

Photodegradation of the Pentaerythritol Wastewater Catalyzed by TiO₂

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The photodegradation of pentaerythritol wastewater catalyzed by TiO₂ was studied in this report. The rutile phase TiO₂-HY with a particle size of 22.6 nm showed the highest degradation efficiency of 90.5 % in solar light under the optimal operating conditions, while the pH value was 6 and the amount of catalyst was 0.06 g.

Key Words: TiO₂, Photodegradation, Wastewater, Pentaerythritol.

INTRODUCTION

Many water-soluble synthetic organic compounds generate lots of wastes during production, use and disposal. In addition, many materials in the production are often non-biodegradable or toxic to microorganisms and have very long half-life periods in the environment^{1,2}. For example, pentaerythritol (PE), which is widely used in paint, lubricant, plasticizer and surfactant industries, is difficult to be degraded because of its strong suppression on the biodegradation, while most of the alcohols are biodegradable^{3,4}. A technology combined hydrolysis and acidification with sequencing batch reactors (HA-SBR) had been used by Yang *et al.*^{5,6} to treat pentaerythritol wastewater, while it needed rigorous conditions and a long time to operate and debug. Therefore, it is necessary to develop a more effective method for the treatment of pentaerythritol wastewater.

As is well known, TiO₂ has been extensively applied in photocatalytic purification of wastewaters containing organic compounds due to its advantages, such as high photosensitivity, low cost, chemical stability and non-toxicity⁷. For example, TiO₂ has been widely used to photocatalyze methyl red⁸, methyl orange⁹, methylene blue^{10,11} and acetone¹². Within this context, we report our studies on the TiO₂ catalytic photodegradation of pentaerythritol wastewater. The TiO₂ catalysts were prepared *via* hydrolysis and sol-gel methods and characterized by XRD and XPS. The photoactivities of TiO₂ particles were precisely evaluated by photocatalytic degradation of pentaerythritol wastewater under different lights.

EXPERIMENTAL

All chemicals were of reagent grade and were used without any further purification. The TiO₂ samples were prepared by the following methods: for the hydrolysis

method, requisite amount of deionized water, hydrochloric acid and activated carbon were mixed in a flask and then 0.2 mol of titanium tetrachloride was added dropwise into the flask under vigorous stirring. After heated at 100 °C for 1 h, 0.2 mol base was added into above solution for 2 h of hydrolysis. The obtained catalyst was dried at 100 °C and calcined at 650 °C to get a powder TiO₂. Such samples are denoted as TiO₂-HY. For the sol-gel method, tetrabutyl titanate was dissolved in ethanol as solution A. Acetic acid and deionized water were mixed in ethanol as solution B. The molar ratio of tetrabutyl titanate, acetic acid, deionized water and ethanol was 1:1:2:10. Then, the above two solution A and B were mixed for 2 h, hydrochloric acid was added to adjust pH. The obtained gel was dried at 100 °C and calcined at 650 °C for 1 h and then pulverized to powder. These sol-gel samples are designated as TiO₂-SG. For doped samples, metal nitrates were added after titanium tetrachloride in the hydrolysis method and were added into the solution B while completely dissolved in the deionized water in the sol-gel method. They are named as TiO₂-Fe-SG, TiO₂-Fe-HY, TiO₂-Cr-HY, TiO₂-Zn-HY and TiO₂-Cu-HY, respectively.

X-Ray diffraction (XRD) was carried out on a Y-2000 X-ray diffractometer with CuK_α radiation. X-Ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 1600 spectrometer using a MgK_α X-ray source for excitation. The pentaerythritol wastewater was got from Baoding Guoxiu Chemical Industry Co., Ltd, which contains pentaerythritol, formaldehyde, acetaldehyde, *etc.* The chemical oxygen demand (COD) of initial pentaerythritol wastewater was about 1.0 g/L. The photocatalytic degradation experiments of pentaerythritol wastewater over TiO₂ catalysts were carried out in the home-built reactors. A high-pressure mercury lamp (Philips HPK-125 W) was used as UV-light irradiation source, as compared to solar light. In a typical run, 1 mL pentaerythritol wastewater was first diluted with 99 mL distilled water and then 0.06 g catalyst was added into 50 mL diluted pentaerythritol wastewater. The solutions were irradiated under the light with stirring for 16 h. The chemical oxygen demand was used to investigate the photocatalytic performance of catalysts. The degradation efficiency (DE) of pentaerythritol wastewater was calculated by the following formula:

$$\text{Degradation efficiency} = \frac{C_0 - C_D}{C_0} \times 100 \%$$

where C₀ and C_D are the COD concentration before and after PE wastewater degradation, respectively.

RESULTS AND DISCUSSION

As is well known, the catalytic photodegradation of organic compounds is a complicated process with a variety of reactions¹³. Thus, selection of a suitable catalyst is crucial to a highly efficient photodegradation of pentaerythritol wastewater. Therefore, the TiO₂ catalysts were first examined to photodegrade the pentaerythritol wastewater under solar light for 8 h. A representative sample of the results is listed in Table-1.

TABLE-1
EXPERIMENTAL RESULTS OF DEGRADATION EFFICIENCY OF
CATALYSTS UNDER SOLAR LIGHT

| Entry | Catalysts | Molar ratio | Base/Acid | DE (%) |
|-------|--------------------------------------|-------------|-------------|--------|
| 1 | TiO ₂ -HY | - | Urea | 42.5 |
| 2 | TiO ₂ -HY | - | NaOH | 43.0 |
| 3 | TiO ₂ -HY | - | NaOH + Urea | 62.5 |
| 4 | TiO ₂ -HY | - | Ammonia | 51.6 |
| 5 | TiO ₂ -SG ^a | - | HCl | 53.8 |
| 6 | TiO ₂ -SG ^b | - | HCl | 52.5 |
| 7 | TiO ₂ -SG ^c | - | Acetic acid | 51.3 |
| 8 | TiO ₂ -SG ^d | - | - | 43.5 |
| 9 | TiO ₂ -Fe-SG ^b | 1:0.01 | HCl | 28.1 |
| 10 | TiO ₂ -Fe-HY | 1:0.05 | NaOH | 16.4 |
| 11 | TiO ₂ -Zn-HY | 1:0.05 | NaOH | 19.8 |
| 12 | TiO ₂ -Cu-HY | 1:1 | NaOH | 15.4 |
| 13 | TiO ₂ -Cu-HY | 1:0.05 | Ammonia | 13.9 |
| 14 | TiO ₂ -Cr-HY | 1:0.05 | Ammonia | 18.1 |

^apH: 2-3; ^bpH: 3-4; ^cpH: 2-3; ^dno acid added.

Reaction conditions: 0.06 g catalysts, 50 mL diluted pentaerythritol wastewater, 8 h.

Experiments showed that the TiO₂-HY, prepared by the combined base, was the most effective catalyst with a degradation efficiency of 62.5 % among all the TiO₂ catalysts studied (Table-1, entries 1-8). On the other hand, additives have proven to be an important factor for improving the activity and stability of catalysts¹⁴. Therefore, a series of modified TiO₂ catalysts were prepared and investigated under the same reaction conditions (Table-1, entries 9-14). Unfortunately, all the modified TiO₂ catalysts exhibited lower activities than the unmodified TiO₂ catalysts, although the Fe-doped sol-gel sample gave relatively high degradation efficiency of 28.1 % among them. Thus, the three samples (Table-1, entries 3, 5, 9) were tested further to clarify their difference in photodegradation of the pentaerythritol wastewater.

XRD patterns of the three catalysts are shown in Fig. 1, indicating that both anatase and rutile phase existed in the above catalysts. TiO₂-HY is predominantly composed of rutile crystal phase, whereas the anatase crystal phase is mainly existed in the TiO₂-Fe-SG. There are no peaks related to Fe found in the XRD pattern of TiO₂-Fe-SG. It is well known that the relatively wide width of the peaks indicated small crystallite size, which can be estimated by Scherrer's equation from the XRD peak broadening analysis. It is worth to note that the crystallite sizes of TiO₂-HY, TiO₂-SG and TiO₂-Fe-SG are 22.6, 44.5 and 63.1 nm, respectively. Thus, it is suggested that the doped of Fe led to the growth of the anatase phase and gave a larger crystallite size, while no phase related to Fe can be detected in the body of the catalyst. It is obvious that the small crystallite size of TiO₂-HY is correlated to the high performance of this catalyst. This is because a small crystallite size causes a blue shift in the light absorption spectrum and favours surface recombination of the

photo-excited holes and electrons, while a larger crystallite size exhibits lower surface area and thus a smaller number of catalytic active sites per unit mass of catalyst^{15,16}.

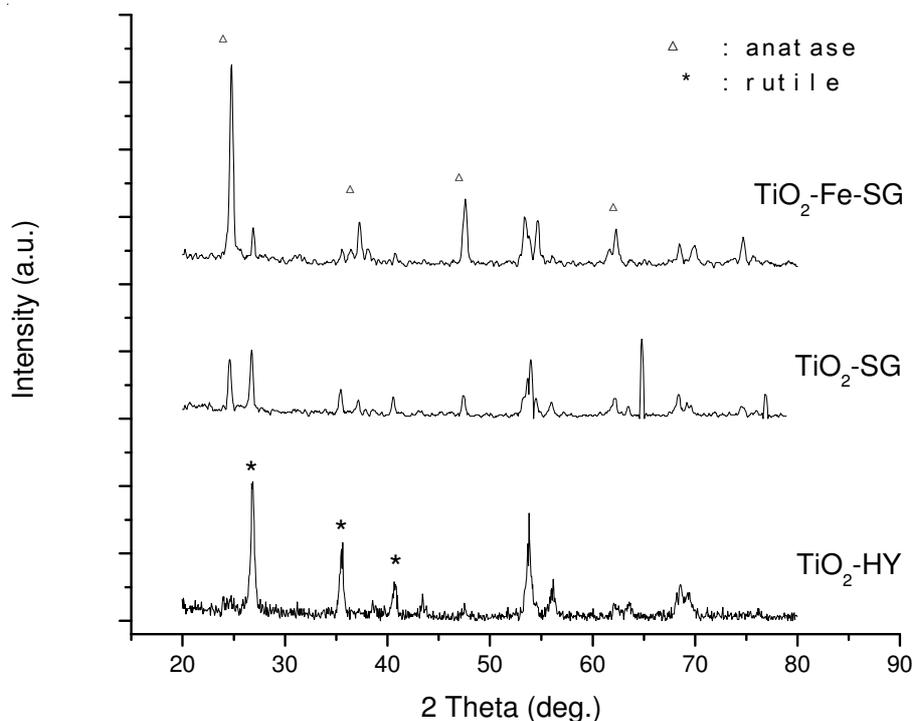


Fig. 1. XRD patterns of the TiO_2 catalysts

In order to investigate the chemical status of elements on the surface of TiO_2 catalysts, the catalysts were characterized by XPS. Fig. 2 gives the high-resolution XPS spectra of the Ti 2p region of the three catalysts. The Ti 2p peaks, observed at 458.0, 458.5 and 458.3 eV, are in good agreement with Ti 2p_{3/2} of the TiO_2 . On the other hand, the peaks of 463.5, 464.2 and 464.1 eV can be ascribed to the Ti 2p_{1/2}. It is clear that the characteristic peaks of TiO_2 -HY display a feature extending to lower binding energy values compared to the other two catalysts, indicating that the probability density distribution of electronic cloud around Ti^{4+} in the TiO_2 -HY is increased. Furthermore, Fe was detected on the surface of the TiO_2 -Fe-SG catalyst with a binding energy of 710.4 eV, thus it is suggested that Fe may be highly dispersed on the catalysts surface.

With consideration of previous reports¹⁷, reaction activities strongly depend on both the structure of the catalysts and the experiment parameters such as pH value, reaction time and light sources. In general, pH value has a crucial influence on the degradation efficiency of some organic compounds in the photocatalytic process. Therefore, the effect of pH value on the degradation efficiency of the pentaerythritol wastewater catalyzed by TiO_2 -HY has been studied in detail (Fig. 3).

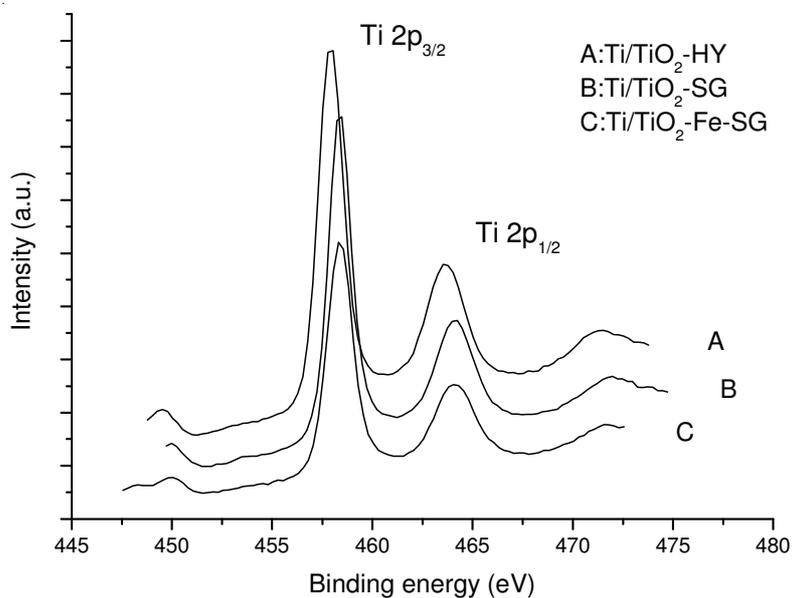


Fig. 2. High-resolution XPS spectra of the Ti 2p region for the catalysts

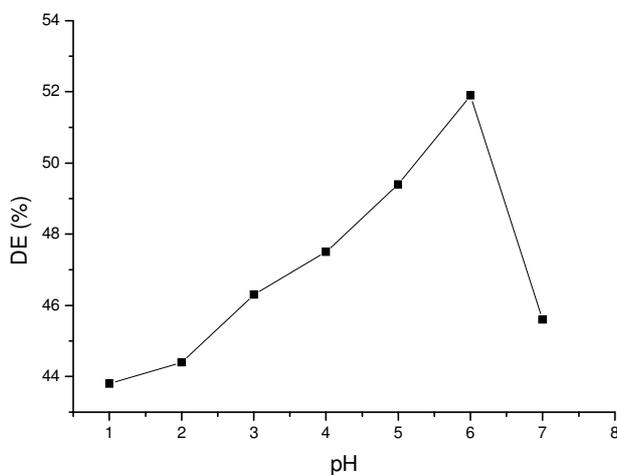


Fig. 3. Effect of pH value on the degradation efficiency; Reaction conditions: 0.06 g catalyst, 50 mL diluted pentaerythritol wastewater, 8 h, solar light

It was found that the degradation efficiency increased from 43.8 to 51.9 % with an increase in pH value from 1 to 6 and then decreased sharply with an increase of pH value up to 7. Therefore, 6 is chosen as the optimum pH value. It is worth pointing out that the weak acidic condition is in favour of the degradation of pentaerythritol wastewater. In weak acidic solution, the photocatalytic degradation of pentaerythritol wastewater was effective probably due to the formation of $\cdot\text{OH}$ according to the following reactions (eqns. 1-4)¹⁸.



It had been proved that photogenerated holes oxidized water or adsorbed $\bullet OH$ at the surface of semiconductor to hydroxyl radicals¹⁹. These highly reactive radicals could then be used to mineralize or at least partially degrade most of organic pollutants.

The effects of the catalysts and the light source on the degradation efficiency are shown in Table-2. This indicates that catalysts exhibit higher degradation efficiency after 16 h irradiation both in solar light and UV-light, compared with the 8 h results under solar light (Table-1, entries 3, 5, 9). Considering that the degradation efficiency of TiO₂-HY are similar for different lights, solar light is chosen as the light source for further practical usage.

TABLE-2
DEGRADATION EFFICIENCY OF CATALYSTS UNDER DIFFERENT LIGHTS

| Entry | Catalysts | Light sources | |
|-------|--------------------------|-----------------|--------------|
| | | Solar light (%) | UV-light (%) |
| 1 | TiO ₂ -HY | 90.5 | 91.4 |
| 2 | TiO ₂ -SG | 89.5 | 89.2 |
| 3 | TiO ₂ -Fe -SG | 50.5 | 75.8 |

Reaction conditions: 0.06 g catalysts, 50 mL diluted pentaerythritol wastewater, 16 h.

The influence of the catalyst amount on the degradation efficiency was also investigated and the results are shown in Fig. 4. This indicates that the degradation efficiency of pentaerythritol wastewater increases from 72.6 to 90.5 % as the dosage of catalyst increases from 0.03 to 0.06 g and then decreases after that. The low degradation efficiency at higher catalyst loading can be due to the deactivation of activated molecules by collision with ground state molecules of titania²⁰. Therefore, 0.06 g is chosen to be the best dosage of catalyst.

In conclusion, a process for the TiO₂ catalytic photodegradation of pentaerythritol wastewater was established in this work. Rutile phase TiO₂ was found to have high degradation efficiency, while anatase phase TiO₂ showed low degradation efficiency for this photodegradation process based on XRD and XPS characterization. The degradation efficiency was 90.5 % in solar light under the optimal operating conditions catalyzed by the TiO₂-HY with a particle size of 22.6 nm, while the pH value was 6 and the amount of catalyst was 0.06 g.

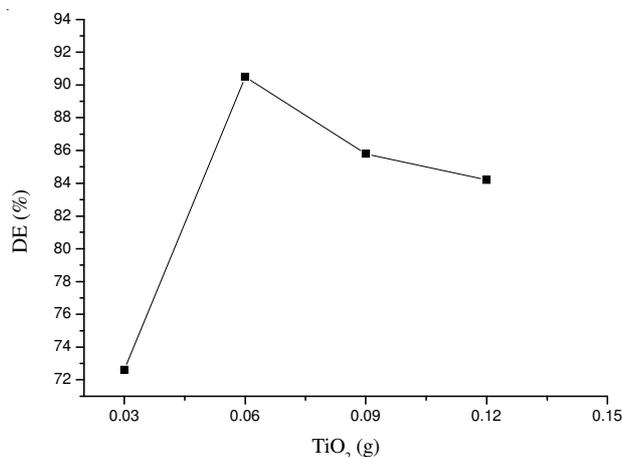


Fig. 4. Effect of amount of TiO₂-HY catalyst on the degradation efficiency; Reaction conditions: 50 mL diluted pentaerythritol wastewater, 16 h, solar light

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