Studies on Phenol Photoconversion by Ag/TiO₂ Photocatalyst

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Abstract – To examine the photoconversion of phenol by Ag/TiO₂ photocatalyst is the main objective in the batch stirred tank reactor. The photocatalyst preparation was carried out by the impregnation of AgNO₃ solution on TiO₂ powder, and then it was calcined at 400 °C under ambient pressure. The catalysts’ characterization was carried out by XRD (X-ray Diffraction), laser particle sizer, SEM (Scanning electron microscopy) and SEM-EDX methods. Using 15W UVC irradiation with 1mM phenol solution, the phenol concentration was monitored by UV-vis spectroscopy during 120 min. Without H₂O₂, the comparison between 1% Ag/ TiO₂ and unmodified TiO₂ photocatalyst, the former gave the highest photoconversion of 16.09% but the latter of 5.03%. The addition of H₂O₂ for 5% Ag/ TiO₂, it could increase the photoconversion up to 53.68% or 3.3 times higher than that previous one. All photocatalysts had anatase as the main phases from XRD results. While SEM results showed that the presence of silver increased the particles agglomeration size from 12.5 to 106.53 micron. The evidence of Ag-Ti species or Ag clusters on the photocatalyst surface, they increased the active sites for phenol adsorption and suppressed recombination of hydroxyl free radicals. The conclusion found that Ag-modified photocatalysts increased the phenol photoconversion with H₂O₂. And it also increased particle size.

Keyword: phenol, photocatalyst, wastewater treatment, titanium dioxide, impregnation catalyst
1. Introduction

Phenol-containing wastewater is the threatening issue to both human-being and ecology worldwide [1]. According to its very toxicity and highly persistence to degrade in nature, then, TiO$_2$ photocatalyst becomes the encouraging method to solve this problem. From the previous results, Zn/TiO$_2$ photocatalyst degraded 78.5% of methyl orange [2] and 38.4% of indigo carmine [3]. The additional examples, V-modified and Cu-modified on TiO$_2$ photocatalysis were reported. But for Ag/TiO$_2$ photocatalyst for phenol removal was not examined in details. So it will become another way to remove phenol under UV irradiation from this research.

This research aimed to study phenol photoconversion by Ag/TiO$_2$ photocatalyst under UV irradiation. The comparison the effects of Ag amount and H$_2$O$_2$ on the phenol photoconversion were mainly examined. The analysis of UV spectrum method, it showed some intermediates formed simultaneously without using the complicated methods. The XRD result shows the rutile-anatase phase while SEM shows the morphology and crystal size from imaging. But this research did not focus on the chemical kinetic of phenol photoconversion. The outcome of this research is to demonstrate the optimum condition to phenol photoconversion for wastewater system. This will sustain the water quality and quantity in the future.

3. Results and Discussion

Phenol had UV spectrum as shown in Fig 1.a) with the characteristic absorption peak at 270 nm. It corresponded to the previous report by Liu [4]. Then, this $\lambda = 270$ nm could apply to draw the calibration curve between phenol concentration and the absorbance.

![Fig. 1, a) UV spectrum of phenol solution.](image)

![Fig. 1 b) Calibration curve of phenol concentration against absorbance at $\lambda_{max}$ 270 nm in this study.](image)

In Fig 1.b, it was plotted between the phenol concentrations in the range of 0.03 mM-1.75 mM with the absorbance. As the increase of the phenol concentration, the absorbance also increased conversely. The calibration with $R^2 = 0.9977$, it was valid to apply for the calculation of phenol photoconversion. It could find out the change of phenol photoconversion...
by Ag/TiO₂ photocatalyst from the effect of Ag modification and H₂O₂ in this study.

3.1 The effect of Ag modification on TiO₂ photocatalyst to phenol photoconversion

![Fig. 2 TiO₂ and Ag/TiO₂ photocatalysts](image)

The calcined catalysts had different color as the Ag-modified type in Fig.2. It meant that Ag modification changed the oxidation state of TiO₂ on each other. The redox reaction on the surface possibly changed the activity of phenol photoconversion.

Using 1.02 mM of phenol solution as the model system, it was found that the absorbance decreased monotonically with time. The decreasing concentrations of phenol were showed in Fig.3-4. By calculation from Eq. 1, the phenol photoconversion were listed in Table 1 and compared.

![Fig. 3 The effect of 1%-5% Ag/ TiO₂ photocatalyst.](image)

\[
\text{phenol photoconversion} = \frac{C_o - C_t}{C_o} \times 100 \quad (1),
\]

where Co and Ct represented the initial and simultaneous concentrations of phenol, respectively.

In Fig. 3, it showed that unmodified TiO₂ photocatalyst had 5.03% of phenol photoconversion. Ag (1%)/ TiO₂ degraded phenol to 16.09% at 120 min. as the maximum value. While Ag (3%) and Ag (5%) photocatalysts, they exhibited 13.23% and 11.46 % of phenol photoconversion, respectively. The evidence revealed that Ag-modified photocatalysts increased the phenol photoconversion significantly. The Ag(1%)/TiO₂ is suitable similar to Fe-TiO₂ photocatalyst [4]. To increase more activity, the addition of H₂O₂ with UV irradiation would be carried out in increase hydroxyl free radicals.

![Fig. 4 The effect of H₂O₂ on Ag/TiO₂ photocatalyst on phenol photoconversion.](image)

3.2 The effect of H₂O₂ on Ag/TiO₂ photocatalysis

From Fig. 4, the addition of H₂O₂ greatly improved the photoactivity at the constant [H₂O₂] = 6.62 mmole. The controlling systems were no TiO₂ and TiO₂ photocatalyst, they showed 60.46% and 32.07% photoconversion, respectively. Then, H₂O₂ addition, it showed the maximum value to 53.95% of Ag (5%)/TiO₂ photocatalyst as in Table 1. It could increase the effectiveness of Ag-Ti interaction on the surface. Or it increased the phenol adsorption on the surface. The Ag-modified TiO₂ photocatalyst showed higher activity like 0.5% V/TiO₂ photocatalyst for methyl orange photodegradation [5-6]. The effect of H₂O₂ improved the photoactivity as the report of Murugesan et al. [7].

![Table 1. The effect of H₂O₂ addition on phenol photoconversion from various Ag/TiO₂ photocatalysts.](image)
phenol photoconversion illustrating in Scheme 1, it had the final products as carbon dioxide and water.

![Fig. 5](image1.png)

Fig. 5 UV spectrum of various intermediates during the phenol photoconversion.

![Scheme 1](image2.png)

Scheme 1 Pathway of phenol photoconversion

### 3.3 CHARACTERIZATION OF TiO$_2$-BASED PHOTOCATALYST

From the photoconversion results and the effect of H$_2$O$_2$, they had to be explained by its surface properties or physical properties. The results of XRD, SEM, and SEM-EDX and laser particle sizer were carried out in this section.

The XRD results of all photocatalyst in Fig 6, they showed that most peaks corresponding to those of JCPDS file 04-0477 and JCPDS file 73-1765 for both anatase (A) and rutile phases (R), respectively. It meant that the presence of Ag did not change the crystal structure of TiO$_2$ in the same way as Amal’s result for Fe-TiO$_2$ photocatalyst [8]. It meant that some Ag atoms formed clusters like Ag$_6$ on the TiO$_2$ anatase surface instead.

![Fig. 6](image3.png)

Fig. 6 XRD results of Ag/TiO$_2$ photocatalysts.

While the SEM results in Fig. 7, it revealed that the Ag modification increased the crystalline size as those of the laser particle sizer in Table 2. The larger crystal plane made phenol adsorption easily to photoconversion. The SEM-EDX results showed the surface Ag/Ti ratio was equal to 0.057 to 2.3 which showed large difference from the bulk Ag/Ti ratio. And it described that very small amount of Ag existing on the surface.

![Fig. 7](image4.png)

Table 2. The particle size and surface Ag/Ti ratio of Ag/TiO$_2$ photocatalysts.

<table>
<thead>
<tr>
<th>Title</th>
<th>particle size (micron)</th>
<th>**surface Ag/Ti ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>*TiO$_2$</td>
<td>0.05-5.0</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>5.0-20.0</td>
<td></td>
</tr>
<tr>
<td>Ag(1%)/TiO$_2$</td>
<td>68.08</td>
<td>0.057</td>
</tr>
<tr>
<td>Ag(3%)/TiO$_2$</td>
<td>99.43</td>
<td>2.1</td>
</tr>
<tr>
<td>Ag(5%)/TiO$_2$</td>
<td>106.53</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Note *TiO$_2$ had bimodal dispersion of particle size. **Surface Ag/Ti ratio was determined by SEM-EDX method.
The effect of Ag on TiO₂ photocatalyst plotted in Fig.8, the result in Table 1 for photoconversion and particle size in Table 2. Focusing on the Ag modification, the increase of Ag increased phenol photoconversion with H₂O₂ addition + UV irradiation. And it induced the agglomeration to larger particle because of electrostatic charging on the surface. From the previous reports for the transition metal modification on photocatalyst resembled to this research [9-10].

From Fig. 8, it concluded that the Ag modification changed the particle size significantly and the phenol photoconversion considerably increased, too. The addition of Ag had speculated to 2 functions for the phenol photoconversion on Ag-Ti active site mainly and to agglomerate particles in the suspension. Because the active site is the key point for the photocatalysis and it requires detailed investigation [11-12].

4. Conclusions

Among various photocatalysts, it was found that Ag (1%)/TiO₂ photocatalyst without H₂O₂, it gave 16.09% for phenol photoconversion. With the addition of H₂O₂, it increased the phenol photoconversion. In case of Ag (5%)/TiO₂ photocatalyst with H₂O₂ + UV irradiation, it showed 53.95% of phenol photoconversion or about 3.3 times higher than those results without H₂O₂. The Ag-TiO₂ catalyst, H₂O₂ and UV irradiation, they are the important components to phenol photoconversion. Moreover, SEM, SEM-EDX and XRD results, they pointed out that Ag modified TiO₂ surface morphology. Laser particle sizer showed that Ag produced larger particle size up to 106.53 micron compare to unmodified TiO₂ of 12.5 micron. The Ag-TiO₂ photocatalyst showed higher phenol photoconversion and it had the relationship between the activity and particle size. The further study will aim to characterize Ag particles sites by TEM, EPMA and XPS (X-ray photoemission spectroscopy) on the photocatalyst surface.

5. ACKNOWLEDGEMENT

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6. REFERENCES