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RESEARCH ARTICLE

Toluene Decomposition by DBD-Type Plasma Combined with Metal Oxide Catalysts Supported on Ferroelectric Materials

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We investigated toluene decomposition with a single-stage plasma catalytic system operated at atmospheric pressure and working at reduced temperature ($T < 75$ °C), where a synergistic catalyst was integrated on ferroelectric $BaTiO_3$ beads with a high dielectric constant. The catalyst species were characterized by FE-SEM and XPS before and after the experiment. The $MnO_2/BaTiO_3$ catalyst showed high stability in igniting plasma during destruction of toluene for 230 hours in a lifetime test.

Keywords: Plasma Catalytic System, Ferroelectric Materials, VOC, Catalyst.

1. INTRODUCTION

Control of volatile organic compound (VOC) emission has become an important issue in that VOCs are not only hazardous to human health, but also harmful to the environment.[1,2] Conventional techniques used to decompose VOCs include adsorption and thermal and thermo-catalytic oxidation.[3] An alternative method for VOC decomposition is non-thermal plasma (NTP) generated at atmospheric pressure, which is an energy-saving approach.[2–5] NTP is a combination of energetic electrons, radicals, ions, and excited active species as well as radiation.[7] In NTP, the electrical energy is primarily used to produce energetic electrons without heating. However, NTP abatement of VOCs shows low selectivity to total oxidation (CO_2 and H_2O) and may result in the formation of undesirable and sometimes toxic by-products.[7] To improve the efficiency of the NTP technique, catalysts can be incorporated into the plasma.[8] In the catalytic plasma technique, there is synergy between plasma excitation and catalysis when the catalyst is placed in the discharge.[3]

Numerous catalysts have been studied in this context. The catalysts are typically metal oxides such as MnO_2, SiO_2, Al_2O_3, Co_3O_4, TiO_2, Ag_2O, and CuO, among others. Among these various metal oxides, MnO_2 has attracted the most attention because of its high ozone decomposition activity.[1] Moreover, ferroelectric materials, such as packed beads, are key the proper functioning of plasma catalytic systems.[6] The transported charge that leads to excitation, dissociation, or ionization in a plasma reaction is proportional to the dielectric constant of ferroelectric materials. Rico et al. described a hybrid catalytic-DBD plasma reactor for the steam reforming of methanol.[10] They demonstrated that copper–manganese oxide catalysts on ferroelectric material interacted synergistically and proposed this system as an efficient alternative to conventional catalytic reactions for the reforming of methanol. However, a major disadvantage of this configuration is the faster deactivation of the catalyst as a result of carbonaceous deposits.[6]

In this study, we investigated toluene decomposition using a single-stage plasma catalytic system operated at atmospheric pressure and reduced temperature ($T < 75$ °C), where the synergetic catalyst was integrated on ferroelectric $BaTiO_3$ beads with a high dielectric constant.

2. EXPERIMENTAL DETAILS

The dielectric materials used were alumina (Al_2O_3), SiO_2 glass, and barium titanate ($BaTiO_3$) beads purchased from Alfa Aesar. Metal oxide catalysts were prepared by mixing an aqueous solution of copper nitrate, cobalt nitrate,

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and manganese nitrate (purchased from Aldrich) to obtain 5 wt% solution. After 1 hour of stirring, the solutions were evaporated, dried, and then calcined at 500 °C for 4 h. The catalysts were characterized by field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS).

The plasma-catalyst reactor has been used in the present work to incoporate the catalyst inside the plasma discharge zone. The reactor consisted of a stainless steel high-voltage electrode with a diameter of 16 mm and a quartz tube with an outer diameter and wall thickness of 22 mm and 1 mm, respectively. The gap distance (2 mm) between the electrodes was filled with 50 g of catalyst (beads) with an average size of 1 mm. The gas flow rate was maintained at 1 L/min with 100 ppm toluene in air balance. An AC power supply with a voltage that could be varied between 1 and 20 kV and a frequency that could be carried between 10 and 20 kHz was used to ignite the plasma. The concentration of toluene in the outlet of the reactor at each applied voltage was measured with a gas chromatograph (Agilent 6890 N).

3. RESULTS AND DISCUSSION

We initially investigated the effect of beads as a packing material between the electrodes. Firstly, to evaluate the effects of the Al_2O_3, SiO_2 glass, and $BaTiO_3$ beads on toluene decomposition, toluene was passed through the packed reactor without igniting the plasma discharge. No conversion of toluene was detected under our experimental conditions. Toluene conversion as a function of average applied voltage with packed Al_2O_3, SiO_2 glass, $BaTiO_3$ beads, or plasma alone is shown in Figure 1. Toluene was mainly decomposed to CO_2 and CO gaseous products. Small amounts, less than 1% hydrocarbon or intermediate oxidation products were detected in the effluent gas. The combined reaction system with plasma and catalyst enhanced total oxidation product selectivity rather than NTP reaction system alone. Toluene conversion increased from zero to a certain value at a well-defined applied voltage for each packed material. In the case of plasma alone (without packed materials), increasing the input voltage from 4 to 7 kV increased the toluene conversion rates, which reached 25% at 5.5 kV and 78% at 7 kV. The toluene conversion rate was similar to that of Al_2O_3, SiO_2 glass beads, and plasma alone at all voltages. However, the conversion of toluene using $BaTiO_3$ beads with high dielectric constant ($\varepsilon \approx 1{,}500$) as a ferroelectric material was enhanced compared to that of SiO_2 glass ($\varepsilon \approx 5$) and Al_2O_3 ($\varepsilon \approx 9$) beads at the same voltage. As reported previously, the higher the relative dielectric constant, the higher the conversion efficiency.[10]

We next investigated the synergistic catalytic performance of MnO_2, Co_3O_4, and CuO on ferroelectric $BaTiO_3$ beads with respect to toluene conversion. Toluene conversion as a function of applied voltage is presented in Figure 2. Toluene conversion increased monotonically up to 6 kV and $MnO_2/BaTiO_3$ was the most active of all the catalysts tested with complete toluene conversion achieved at 5 kV. The toluene conversion efficiency of the catalysts at 5 kV was as follows: $MnO_2/BaTiO_3 > Co_3O_4/BaTiO_3 > CuO/BaTiO_3 > BaTiO_3 \cdot MnO_2$ is a metal oxide catalyst and has potential activity in redox reactions.[8, 11] Metal ions (Mn^{n+}), oxides (O^{2-}) and defect sites of various oxidation states are exposed on the surface of MnO_2 particles.

MnO_2 also has various degrees of coordination unsaturation, and it has acid and base properties. Therefore, the synergistic effect of manganese oxide and $BaTiO_3$ with regard to the acceleration of the decomposition of O_3 to active oxygen species facilitated toluene conversion and was energy-efficient due to the low amount of input voltage consumed by the plasma catalytic system.

The long-run performance of the synergistic MnO_2/$BaTiO_3$ catalyst inside the plasma discharge zone operated at a constant voltage of 5.0 kV for 230 h is shown in Figure 3. The fact that this process was driven at low temperatures (maximum temperature of 75 °C) indicates that

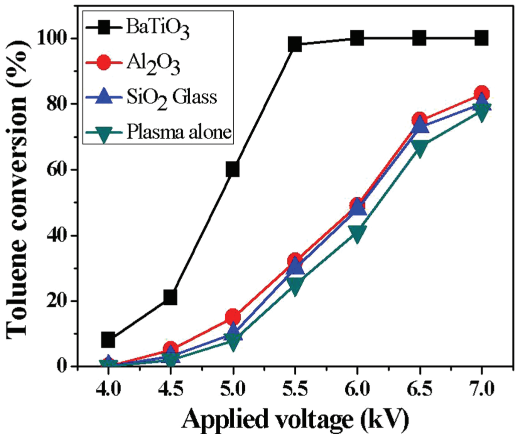

Fig. 1. Toluene conversion as a function of the average applied voltage for packed Al_2O_3, SiO_2 glass, $BaTiO_3$ beads, or plasma alone.

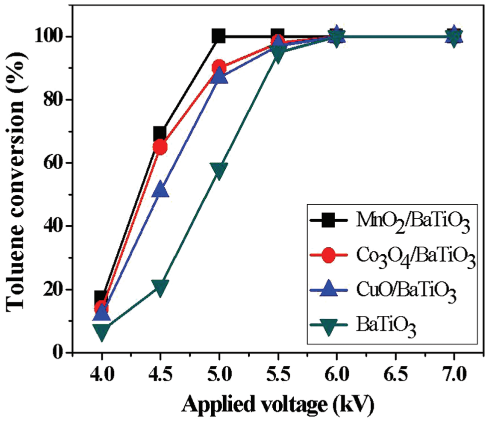

Fig. 2. Toluene conversion as a function of average applied voltage for MnO_2, Co_3O_4, or CuO on the ferroelectric $BaTiO_3$ beads.

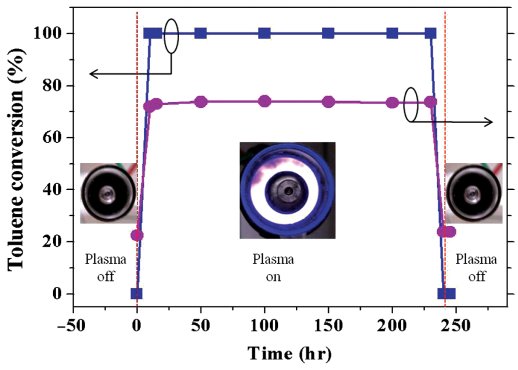

Fig. 3. The lifetime performance of the $MnO_2/BaTiO_3$ catalyst in a plasma catalytic reaction at 5.0 kV for 230 h.

almost all toluene was converted by the plasma catalytic reaction without the requirement for additional external heating. As seen from the figure, the $MnO_2/BaTiO_3$ catalyst maintained the same activity throughout the course of the reaction. This confirms the long-run stability of the $MnO_2/BaTiO_3$ catalyst in plasma during the destruction of VOCs.[6]

SEM images of $MnO_2/BaTiO_3$ before and after the plasma catalytic reaction at 5.0 kV for 230 h are shown in Figure 4. The MnO_2 particles on the $BaTiO_3$ were much smaller and more dispersed after the 230 h reaction in the plasma catalytic reactor than before the reaction. Zhang et al. demonstrated that glow discharge treatment leads to higher and more stable dispersion of active species over the support.[10] Furthermore, we found that the catalyst we used had good activity and stability, consistent with previous studies.

The chemical states of $MnO_2/BaTiO_3$ before and after the plasma catalytic reaction for 230 h were examined by XPS analysis. The Mn 2p and O 1s XPS spectra before and after the reaction are shown in Figures 5(a) and (b), respectively. The binding energy of the Mn 2p peak was determined to be at 642 and 653 eV for both catalysts, indicating that the +2 and +4 oxidation states were well preserved after the reaction (Fig. 5(a)).[2,5] The binding energies of the O 1s peaks at 530 (O^{2-}) and 533 eV (OH^-) of both catalysts were also preserved after the reaction. However, the O 1s peak at 530 eV had a lower energy after the reaction. It has been shown that ultrafine particle catalysts have a less perfect crystal lattice when a large number of oxygen vacancies are present, which induces higher catalytic activity.[12] Some unusual chemical activities have been reported for cases where plasma species were involved in the catalyst surface reactions, which has motivated efforts to apply plasmas directly to obtain more effective catalysts.[13–14] We demonstrated that plasma enhanced the dispersion of the active species of MnO_2 and improved the stability as well as the activity of the catalysts.

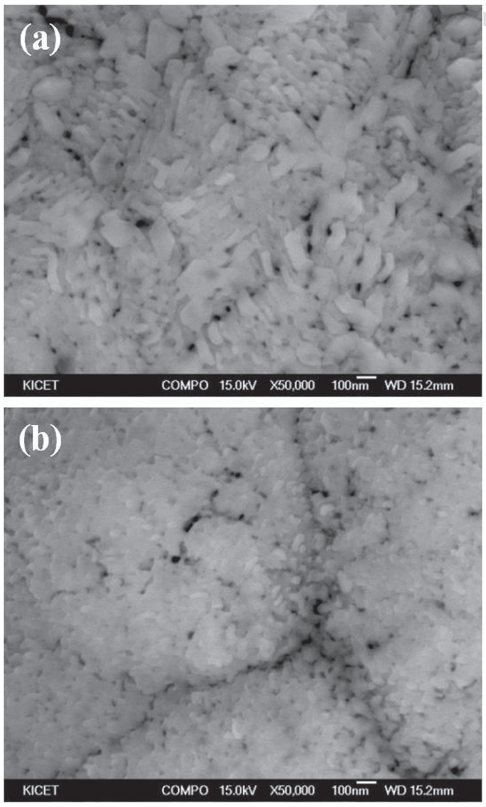

Fig. 4. The SEM images of $MnO_2/BaTiO_3$ for 230 h; before (a) and after reaction (b).

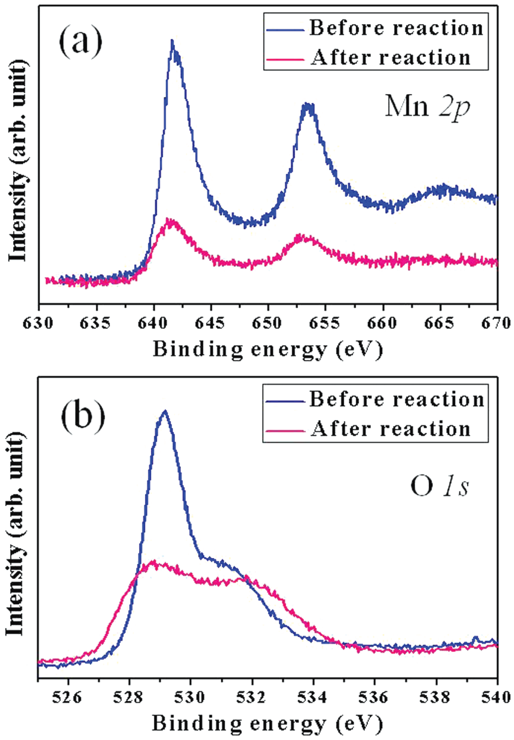

Fig. 5. The XPS spectra of $MnO_2/BaTiO_3$ before and after reaction for 230 h; (a) Mn 2p spectra and (b) O 1s spectra.

4. CONCLUSION

We investigated toluene decomposition in a plasma catalytic system where a catalyst was integrated on ferroelectric $BaTiO_3$ beads. The order of toluene conversion at 5 kV was $MnO_2/BaTiO_3 > Co_3O_4/BaTiO_3 > CuO/BaTiO_3 > BaTiO_3$. In a lifetime test, the $MnO_2/BaTiO_3$ catalyst showed high stability in igniting plasma during the destruction of toluene for 230 hours.

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