Enhanced Photocatalytic Decomposition of Gaseous Isopropyl Alcohol in a Polymer Electrolyte Cell

Wei-Ming Hou, Young Ku*

Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 106, Taiwan

ABSTRACT

Electrochemical enhancement of the photocatalytic decomposition of isopropyl alcohol in gas phase was carried out in a polymer electrolyte cell. An external electrical field was created in the gas-phase photocatalytic reaction due to the presence of solid electrolyte. The effects of bias potential, relative humidity, initial isopropyl alcohol concentration and UV light intensities were investigated for the photoelectrocatalytic process. Photoelectrocatalytic decomposition of isopropyl alcohol was observed to be less sensitive to humidity for experiments that applied a bias potential higher than 2.5 V. Electrical current densities of photoanode were highly correlated to the variations in bias potential, relative humidity level and UV light intensity, although independent of inlet isopropyl alcohol concentrations. Humidity had an ambiguous effect on the membrane conductivity of polymer electrolyte and photocatalytic decomposition rate of isopropyl alcohol with the application of bias potential. The experimental results also showed that the energy consumed in the photoelectrocatalytic process was much less than that needed by the photocatalytic process to achieve a similar level of isopropyl alcohol decomposition.

Keywords: Photoelectrocatalysis; Nafion; Humidity; Applied bias; Gas phase.

INTRODUCTION

Photocatalytic oxidation process using semiconductive materials is a promising advanced oxidation technology in the fields of water and air treatment because of the relatively mild reaction conditions required to achieve satisfactory decomposition of refractory pollutants. However, the rapid recombination between photogenerated electrons and holes seriously restricts the effectiveness of photocatalytic processes, resulting in low quantum yields for most photocatalytic reactions (Chen and Ku, 2007; Ku et al., 2010a). Several modification methods for photocatalytic process were proposed to inhibit electron-hole recombination, including photocatalyst modification via doping with cations (Mn²⁺, Cr³⁺, Fe³⁺, V⁵⁺, etc.) (Nowotny et al., 2008; Dholam et al., 2009; Akpan and Hameed, 2010), depositing metal particles (Pt, Ag, etc.) (Chen et al., 2007; Kuo et al., 2007) or metal oxides (NiO, ZnO, etc.) (Ku et al., 2011a, b) on photocatalyst surface and modifying the structure of photocatalyst (nanotube, nanorod, etc.) (Wang et al., 2009; Ku et al., 2010b, c; Xin et al., 2011), and process intensification via addition of sacrificial agent (methanol, ethanol, Na₂S, ethylene diamine tetraacetic acid, etc.) (Galińska and Walendziewski, 2005; Ku et al., 2011a) or application of bias potential (Ku et al., 2006; Ku et al., 2010a; Shang et al., 2011). The bias-assisted photocatalytic process (also called photoelectrocatalytic process) is a promising technique to decrease electron-hole recombination and save energy (Shang et al., 2007; Ku et al., 2010a; Liu et al., 2011). By applying bias potential to the photocatalyst, an external electrical field is occurred to drive the photogenerated electrons and holes in opposing directions and thus decreases the electron-hole recombination (Ku et al., 2006). To enhance the photocatalytic decomposition, the energy consumption of applying bias potential was reported to be much more efficient comparing with applying higher light intensity (Ku et al., 2010a).

Applications of bias potential to photocatalytic reactions are usually carried out in liquid phase and restricted for decomposition of gaseous contaminants because most electrolytes are in the form of solution. The employment of solid electrolytes exhibits a critical role to develop an electrochemical circuit in gas phase, and therefore to facilitate electrochemical-catalytic reactions, such as for the application of fuel cells and gas sensors (Georgieva et al., 2009). Nafion membrane is one of the commonly utilized solid electrolytes to apply the bias potential to the photocatalytic reactions due to its mild operation of room temperature (Georgieva et al., 2009; Seger and Kamat, 2009). The construction of proton exchange membrane (PEM) fuel cells using Nafion as solid electrolyte exhibits promise for

Humidity revealed controversial impacts on photocatalytic process in gas phase, leading to competition adsorption of water molecules with organic species for active sites on photocatalyst surface, or the generation of hydroxyl radicals by the photocatalysis of water molecules (Wang and Ku, 2003; Pichat, 2010). Moreover, the performance of PEM fuel cell is also significantly affected by the presence of humidity. The power generation of a PEM fuel cell was increased with increasing water molecules in gas phase because of the improved proton conductivity of Nafion membrane (Zhang et al., 2008; Miller and Bazylak, 2011). However, the diffusion of fuel gas on the electrodes would be retard by excess water molecules due to water flooding (Weng et al., 2007).

The objective of this study is to investigate the photoelectrocatalytic decomposition of isopropyl alcohol (IPA) in gas phase. A photoelectrochemical reactor using solid polymer electrolyte was fabricated based on the structure of PEM fuel cell. The bias potential was applied in the presence of solid polymer electrolyte to create an electrical circuit in the gaseous photocatalytic process. The effects of applied bias, humidity, initial isopropyl alcohol concentration and light intensity were investigated on the photoelectrocatalytic and photocatalytic processes. The present study provides further insight for potential applications of the gaseous photoelectrocatalytic process for air pollution control.

METHODS

All chemicals used in this study were analytical grade and utilized as received without any further purification. The 10 wt% TiO2 slurry was prepared by dispersing 50 g Aerosol P-25 TiO2, a mixture of anatase and rutile, into 450 g of ethanol solution. The slurry solution was stirred violently for 30 minutes and then conicated for 8 hours. A drilled stainless steel plate (24 × 24 mm) was used as the immobilizing support of TiO2. The drilled stainless steel plate, with one face covered by a tape, was dipped into the TiO2 slurry solution for 10 seconds and then dried in flowing nitrogen gas. After the dip-coating process repeated for 3 times, the TiO2-coated steel plate was dried at 80°C overnight and then used as photoanode in this study. Another drilled stainless steel plate (24 × 24 mm) immersed in ethanol, aceticone and deionized water in sequence was served as cathode electrode. The similar fabrication procedure for photoanode was published in Ref. (Hou and Ku, 2013). Crystal phase and distribution of TiO2 particles coated on the photoanode was characterized by an X-ray diffractometer (XRD, D2 Phaser, Bruker) and field-emission scanning electron microscopy (FESEM, JSM-6500F, JEOL), respectively.

As shown in Fig. 1, the structure of photoelectrochemical reactor used in this study was designed to follow the structure of PEM fuel cell. The commercial membrane electrode assembly (Horizon Fuel Cell Technologies) consisted of a Nafion membrane was used as solid electrolyte to transport protons. The photoanode and cathode electrodes positioned on opposite sides of the Nafion membrane were tightly sandwiched by two acrylic flow-field plates to provide good contact between the electrodes and Nafion membrane. The ledges of photoanode and cathode were separately attached to make an electrical contact with a potentiostat.

Photoelectrocatalytic decomposition of gaseous IPA in this reactor was evaluated under UV light illumination. The schematic diagram of experimental system is depicted in Fig. 2 consisted of a VOC generation unit, a humidity-tuning unit, a photoelectrochemical reactor, a bias supplier, an UV light source and a detection unit. IPA-laden gas steam with specific concentrations was prepared by varying mixing ratio of calibrated IPA stream and dewatered air in a gas mixer. The humidity of IPA-laden stream was varied by adjusting the air flow passing through the water vaporizer and was measured by a humidity meter (HF532, Rotronic). In order to avoid the condensation of IPA and humidity, a flexible electrical heating tape was wrapped around the gas pipeline keeping the gaseous stream at 40°C. IPA-laden stream was flowed through the photoreactor without UV irradiation for 30 minutes to saturate the adsorption of IPA on the TiO2 film; UV light was then emitted from a 10 W UV-LED (NES110UV, Lustron, primary at 400 nm) and projected onto the photoanode. UV light intensity was controlled by a programmable DC power supply (SPS150-8, Amrel) and was measured by a photometer (IL1400A, International Light) equipped with a UV detector (SEL005/WBS320/TD, International Light). The bias potential and electrical current density of photoanode were provided and measured by the potentiostat (PGSTAT30, Autolab). Outlet gas stream was sampled by an autosampler (Valco, E2C6UWT) and analyzed by a gas chromatograph (China Chromatography, GC 2000) equipped with a RTX-624 capillary column and a flame ionization detector (FID).

In order to differentiate the enhancement contributed by bias potential for inhibiting the recombination of electron-hole pairs, synergetic factor was determined for quantitative calculation. The synergetic factor, SPEC, is calculated using the decomposition of IPA by photoelectrocatalytic, photocatalytic and electrolytic processes for experiments conducted under similar conditions and expressed as follows:

$$S_{PEC} (\%) = \frac{R_{PEC} - (R_{PC} + R_{E})}{R_{PEC}} \times 100 \quad (1)$$

where RPEC, RPC and RE are the decomposition for experiments conducted with photoelectrocatalytic,
photocatalytic and electrolytic processes.

RESULTS AND DISCUSSION

Characterization of Photoanode

The SEM image and XRD pattern of prepared TiO$_2$-coated photoanode are illustrated in Fig. 3. The surface morphology of coated TiO$_2$ layer demonstrated in Fig. 3(a) indicates that the smooth TiO$_2$ layer was structured by spherical TiO$_2$ particles in the range of 30 to 60 nm, and the cracks were possibly generated due to the evaporation of ethanol. The thickness of TiO$_2$ layer shown in Fig. 3(b) was at about 25 μm. The diffraction peaks of XRD pattern shown in Fig. 3(c) for the TiO$_2$-coated photoanode at 2θ = 25.2° and 27.2° were assigned to the reflections of (101) and (110) planes of TiO$_2$, respectively. Moreover, the diffraction peaks at 2θ = 43.8° and 44.7° indexed to iron nickel and alpha iron was contributed from stainless steel substrate.

Fig. 1. Schematic diagram of the photoelectrochemical reactor.

Fig. 2. Schematic diagram of the photoelectrocatalytic system used for decomposition of gaseous IPA.
Effect of Applied Bias Potential on Gaseous Photoelectrocatalytic Process

The effect of applied bias on the decomposition of gaseous IPA by electrolytic, photocatalytic and photoelectrocatalytic processes in the presence of 10% relative humidity is depicted in Fig. 4(a). No IPA decomposition was observed by electrolytic process for experiments conducted with applied bias less than 2 V; merely about 8% IPA was decomposed for experiments conducted with applied bias potentials of 2.5 or 3 V. IPA decomposition by photocatalytic process without any applied bias potential was approximately 70%. It was observed that IPA decompositions by photoelectrocatalytic process were higher than those by photocatalytic process. IPA decomposition was increased by roughly 13% with applied bias potentials of 2.5 or 3 V for photoelectrocatalytic process. The enhancement could be attributed that the photogenerated electrons might be efficiently driven by the applied bias potential out of the photoanode to the external circuit to decrease recombination of electrons and holes (Ku et al., 2010a).

Fig. 4(b) demonstrates the variation of electrical current density of the photoanode for experiments conducted with various applied biases in the range from 0.5 to 3 V. Drastic increase of electrical current densities was observed for experiments conducted with applied bias higher than 1.5 V. It could be attributed that protons, charge carriers within Nafion membrane, were generated for experiments conducted with applied bias potential higher than the voltage for water splitting (E = 1.23 V) (Itoh et al., 2000). The electrical current densities were drastically amplified due to increasing applied bias potential in the range from 1 to 2.5 V. A saturated value of electrical current densities was observed for experiments conducted with bias higher than 2.5 V, which was attributed that the diffusion of water molecules for experiments carried out in the presence of 10% relative humidity supplemented limiting proton for solid electrolyte (Sawada et al., 2008). The electrical current densities measured for the photoelectrocatalytic process were obviously lower than those measured for the electrolytic process. According to the previous studies (Wang and Ku, 2003; Zhao and Yang, 2003; Pichat, 2010), water molecules
were consumed to the formation of hydroxyl radicals involving the electron transfer of photo-excited TiO$_2$ with adsorbed water molecules and hydroxyl ions. In addition, a humidified Nafion membrane exhibits effective proton conductivity because proton only can migrate through the solid polymer electrolyte membrane with water molecules (Rosseler et al., 2011). Zhang et al. (2008) presented that the proton transfer conductivity of Nafion membrane was decreased with decreasing water content in membrane, as a function of relative humidity. Comparing with the electrolytic process, the lower electrical current densities observed from photoelectrocatalytic process were considered that water molecules were consumed after UV light illumination, decreasing the amount of charge carriers and membrane conductivity because of the lack of proton production and water molecules for Nafion membrane, respectively.

**Effect of Relative Humidity on Gaseous Photoelectrocatalytic Process**

The presence of humidity is reported to exhibit controversial impacts on photocatalysis in gaseous phase (Wang and Ku, 2003; Pichat, 2010; Rosseler et al., 2011). Photocatalysis of water molecules might generate hydroxyl radicals to enhance the oxidation reactions; however, the excessive adsorption of water molecules on the active sites might also retard the photocatalytic reactions (Wang et al., 2003; Chou and Ku, 2010). IPA decomposition by photoelectrocatalytic, photocatalytic and electrolytic processes for experiments carried out in the presence of various relative humidity levels from 10 to 40% is presented in Fig. 5(a). Decomposition of IPA by photocatalytic and photoelectrocatalytic processes was decreased with increasing humidity levels. The decrease of IPA decomposition is
attributed to the competition between water and IPA molecules for the active sites on highly hydrophilic TiO$_2$ surface. The slight increase of IPA decomposition for experiments conducted by electrolytic process with increasing relative humidity was ascribed to the increasing effective bias potential for the photoanode depicting as follow (Roy et al., 2011):

$$V_{\text{eff}} = V_{\text{app}} - IR$$  \hspace{1cm} (2)

where $V_{\text{eff}}$ is the effective bias potential, $V_{\text{app}}$ is the applied bias potential, $I$ is the current and $R$ is resistivity of the solid electrolyte. Increasing relative humidity decreased the resistivity of the solid electrolyte, and supplemented more proton for Nafion membrane (Xu et al., 2007; Zhang et al., 2008). Therefore, the electrolytic decomposition of IPA was elevated by increasing effective bias potential applied on the photoanode. Effect of relative humidity on synergetic factors for experiments conducted with 2.5 V applied bias potential was shown in Table 1. The synergetic factors were increased from 6.5% to 20.9% in the range of relative humidity from 10 to 40%. As IPA decomposition by electrolytic process slightly increased with increasing relative humidity, the increase of synergetic factors indicated that the retard level of photoelectrocatalytic decomposition of IPA was less than that of photocatalytic decomposition of IPA. It could be supposed that the increasing effective bias potential with increasing relative humidity applied on the photoanode efficiently drove the photogenerated electrons into the external circuit. Besides,
Table 1. Effect of relative humidity on the synergetic factor determined by photoelectrocatalytic, photocatalytic and electrolytic processes.

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>Synergetic factor* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.5</td>
</tr>
<tr>
<td>20</td>
<td>13.8</td>
</tr>
<tr>
<td>30</td>
<td>17.1</td>
</tr>
<tr>
<td>40</td>
<td>20.9</td>
</tr>
</tbody>
</table>

* All experiments conducted with photoelectrocatalytic process were applied with 2.5 V bias potential and 37.8 mW/cm² of UV light intensity.

Electrical current densities for both electrolytic and photoelectrocatalytic processes were increased linearly with increasing relative humidity due to the increase of membrane conductivity of Nafion, as depicted in Fig. 5(b). The experimental results also demonstrated that the level of relative humidity could be estimated by the electrical current density of photoanode. Therefore, the presence of water molecules for photoelectrocatalytic process demonstrates a controversial effect to promote membrane conductivity of Nafion and retard the photocatalytic reaction.

Fig. 6 presents photoelectrocatalytic decompositions of IPA for experiments conducted with various applied bias and relative humidity. Comparing with the rapid decrease of IPA decomposition by the photocatalytic process from 70% to 45% with increasing relative humidity, IPA decomposition by the photoelectrocatalytic process was gradually decreased from 83% to 69% at the applied bias of 2.5 V. IPA decomposition by photoelectrocatalytic process with applied bias higher than 2.5 V was less sensitive to humidity than that by photocatalytic process. The experimental results revealed that photoelectrocatalytic process in the photoelectrochemical reactor is a technically feasible air treatment practice even in humid conditions.

Effect of Inlet IPA Concentration on Gaseous Photoelectrocatalytic Process

Experimental results shown in Fig. 7(a) revealed that IPA decomposition by photoelectrocatalytic and photocatalytic processes was decreased for experiments conducted with increasing inlet IPA concentration. Similar results were also provided for the decomposition of benzene (Wang and Ku, 2003) and acetone (Ku et al., 2005), and the reduction of NO (Chou and Ku, 2010). The decrease of IPA decomposition was attributed to the limited active sites on the TiO₂ surface available for the adsorption of IPA. However, the electrical current density presented in Fig. 7(b) was maintained at a steady value for experiments conducted with various inlet IPA concentrations. It could be further verified that the proton as the charge carrier within Nafion membrane was not contributed from the IPA decomposition, but from water molecules.

Effect of UV Light Intensity on Gaseous Photoelectrocatalytic Process

The effect of UV intensity on the IPA decomposition by photoelectrocatalytic and photocatalytic processes at a residence time of 0.34 second is shown in Fig. 8(a). Decomposition rate of IPA for both processes was increased with increasing UV intensity because the generation of photogenerated electrons and holes was promoted. However, the promotion of increasing UV intensity on IPA decomposition was decreased for experiments conducted with light intensity higher than 25.2 mW/cm² because excessive light energy can not be absorbed by the limited surface of TiO₂ particles, similar to the results reported previously for benzene decomposition by photocatalytic process (Wang and Ku, 2003).

![Photoelectrocatalytic decomposition of IPA as a function of applied bias for experiments conducted with various relative humidity levels.](image)
Electrical current density of the photoanode depicted in Fig. 8(b) was found to be decreased linearly with increasing UV light intensity, indicating the decrease of membrane conductivity of Nafion possibly due to the photocatalytic decomposition of water molecules. It was conjectured that the decreasing water molecules would reduce the water content within polymer electrolyte membrane with increasing light intensity, and therefore decrease the proton transfer conductivity of Nafion.

**Proposed Mechanism for Photoelectrocatalytic Process in a Polymer Electrolyte Cell**

The proposed scheme for decomposition of gaseous IPA in the photoelectrocatalytic reactor was illustrated in Fig. 9. The application of bias potential could enhance the decomposition efficiency because the generation of electrical field retards the rapid recombination of photogenerated electrons and holes. For experiments conducted with the applied bias potential higher than the voltage for water splitting, photocatalysis and water electrolysis should be both considered. Therefore, the reaction mechanism at photoanode could be expressed as follow:

\[
\text{TiO}_2 + \text{hv} \rightarrow e^- + h^+ \quad (3)
\]

\[
(\text{CH}_3)_2\text{COH} + h^+ \rightarrow \text{oxidized products} \quad (4)
\]

\[
\text{H}_2\text{O} + h^+ \rightarrow \cdot\text{OH} + \text{H}^+ \quad (5)
\]

\[
\text{OH}^- + h^+ \rightarrow \cdot\text{OH} \quad (6)
\]
Fig. 8. Effect of UV light intensity on the (a) IPA decomposition by the photoelectrocatalytic and photocatalytic process; and (b) electrical densities of photoanode.

\[ e^- + h^+ \rightarrow \text{luminescence or thermal heat} \quad (7) \]

\[ 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4e^- \quad (8) \]

where \( e^- \) and \( h^+ \) are the photogenerated electrons and holes, respectively. The proton generated from the water electrolysis was driven through the Nafion membrane to the cathode by the application of bias potential, and then reacted with the electrons to generate hydrogen:

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (9) \]

**Energy Consumption of Photoelectrocatalytic Process**

Energy consumption determined for the decomposition of gaseous IPA by photocatalytic and photoelectrocatalytic processes was shown in Table 2. 68.6% IPA was decomposed for experiments conducted by photoelectrocatalytic process with 17.6 mW/cm\(^2\) of UV light intensity, consuming 4.63 \( \times 10^{-3} \) kWh of electrical power. However, 9.18 \( \times 10^{-3} \) kWh was consumed for experiments conducted by photocatalytic process with 31.9 mW/cm\(^2\) of UV light intensity to achieve similar IPA decomposition. The experimental results exhibited that application of bias potential was more energy efficient than the increase of UV light intensity to enhance IPA decomposition.

**CONCLUSIONS**

Photoelectrocatalytic decomposition of gaseous IPA was approached in a polymer electrolyte reactor constructed by
Fig. 9. Proposed scheme for decomposition of gaseous IPA in the photoelectrocatalytic reactor.

Table 2. Energy consumption determined for gaseous IPA decomposition by photoelectrocatalytic process with various UV light intensities and bias potentials.

<table>
<thead>
<tr>
<th>UV light intensity (mW/cm²)</th>
<th>Bias potential (V)</th>
<th>Removal ratio (%)</th>
<th>Energy consumption (kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.6</td>
<td>2.5</td>
<td>68.6</td>
<td>$4.63 \times 10^{-3}$</td>
</tr>
<tr>
<td>17.6</td>
<td>0</td>
<td>44.2</td>
<td>$4.24 \times 10^{-3}$</td>
</tr>
<tr>
<td>25.2</td>
<td>0</td>
<td>59.3</td>
<td>$6.65 \times 10^{-3}$</td>
</tr>
<tr>
<td>31.9</td>
<td>0</td>
<td>66.6</td>
<td>$9.18 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Reaction conditions: $C_{IPA} = 20$ ppmv; flow rate of anode = 100 sccm; humidity ratio = 10%; light intensity = 37.8 mW/cm².

the structure of PEM fuel cell. The presence of solid polymer electrolyte was feasible to apply bias potential in the gaseous photocatalytic reaction. Decomposition of gaseous IPA was efficiently enhanced by photoelectrocatalytic process because the photogenerated electrons were efficiently driven from TiO₂-coated photoanode into external circuit by the application of bias potential, further inhibiting electron-hole recombination. Water molecules demonstrated as a controversial effect for gaseous photocatalytic process in the polymer electrolyte reactor as supplier of proton as charge carrier, promoter for proton transfer within Nafion membrane and a competitive adsorber for active sites on the photocatalyst surface. Electrical current densities of photoanode were increased with increasing bias potentials and relative humidity levels, but decreased with increasing UV light intensities. The electrical current densities for experiments conducted with various inlet IPA concentrations were determined at a steady value, indicating that the proton was mainly supplied from water molecules. The synergetic factors of photoelectrocatalytic process were increased with increasing relative humidity because of the variation of conductivity of Nafion membrane. Comparing with increasing UV light intensity, 50% energy reduction was achieved by applying bias potential on the photocatalytic process. Experimental results provided that photoelectrocatalytic process in gas phase was an efficient air treatment in real humid conditions.

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