Application of Three-phase Fluidized Photocatalytic System to Decompositions of Acetic Acid and Ammonia

Yeon-Hee Son, Min-Kyu Jeon, Ji-Young Ban, Misook Kang*†, and Suk-Jin Choung†

Department of Chemical Engineering, School of Environmental Applied Chemistry,
*Industrial Liaison Research Institute, Kyung Hee University, Yongin, Gyeonggi 449-701, Korea

Received June 17, 2005; Accepted August 16, 2005

Abstract: To enhance the performance for acetic acid and ammonia destruction, a fluidized photo-catalytic system was designed in this study. TiO₂ and Al-TiO₂ photocatalysts were obtained by the sol-gel method, and they were characterized by XRD, SEM, XPS, and TPD analyses for acetic acid and ammonia. The XRD pattern for Al-TiO₂ developed a stable anatase structure after thermal treatment at 700 °C, but pure TiO₂ was rapidly transformed into the rutile type after thermal treatment at 700 °C. In terms of the surface properties, the 10.0 mol-% Al-TiO₂ formed a larger (185 m²/g) area when compared with that formed by pure TiO₂ (52 m²/g). The XPS results showed that Al-TiO₂ possessed a higher hydrophilic property than did pure TiO₂. In addition, the amount of acetic acid and ammonia adsorbed was higher in Al-TiO₂ when compared with that in pure TiO₂. The decompositions of acetic acid and ammonia were enhanced in a fluidized photoreactor relative to those obtained in a conventional steady photoreactor, particularly when Al-TiO₂ was used as the photocatalyst; the conversions to N₂ (ammonia decomposition) and CO₂ (acetic acid decomposition) reached above 90 % until 600 min when bubbling air (1 L/min) into a 0.5 g/L Al-TiO₂ fluidized photo-system; the conversion to N₂ (ammonia decomposition) was 70 % in a conventional steady photoreactor. Undesirable NOₓ and NO₃⁻, which were detected as by-products of the ammonia photo-degradation, were present at only ca. 1 ~ 2 ppm as determined from FT-IR spectra and ion chromatograms. These components were more depressed on Al-TiO₂.

Keywords: Al-TiO₂ fluidized photoreactor, acetic acid, ammonia decomposition

Introduction

Ammonia and acetic acid are serious pollutants in waste water that bring about eutrophication of rivers and lakes [1]. These bodies of water must be treated using biological techniques, adsorption, and thermal incineration. Recently, catalytic decomposition of these species in waste water using metal-TiO₂ photocatalysts has attracted much attention [2-6]. In particular, most researchers have hoped to convert all of the ammonia molecules into N₂ using photocatalytic redox reactions: 4NH₃ + 3O₂ → 2N₂ + 6H₂O. However, it has been reported that when metal-incorporated TiO₂ photocatalysts are used for ammonia decomposition, considerable amounts of N₂O, NOₓ, and NO₃⁻ are formed. In addition, the values of pH in acetic acid or ammonia solutions (100 ~ 500 ppm) are distributed from 2 to 11. Therefore, it is very important for the catalyst to be structural stable during photocatalytic reactions in acidic and basic aqueous solutions. In our previous study, an attempt was made to introduce Al-TiO₂ to benzene photodecomposition through H₂O addition [7]. We discovered that the addition of H₂O in Al introduction improves benzene photodecomposition relative to that mediated by pure TiO₂; in addition, the anatase structure of Al-TiO₂ remained stable during photoreaction. On the other hand, these photocatalytic applications have limitations when used in industrial situations because the observed performances are very low. To improve the photocatalytic decomposition, a three-phase fluidized photoreactor was designed in this study. The three-phase reactors, involving contact among gases, liquid, and solid phases, have gained increasing importance in a wide range of industrial applications [8,9]. Such reactors are preferred because of the simplicity of their construction and operation, low operating
costs, and flexibility over the liquid and solid phase residence times. The advantages of three-phase reactors are: 1. Intense contact between the phases; 2. High degree of mixing that results in isothermal operation; 3. High values of effective interfacial area and overall mass transfer coefficient can be obtained; 4. Large heat capacity of the liquid phase and high heat transfer coefficients are advantageous in temperature control; 5. Catalysts can be continuously added and withdrawn without any erosion or plugging problems; 6. Cushioning effect of the liquid reduces particle abrasion. Because of these advantages, three-phase fluidized bed reactors have been used widely: for example, in coal conversion process, catalytic hydrogenation, and hydro-desulfurization of residual oil. Current applications for wastewater treatment and biochemical processes are commonly encountered.

Therefore, the main objective of this study was to enhance the photocatalytic decompositions of acetic acid and ammonia using a three-phase fluidized reactor operated under atmospheric conditions. We obtained TiO$_2$ and Al-TiO$_2$ photocatalysts by applying the sol-gel method; these materials were applied to decompose acetic acid and ammonia solutions.

**Experimental**

**Catalyst Preparation**

The conventional sol-gel method was employed for the preparation of TiO$_2$ and Al (5.0- and 10.0-mol-%)-TiO$_2$ catalysts, as shown in Figure 1. The reagents used for the preparation of the sol-mixture were titanium tetraisopropoxide (TTIP, 99.95 %, Junsei Chemical, Japan) and aluminum isopropoxide (99.99 %, AIP, Junsei Chemical, Japan), which were used as the titanium and aluminum precursors, respectively. Ethanol (Wako Pure Chem., Ltd.) was used as a solvent. TTIP and the aluminum precursor were mixed with the alcoholic solvent in a 300-mL beaker. TTIP was hydrolyzed by the OH groups of water (0.4 mol), and then the solution was aged at 80–90 °C for 6 h. The precipitated white powders were washed with distilled water and then dried at 100 °C for 24 h. Finally, crystallization of TiO$_2$ and Al-TiO$_2$ with anatase structure, occurred after calcination at 500 °C for 3 h.

**Characterization of Synthesized Catalysts**

The synthesized samples (TiO$_2$ and Al-TiO$_2$ powders) were identified using powder X-ray diffraction analysis (XRD, model PW 1830 from Philips) and nickel-filtered CuK$_\alpha$ radiation (30 kV, 30 mA) at 2-theta angles from 20 to 70°. The scan speed was set at 10 degrees/min while the time constant was set at 1 sec.

The particle sizes and shapes of the TiO$_2$ and Al-TiO$_2$ powders were investigated using scanning electron microscopy (SEM, model JEOL-JSM35CF). The power was set at 15 kV.

The UV-visible spectrum was obtained using a JASCO V-570 spectrometer equipped with a reflectance sphere. The spectral range varied from 200 to 800 nm.

The BET surface area and pore size distribution (PSD) of the sample were measured through nitrogen gas adsorption in a continuous flow method, using a chromatograph equipped with a TCD detector for the liquid nitrogen temperature. A mixture of nitrogen and helium was discharged as the carrier gas using the GEMINI2375 model from Micrometrics.

XPS spectra were acquired using an ESCA 2000 and Al K$_\alpha$ X-rays (15 kV, 350 W). The spectra were then collected for 20–90 min, depending on the peak intensities, at an energy level of 23.5 eV. XPS peaks were identified using tabulated binding energy values from XPS handbooks, they yielded information on the chemical composition and bonding environments.

Acetic acid and NH$_3$-temperature programmed desorption (TPD) measurements were performed on a conventional TPD system equipped with a TCD cell. The catalysts were exposed to He gas at 550 °C for 2 h to remove water and impurities on the surface. After the pretreatment, the samples were exposed to acetic acid and ammonia atmospheres for 1 h. Finally, the programmed heating was set to 600–700 °C at a rate of 10 °C/min. The amount of desorbed gas was monitored continuously using a TCD cell.

**Analysis of Acetic Acid and Ammonia Decomposition**

The decompositions of acetic acid and ammonia were performed using a continuous three-phase fluidized photo-
reactor designed in our laboratory (Figure 2). The reactor column has an outer diameter of 7.5 cm and inner diameter of 6.5 cm, with a height of 118 cm; it was made of pyrex. In preparation for acetic acid and ammonia decompositions, TiO₂ and Al-TiO₂ powders (0.5 g/1 L) were added into the pyrex cylinder reactor with a 3-L volume of water. The flowed concentration of acetic acid and ammonia were fixed (300 and 80, ppm respectively), and the injected rate was 1~2 L/min. A UV-lamp (39 W/cm², 90 cm length x 2.0 cm diameter, YongWha Lamp, Korea) operated at 254 nm was used.

Analyses of the concentrations of acetic acid and ammonia before and after the photodecomposition reactions were performed using a gas chromatograph (Shimadzu GC 17A) equipped with FID/TCD detectors (HP-1 capillary column). The removal (in percentage values) was based on the disappearance of pollutants during the decomposition process. All experiments were performed at room temperature and atmospheric pressure. A Fourier Transform Infrared (FT-IR) spectrometer (Shimadzu, FTIR-8400) and Ion Chromatograph were used to conduct the quantitative gas analyses of the products after ammonia decomposition at a reaction time of 60 min.

Results and Discussion

Characterization of Catalyst

Figure 3 shows the XRD patterns of the TiO₂ and Al-

Figure 2. Schematic illustration of the three-phase fluidized photoreactor apparatus.

Figure 3. The changes in the XRD patterns of TiO₂ and Al-TiO₂ upon thermal treatment.

TiO₂ powders under various calcination temperatures. In general, the TiO₂ photocatalyst having an anatase structure exhibited better VOC decomposition performance relative to catalysts having other structures, such as rutile, brookite, and amorphous. As shown in Figure 3, all the samples exhibited a well-developed anatase structure (symbol A) at temperatures above 500 °C. In the case of pure TiO₂ (Figure 3a), the rutile structure (symbol R) occurred at 700 °C; however, the anatase structure remained stable at temperatures up to 700 °C in the case of the Al-TiO₂ sample (Figure 3b). Therefore, the increase in the aluminum amount resulted in a corresponding increase in the thermal stability of the anatase structure. In addition, special peaks for Al₂O₃ were not observed in any of the samples. This observation indicates that the Al³⁺ ion was inserted well within the Ti⁵⁺ sites. On the other hand, the peak width was slightly broader in the case of Al-TiO₂ relative to that of the pure TiO₂ particles. In general, the width of the XRD peak corresponds to the crystallite sizes of the materials. If the peak width is broad, the crystallites form smaller sizes.
Therefore, Figure 3 confirms that the Al-TiO₂ particles were smaller and more stable thermally than were the pure TiO₂ particles.

SEM images of the TiO₂ and Al-TiO₂ photocatalysts are shown in Figure 4. All of the catalysts possess relatively uniform and spherical shapes, but the particle sizes could not be evaluated from these SEM images. The 10.0-mol% Al-TiO₂ catalyst exhibited a slightly smaller particle size when compared with those of the other catalysts.

Table 1 summarizes the physical properties of the catalysts. When aluminum was added into the titanium dioxide, new bulk pores were generated having sizes ranging of 47–57 nm and pore volumes of 0.13–0.27 mL/g. This result may be attributed to the fact that the Al-TiO₂ framework had a negative charge, which is identical to the Al³⁺ ion that was substituted into the Ti⁴⁺ ion sites. Therefore, the interaction among the Al-TiO₂ nano-sized particles increased, generating new bulk pores that occurred among the nano-sized Al-TiO₂ particles. On the other hand, the higher aluminum content also raised the BET surface area, which reached 185 m²/g at 10.0 mol% aluminum. This phenomenon is due to the smaller particle size and the new bulk pores exhibited by Al-TiO₂. In addition, we estimated the zeta-potential values at pH 2.0, 7.0, and 11.0 (in DI water); the surface charges exhibited positive and negative values in acidic solution (pH 2) and at pH above 7, respectively. In particular, the values in acidic solution were larger for pure TiO₂; they were relatively larger for Al-TiO₂ in basic solution. This result means that the surfaces of pure TiO₂ and Al-TiO₂ were more stable in acidic and at basic solutions, respectively.

Quantitative XPS analyses for O1s were performed on the TiO₂ and 10.0 mol% Al-TiO₂ particles (Figure 5). Gaussian fitting was used for curve resolutions of the O1s peaks (first peak: 529.5; second peak: 531.4 eV) in the two spectra. In particular, the secondary peak value was indicated in the bulk oxide (O²⁻) and hydroxyl (OH⁻) species on the TiO₂ surface, which related to the hydrophilic character [9,10]. This peak shifted to a higher

<table>
<thead>
<tr>
<th>Table 1. Physical Properties of TiO₂ and Al-TiO₂ Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta potential (mV)</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>pH 2.0</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>5 mol-% Al-TiO₂</td>
</tr>
<tr>
<td>10 mol-% Al-TiO₂</td>
</tr>
</tbody>
</table>
binding energy, and its intensity increased upon the addition of the aluminum component into the TiO₂ framework. This result explains two features. The first is that the peak shift suggests that oxygen species in Al-TiO₂ changed to higher oxidation states relative to those in pure TiO₂. The second is that the larger O1s secondary peak suggests that the Al-TiO₂ sample was more hydrophilic than pure TiO₂.

Figure 6 shows the UV-visible spectra of the TiO₂ and Al-TiO₂ particles. In general, the absorption of Ti⁴⁺ (tetrahedral symmetry) appears at ca. 350 nm. The maximum absorption bands in the Al-TiO₂ samples were shifted slightly to shorter wavelengths when compared with that of pure TiO₂. This result implies that the band gaps in the Al-TiO₂ samples was larger than that in pure TiO₂.

To confirm the effect of the addition of aluminum into the TiO₂ framework, an NH₃-TPD test was performed. Figure 7 shows an resulting profiles. Generally, these profiles consist of two peaks: one that appears in a low-temperature range (ca. 200～300 °C), and another that appears in a high-temperature range (ca. 450～550 °C).

---

**Figure 5.** XPS spectra for the O1s levels of the TiO₂ and 10.0-wt-% Al-TiO₂ samples.

**Figure 6.** UV-visible spectra of the TiO₂ and Al-TiO₂ samples.

**Figure 7.** NH₃-TPD profiles of the TiO₂ and Al-TiO₂ samples.

**Figure 8.** TG curves for desorbed acetic acid for the TiO₂ and Al-TiO₂ samples.
The low- and high-temperature peaks correspond to the weak and strong acid sites, respectively. In the case of pure TiO₂, only one peak assigned to physical adsorption was evident (at ca. 100 °C), while three peaks (at ca. 150, 250, and 550 °C) appeared for the 10.0 mol% Al-TiO₂ sample. This finding indicates that new acid sites on the TiO₂ photocatalyst framework are generated by the addition of aluminum.

Figure 8 provides a comparison of the amount of acetic acid desorbed in the photocatalysts, which were calculated based on the TG curve. With an increase in the amount of Al, the amounts of adsorbed acetic acid increased. In particular, the desorbed amount reached 14 % in 10.0 mol% Al-TiO₂. From the results of Figures 7 and 8, we confirmed that the decompositions of acetic acid and ammonia increased in Al-TiO₂ relative to those in pure TiO₂.

Decompositions of Acetic Acid and Ammonia in a Three-phase Fluidized Photo-system.

Figure 9 provides the conversions for the acetic acid and ammonia removals over TiO₂ and Al-TiO₂ in a three-phase fluidized photocatalysis reactor. In the case of acetic acid decomposition (300 ppm), the conversion increased after aluminum had been added; the conversion to CO₂ reached ca. 90 % and it remained at this level for 600 min on 10 mol% Al-TiO₂. The ammonia removal (80 ppm) was also enhanced on Al-TiO₂ relative to that of pure TiO₂; the conversion to N₂ reached above 95 % in 10 mol% Al-TiO₂. The ammonia conversion reached 70 % in a conventional steady photoreactor. From this result, we confirmed that the fluidized photoreactor was more useful to remove highly concentrated acetic acid and ammonia.

FT-IR spectroscopic data analyses indicate the products that formed after ammonia decomposition for 1 h; we present the results in Figure 10. We have confirmed that the oxygen or OH radicals, which were induced from H₂O and UV radiation, reacted with ammonia to form N₂, NO, NO₂, and H₂O through a series of probable reactions. Undesirable NO and NO₂ products, however, were more depressed in Al-TiO₂ relative to the amounts formed in pure TiO₂. In addition, we confirmed from ion chromatography results that the total amounts of NO and NO₂ were merely ca. 1 ~ 2 ppm.

To examine the structural stability of the samples during ammonia decomposition over TiO₂ and Al-TiO₂, the XRD patterns were measured, before and after the reaction; the results are shown in Figure 11. The specific peak position of the anatase structure did not change after ammonia destruction. However, the peak intensity decreased for all of the samples; this decrease was particularly remarkable.
for pure TiO₂. From a previous study, we reported that the anatase structure of Fe-TiO₂ transformed into the rutile phase after methanol destruction [10]. From this present result, we confirmed that a suitable suppletion of Al into TiO₂ provides structural stability, and as a result, enhances the decomposition of ammonia.

**Conclusions**

To enhance the performance of a acetic acid and ammonia destruction, we designed a fluidized photocatalytic system. The main results are summarized as follows.

1) XRD analyses indicated that the thermal stability was enhanced in Al-TiO₂ relative to that in pure TiO₂. The anatase structure remained stable up to 700 °C. In addition, the 10.0 mol% Al-TiO₂ sample formed a larger (185 m²/g) area than that formed by pure TiO₂ (52 m²/g).

2) XPS analyses indicated that Al-TiO₂ possessed a higher hydrophilicity thandid pure TiO₂.

3) The amounts of acetic acid and ammonia adsorbed were higher in Al-TiO₂ than that in pure TiO₂.

4) The decompositions of acetic acid and ammonia were enhanced in the fluidized photoreactor relative to that in a conventional steady photoreactor. When 10 mol% Al-TiO₂ was used as a photocatalyst, the conversions of acetic acid and ammonia to CO₂ and N₂ reached above 90 % after 600 min, with air bubbling at 1 L/min, in the 0.5 g/L Al-TiO₂ fluidized photo-system.

These results confirm that VOC removal is more useful when performed in a fluidized photoreactor than it is in a conventional steady photoreactor, particularly when Al-TiO₂ is used as the photocatalyst.

**Acknowledgment**

This study was supported by the Korea Institute Environmental Science and Technology (2005-01003-0034-1). The authors are grateful for financial support.

**References**