Methyl Orange Removal in a Liquid Photo-System with Nanometer Sized V/TiO₂ Particle

Misook Kang†, Dong-Hyuk Choi*, and Suk-Jin Choung*

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

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Abstract: This study focuses on the removal of methyl orange (sodium p-dimethylaminoazobenzene sulfonate), a representative dye compound, in a liquid photo-system using nanometer-sized V/TiO₂ synthesized by commercial sol-gel method. The V/TiO₂ particles exhibited a mixture structure of anatase and rutile with a particle size below 70 nm; the surface areas of V/TiO₂ were large (15.0 m²/g) compared with that of pure TiO₂ (7.0 m²/g). The XRD pattern for V/TiO₂ revealed that the vanadium component was substituted well into the titanium ion sites until it reached an amount of 5.0 wt%. The XPS result confirmed that V/TiO₂ had a higher hydrophilic property than did pure TiO₂. In addition, when the vanadium component was added, new Brønsted acid sites were generated. Based on these results, the photodecomposition of methyl orange in liquid reaction was enhanced over V/TiO₂ when compared to that over pure TiO₂, especially when using the 5.0 wt% vanadium addition sample. Furthermore, the photoactivity of V/TiO₂ increased remarkably with H₂O₂ addition in an aqueous solution. From ion chromatogram data, NO₃⁻, NO₂⁻, CO₃²⁻, and SO₄²⁻ ions appeared as products of the methyl orange photodegradation. From the results, it could be suggested that complete photo-oxidation dominated in V/TiO₂ relative to that in pure TiO₂.

Keywords: V/TiO₂, XPS, H₂O₂ addition, methyl orange, ion chromatography

Introduction

The world faces a tremendous set of environmental problems. Thus, an extensive range of research activities are being carried out in a search for advanced chemical, biochemical, and physicochemical methods to eliminate hazardous chemical compounds from the air and water [1-3]. Many studies have been under taken on the photocatalytic treatment of environmental pollutants using semiconductors such as TiO₂, Fe/TiO₂, and Zn/TiO₂. When a semiconductor made of TiO₂ absorbs a photon and is promoted to an excited state, an electron is transferred from a valence band to the conduction band where it can function as a reducing moiety, leaving a hole in the valence band that is strongly oxidizing. The energy gap between the valence and conduction bands in pure TiO₂ is 3.2 eV, so UV light is necessary to excite the electrons on TiO₂ surface. To activate the photocatalysts using UV light with longer wavelengths, many researches have focused recently on the doping/mixing of other sulfides or oxides, such as CdS, Fe₂O₃, ZnO, or PtO [4-6] in the TiO₂ anatase structure, which exhibits a lower band gap energy. Unfortunately, many metal-incorporated TiO₂ derivatives did not give better photoactivity. Previous studies attempted to introduce Al or Fe/TiO₂ having higher hydrophilic properties to the photodecomposition of in benzene gas phase reaction [7,8]. As a result, the benzene photodecomposition was enhanced in these samples compared with that of pure TiO₂ in particular, through H₂O addition. However, H₂O addition could result in structural damage. Therefore, efforts were made to come up with more-stable photocatalysts with higher hydrophilicity and good photoactivity. On the other hand, decomposing colored compounds with nitrogen or sulfur component has also been attempted. In general, it is well known that the removal of nitrogen and sulfur compounds is difficult in liquid photoreactions because of

† To whom all correspondence should be addressed.
(e-mail: mskang@khu.ac.kr, msk1205@chol.com)
catalytic deactivation [9,10]. Therefore, methyl orange, a representative dye compound, was selected in this study because it consists of carbon, nitrogen, and sulfur atoms. This present study, therefore, focused on the synthesis and characterization of selected nano-sized V/TiO₂ particles, and the relationship between photocatalytic activity toward methyl orange and the surface properties of V/TiO₂. In addition, using ion chromatography, this study attempted to identify the final products resulting from methyl orange photodegradation.

**Experimental**

**Catalyst Preparation**

A conventional sol-gel method (Figure 1) was employed for the preparation of TiO₂ and V (1.0, 5.0, 10.0 wt-%)/TiO₂ catalysts. The reagents used for the preparation of the sol-mixture were titanium tetraisopropoxide (TTIP, 99.95%, Junsei Chemical, Japan) and vanadium oxide (99.99% V₂O₅, Junsei Chemical, Japan), which were used as the titanium and vanadium precursors. Ethanol (Wako Pure Chem., Ltd.) was used as a solvent. First, vanadium oxide was completely dissolved in an HNO₃ solution. The solution was then mixed with the TTIP in the alcoholic organic solvent in a 300-mL beaker. The pH value was fixed at 1. TTIP was hydrolyzed by the OH groups during evaporation at 80°C for 6 h. The white precipitated materials were washed with distilled water and then dried at 100°C for 24 h. Finally, crystallization of the TiO₂ and V/TiO₂ with anatase structure occurred after calcination at 500°C for 3 h.

**Characterizations of Synthesized Catalyst**

The synthesized powders, V/TiO₂ powders, were identified using powder X-ray diffraction analysis (XRD, model PW 1830 from Philips) with nickel-filtered CuKa radiation (30 kV, 30 mA) at 2-theta angles from 5 to 70°. The scan speed was 10°/min and the time constant was 1 sec.

The particle sizes and shapes of the V/TiO₂ powders were observed through scanning electron microscopy (SEM or FESEM, model JEOL-JSM35CF). The power was set at 15 kV. The BET surface area of the sample and pore size distributions (PSD) were measured through nitrogen gas adsorption in a continuous flow method using a chromatograph equipped with a TCD detector at liquid nitrogen temperature. A mixture of nitrogen and helium flowed as the carrier gas using a GEMINI2375 model apparatus (Micrometrics). The sample was treated thermally at 350°C for 3 h before nitrogen adsorption.

At this point, XPS peaks could be identified using tabulated binding energy values from XPS handbooks yielding information on the chemical composition and bonding environments. XPS spectra were acquired using ESCA 2000. The spectra, which were generated by AlK X-rays (15 kV, 350W), were collected for 20~90 min, depending on the peak intensities, at an energy of 23.5 eV.

NH₃-Temperature programmed desorption (TPD) measurements were undertaken 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 any impurities on the surface. After pretreatment, the samples were exposed to ammonia for 1 h. Finally, programmed heating at a rate of 10°C/min was effected, followed by heating to 700°C. The amount of desorbed gas was monitored continuously with a TCD cell.

**Methyl Orange Decomposition and Analysis**

The decomposition of methyl orange was performed using three-phase fluidized bed photoreactors designed in the laboratory (Figure 2). In preparation for the methyl orange decomposition, V/TiO₂ powders (0.1, 0.5, and 1.0 g per total reaction solution of 1000 mL) were added into an acrylic cylinder reactor of 2.5 L volume. The concen-
Results and Discussion

Characterization

Figure 3 shows the XRD patterns of V/TiO₂ powders after calcination at 500°C for 3 h. All samples exhibited the mixture of anatase and rutile (about 20%) structures. In general, pure TiO₂ could be maintained in an anatase structure until thermal treatment at 650°C, and this material exhibited higher performance for VOC decomposition when compared with catalysts of other structures, such as rutile, brookite, and amorphous TiO₂. On the other hand, the mixture of 70~80% anatase and 20~30% rutile is known to show higher photoactivity. As shown in Figure 3, all of the samples synthesized by the sol-gel method in this study showed a structural mixture, even at lower thermal treatment (500°C). With an increase in the vanadium amount, the peak intensity decreased. In particular, when 10.0 wt% vanadium was added, we observed peaks assigned to V₂O₅ existing outside the framework. This result indicates that, until 5.0 wt%, vanadium substituted well into the titanium ion site.

Figure 4 shows FESEM images of the particle shape and size distribution of V/TiO₂ catalysts. The catalysts consist of a relatively uniform mixture of spherical and rhombic particles with sizes of about 20~70 nm. With an increase of the vanadium amount, the particle size also increased.

Table 1 summarizes the physical properties of the catalysts. The real composition on the surface attained by EDAX was slightly smaller than the amount of precursor added in the sol preparation. With an increase of the vanadium amount in the sol preparation, the included vanadium amount also increased in the nano-sized particles. The Table also gives the pore volumes and pore diameters. When vanadium was added into the titanium site, new bulk pores with a size of ca. 20.0 Å were generated. The pore volume also increased with an increase of the vanadium amount. The BET surface area also increased. The surface area in pure TiO₂ is known to be 50.0 m²/g. In this study, we observed surface areas...
that were very small in all samples.

To confirm the effect of vanadium addition into the titanium framework, the NH3-TPD test was performed. Figure 5 shows the resulting profiles. Generally, these profiles consist of two peaks: one appearing at a low temperature range (ca. 200 ~ 300°C), and the other appearing at a high temperature range (ca. 450 ~ 550°C). The low- and high-temperature peaks correspond to weak and strong Brønsted acid sites, respectively. In the case of pure TiO2, only one peak assigned to H2O desorption was found at ca. 100°C, while three peaks, around 150, 250, and 550°C, appeared in the 10.0 wt% V/TiO2 sample. This result explains that the new Brønsted acid sites on the TiO2 framework were generated by the addition of vanadium. It was, therefore, confirmed that these Brønsted acid sites could partially affect the removal of the nitrogen component of methyl orange.

Quantitative XPS analysis was performed on the TiO2 and V/TiO2 particles. Figure 6a gives the typical survey and high-resolution spectra. The survey spectra of the TiO2 and V/TiO2 particles contained Ti 2p and O1s peaks from TiO2. The Ti 2p1/2 and Ti 2p3/2 spin-orbital splitting photoelectrons for all samples were located at binding energies of 463.5 and 458.3 eV, respectively [Figure 6(a)]. The binding energy increased with vanadium addition. In general, the increase of binding energy means the increase of the oxidation state of the metal. Therefore, it was confirmed that the titanium oxidation

| **Table 1. The Physical Properties of TiO2 and V/TiO2 Particles** |
|-----------------|--------|--------|--------|
| **Catalysts**   | **TiO2** | **1.0 wt%** | **5.0 wt%** | **10.0 wt%** |
| **Composition** |        |        |        |        |
| on surface     | V      | -      | 0.65   | 4.24   | 7.86   |
| **atomic %**   | Ti     | 26.08  | 30.05  | 35.56  | 24.50  |
|                | O      | 73.92  | 69.30  | 60.20  | 67.64  |
| **Surface Area (m²/g)** | 7.3739 | 10.0870 | 16.5178 | 14.5672 |
| **Pore Volume (cm³/g)** | 0.003678 | 0.005009 | 0.008241 | 0.007261 |

**Figure 5.** NH3-TPD profiles of TiO2 and V/TiO2 after calcination. a) TiO2, b) 1.0 wt% V/TiO2, c) 5.0 wt% V/TiO2, and d) 10.0 wt% V/TiO2.

**Figure 6.** XPS spectra of TiO2 and V/TiO2 after calcination. a) TiO2, b) 1.0 wt% V/TiO2, c) 5.0 wt% V/TiO2, and d) 10.0 wt% V/TiO2.
state (Ti$^{4+}$) in V/TiO$_2$ increased more relative to that of titanium that of in pure TiO$_2$. The Gaussian values were used in the curve resolution of the individual O1s peaks (Figure B; first peak O1: 530.0 eV; second peak O2: 531.0 eV) in the two spectra. The two curve-resolved O1s signals could be assigned to Ti$^{4+}$-O and Ti$^{3+}$-O, respectively. The locations of the binding energies for the second peak agreed well with the reported values for the bulk oxide (O$^{2-}$) and the hydroxyl (OH) species. The first peak area became larger with an increase of the vanadium component into the TiO$_2$ framework. In general, the higher the peak, the greater the hydrophilicity.

**Methyl Orange Decomposition**

Figure 7 gives the methyl orange removal over TiO$_2$ and V/TiO$_2$ in the batch photoreactor system. Methyl orange of 50.0 ppm completely decomposed after 6 h when using both of TiO$_2$ and 5.0 wt% V/TiO$_2$ catalysts (Figure 7a). However, the decomposition rate was slightly faster in V/TiO$_2$ compared with pure TiO$_2$. On the other hand, the methyl orange degradation rate was fastest over 5.0 wt% V/TiO$_2$ than in the other V/TiO$_2$ samples. As mentioned in the XRD result, the 5.0 wt% vanadium was substituted stably into the TiO$_2$ framework. Based on these results, we conclude that the optimum vanadium amount for effective methyl orange removal is 5.0 wt%.

Figure 8 shows the methyl orange removal over 5.0 wt% V/TiO$_2$ under various conditions. Firstly, the optimum O$_2$ bubbling concentration was determined under the following reaction conditions: 5.0 wt% V/TiO$_2$, 50.0 ppm methyl orange, pH 7.0, and 48 W/cm$^2$ UV radiation (Figure 8a). The O$_2$ bubbling concentration was not affected by methyl orange removal in the aqueous photo-

**system. This situation arose because the O$_2$ needed for methyl orange removal is influent in water. Figure 8b shows the effect of the amount of added catalyst in the photosystem under the following reaction conditions: 500 mL/min O$_2$ bubbling, 5.0 wt% V/TiO$_2$, 50.0 ppm methyl orange, pH 7.0, and 48 W/cm$^2$ UV radiation. The complete decomposition time for methyl orange was 4 h, which was common in almost all of the samples, except at a concentration of 1.0 g/L. In particular, when 0.3 g/L was added, the methyl orange decomposed the fastest. On the other hand, with an increase of methyl orange, the decomposition time was longer (Figure 8c) under the following reaction conditions: 500 mL/min O$_2$ bubbling, 5.0 wt% V/TiO$_2$, pH 7.0, and 48 W/cm$^2$ UV radiation. Finally, the UV intensity effect (Figure 8d) was investigated under these reaction condition: 500 mL/min O$_2$ bubbling, 5.0 wt% V/TiO$_2$, and pH 7.0. As we observe in Figure 8c, when the UV intensity increased, the methyl orange decomposed faster. In particular, the decomposition was complete after 3 h at a UV intensity of 72 W/cm$^2$.

The methyl orange decomposition rate may be affected by the environment of the aqueous solution. Therefore, the effects of pH and the addition of H$_2$O$_2$ were also checked and the results are shown in Figure 9 (a and b). The pH change gives various H$^+$ and OH$^-$ ions while H$_2$O$_2$ addition gives various OH radicals that may affect methyl orange photodecomposition. Surprisingly, the change in pH and the addition of H$_2$O$_2$ have strong effects on methyl orange removal. As shown in Figure 9a, when 10.0 mL of H$_2$O$_2$ was added, the decomposition rate was shortened to 30 min (compared with 4 h without H$_2$O$_2$ addition) under the following reaction conditions:
Figure 8. The effects of reaction conditions on methyl orange photodecomposition over 5.0 wt% V/TiO₂. a) Effect of O₂ bubbling concentration, b) effect of catalyst amount, c) effect of methyl orange concentration, and d) effect of UV-radiation intensity. Reaction conditions: methyl orange concentration, 20 ~ 100 ppm; O₂ bubbling, 500 ~ 1500 mL/min; catalyst weight, 5.0 wt% V/TiO₂, 0.1 ~ 1.0 g; UV-light intensity, 254 nm; 24 ~ 72 W/cm²; batch system.

Figure 9. The effects of H₂O₂ addition and pH change on methyl orange photodecomposition over 5.0 wt% V/TiO₂. a) Effect of H₂O₂ addition, b) effect of pH.
500 mL/min O₂ bubbling, 5.0 wt% V/TiO₂, pH 7.0, and 48 W/cm² UV radiation. This result was ascribed to the increase in OH radicals by the addition of H₂O₂. However, even with further H₂O₂ addition, the removal rate was not enhanced. From this result, the optimum H₂O₂ amount was identified to be 10.0 mL/L to remove 50.0 ppm of methyl orange. On the other hand, the methyl orange decomposition was enhanced in both acidic and basic solutions compared with that in neutral solution. The basic solution, of course, was more affected by the methyl orange decomposition than was the acidic solution. This result explains that not only OH⁻ ions but also H⁺ ions affect the methyl orange photo decomposition.

The final products after photoreaction for methyl orange removal over 5.0 wt% V/TiO₂ were identified through an ion chromatogram analysis (Figure 10): Cl⁻ in water, NO₃⁻, NO₂⁻, CO₃²⁻, and SO₄²⁻ were observed. With reaction time, the amount of NO₂⁻ ion increased remarkably, and then it decreased at the reaction termination after 6 h. From this result, it could be suggested that, first, the methyl orange is decomposed to various carbon, nitrogen, and sulfur ions, and then the oxidation step progress to give NO₂⁻, NO₃⁻, CO₃²⁻, and SO₄²⁻ ions. In particular, CO₃²⁻ and SO₄²⁻ ions were easily vaporized as CO₂ or SO₂ gas components. Therefore, the amount in the solution shows a relatively small amount of NO₂⁻. This result confirms that the photo-oxidation ability of V/TiO₂ was very useful for dye compounds like methyl orange.

Conclusions

This study focuses on the removal of methyl orange, a representative dye compound, in a liquid photosystem using a nanometer-sized V/TiO₂ synthesized using the sol-gel method. The following are the main conclusions of this study:

1. The V/TiO₂ particles exhibit a mixed structure of anatase and rutile with a particle size below 70 nm. The surface areas of the V/TiO₂ were large (15.0 m²/g) when compared with that of pure TiO₂ (7.0 m²/g).

2. In the XRD pattern for V/TiO₂, we identified that the vanadium component was well substituted into the titanium ion site until it reached an amount of 5.0 wt%. From the XPS results, we confirmed that V/TiO₂ had a higher hydrophilicity than did pure TiO₂.

3. The NH₃-TPD curve shows that when the vanadium component was added, new Bronsted acid sites were generated.

4. The photodecomposition of methyl orange in liquid reaction was enhanced over V/TiO₂ when compared to that over pure TiO₂, especially in the 5.0 wt% vanadium addition sample.

5. The photoactivity of V/TiO₂ increased remarkably with H₂O₂ addition in the aqueous solution.

6. The ion chromatogram data confirmed that NO₂⁻, NO₃⁻, CO₃²⁻, and SO₄²⁻ ions were the final products of methyl orange photodegradation.

From these results, it could be suggested that complete photo-oxidation was more dominant over V/TiO₂ than it was over pure TiO₂.

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