig. 8. The amount of TiO_2 fixed on glass beads was 3 wt.%. As shown, the TiO_2 addition in this system was strongly affected the toluene decomposition. The decomposition performance for toluene increased notably with an increase of the pulse voltage. Of course, the tendency was accorded to the result of Figs. 6 and 7. However, the conversion more enhanced in TiO_2 catalytic system and reached 70% at 13 kV. In photocatalyst system with power of 24 W and UV-irradiation of 254 nm, the conversion of toluene decomposition was below 40% after 120 min. From this result, it was confirmed that plasma/TiO_2 catalytic system was more useful in the decomposition of toluene compared with photocatalytic system.

Fig. 9 shows the change of conversion of toluene in condition of TiO_2/O_2 plasma system with a change of current (60 and 100 MHz). As shown in Fig. 7, the decomposition performance of toluene remarkably increased with an increase of the pulse voltage.

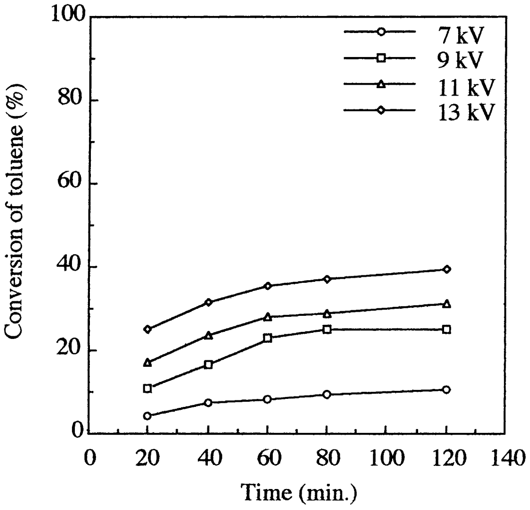


Fig. 7. Toluene decomposition under only O_2 plasma without TiO_2 catalyst.

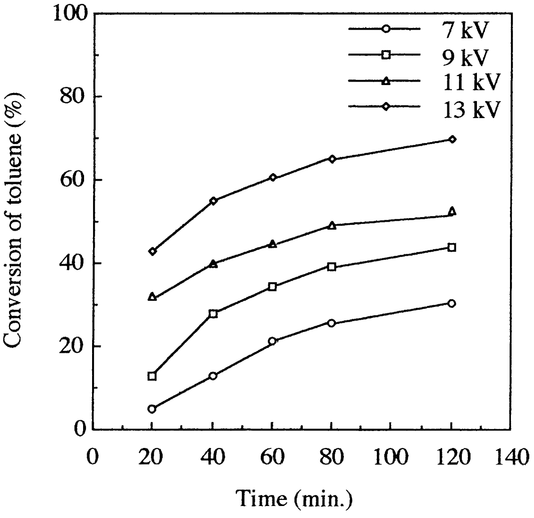


Fig. 8. Toluene decomposition under TiO_2/O_2 plasma system.

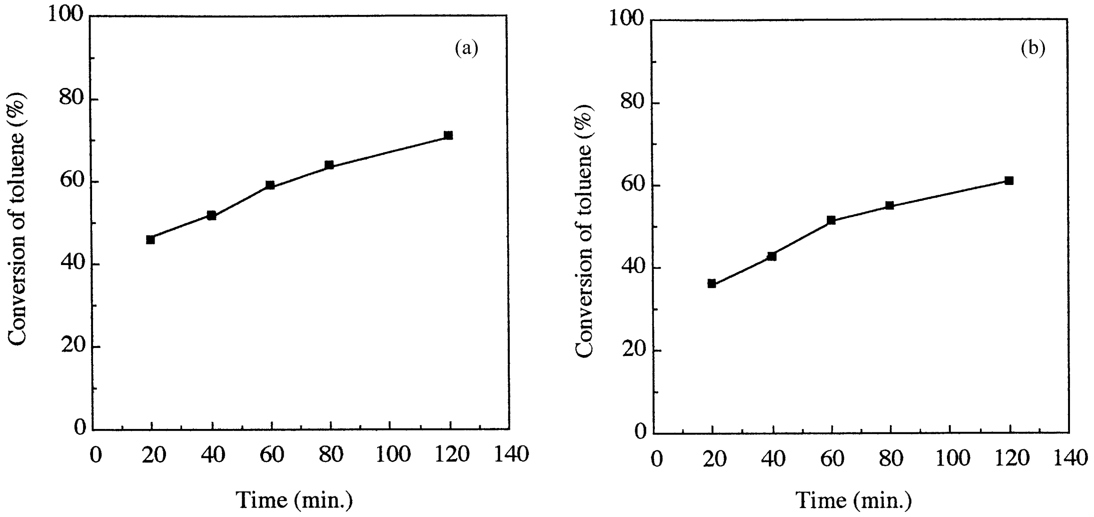


Fig. 9. Toluene decomposition with current intensity under TiO_2/O_2 plasma system. (a) For 60 MHz; and (b) For 100 MHz.

Whereas, the performance of toluene decomposition decreased with an increase of current. However, the change was very slight. The difference of performance was about 15% after 120 min under 60 and 100 MHz conditions. From this, it was confirmed that the pulse voltage more affected the decomposition of toluene compared with the current.

3.2.3. *Comparison of decomposition of toluene over photocatalyst and plasma-catalyst systems, and effect of support*

On the other hand, the performance of toluene decomposition between in photocatalyst system (UV-irradiation: 254 nm, 24 W/m^2) and plasma-catalyst system are compared in Fig. 10. As mentioned above, the decomposition of toluene in TiO_2/O_2 plasma system enhanced compared with in photocatalyst system. As shown, in photocatalytic system, the performance for toluene decomposition increased with reaction time as like S-line type. However, in plasma system, the increase tendency displayed a straight-line type. In particular, the difference of toluene conversion between plasma and photocatalytic systems was very large about 30%. This is attribution to power of plasma, which was stronger than photo radiation. The excitation of electron rapidly increased, consequently, the decomposition of toluene rapidly also increased.

On the other hand, as shown Fig. 11, when the γ-alumina support was used, the conversion of toluene decomposition more enhanced, and the conversion reached about 80% after 120 min. This is ascribed to two reasons: one is the attached catalyst amount on support. Much TiO_2 powders were stably attached on γ-alumina compared with that on glass beads.

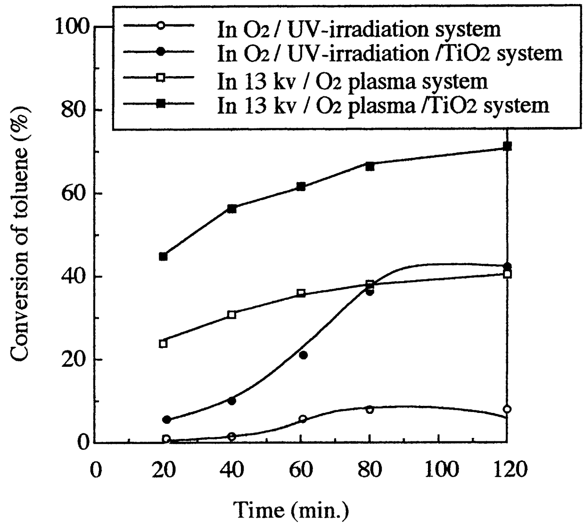


Fig. 10. Comparison of toluene decomposition under TiO_2/O_2 plasma system and under photocatalytic system.

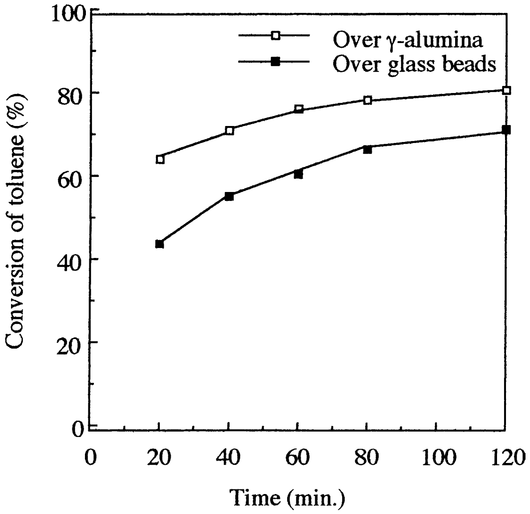


Fig. 11. Effect of support on toluene decomposition under TiO_2/O_2 plasma system.

The other is that the γ-alumina can play role of an electron acceptor, resulted to have the longer lifetime, finally the decomposition of VOCs increased.

From the results of Figs. 6–10, we confirmed that the TiO_2/O_2 plasma system was very useful for decomposition of VOCs.

4. Conclusions

The TiO_2 catalyst with anatase structure was synthesized by a colloidal solution prepared from an improved sol–gel method. In addition, instead of UV-irradiation, the atmospheric pressure plasma source was used for decomposition toluene. The following conclusions were derived from this study.

1. The TiO_2 catalyst exhibited the anatase structure with particle size of about 50–100 nm.
2. The toluene was decomposed in the O_2 plasma condition without TiO_2 catalyst, and the conversion was 40%.
3. The conversion for toluene decomposition remarkably increased in the TiO_2/O_2 plasma condition, and it reached 70% in 13 kV pulse voltages after 120 min.
4. With an increase of the pulse voltage intensity, the toluene conversion increased, but, in spite of increase of current intensity, the conversion of toluene was not enhanced.
5. The conversion for toluene decomposition was up to 80% in O_2 plasma/TiO_2 coated on γ-alumina condition.

From these results, it could be concluded that the TiO_2/O_2 plasma system was very useful for decomposition of VOCs.

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