Photoactivity of Fe and Zn-doped TiO₂ in phenol degradation under visible light

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Abstract. This study developed bandgap energy of TiO₂ into the visible region for the photo-activation. The photocatalytic performance of TiO₂ was improved when Fe-doping at 2% and 4% by weight, Zn-doping at 2% and 4% by weight, and doping Fe/Zn 1+1% and 2+2% by weight using flame spray pyrolysis as a synthesis method. Brunauer-Emmett-Teller (BET), ultraviolet-visible spectroscopy (UV-Vis), and x-ray diffraction (XRD) were used to characterize the properties of synthesized and all doped TiO₂ photocatalysts. To prove the effectiveness, all the modified TiO₂ were also compared with the pure synthesized TiO₂ by performing photodegradation of phenol under 1hr visible light. The remaining phenol concentration was estimated using gas chromatography-flame ionization detector (GC-FID). Doped TiO₂ enhances smaller grain size, larger specific surface area and narrower the bandgap energy after comparing with the pure synthesized TiO₂. Zn-doped leads to large surface area that improved the photocatalytic activity of catalyst. However, there was no significant synergistic effect between Fe and Zn doping. The optimum condition for phenol photodegradation was at about 4%Fe doped TiO₂.

1 Introduction

Advanced Oxidation Process (AOP), the application of photocatalysis for detoxification of wastewater, has been discovered as one of clean technology to remove organic and inorganic compounds, pesticides, eradication toxins, and destruction contaminants. This technique uses semiconductors in photocatalysis since they display a great ability with a low cost, and environment friendly. Various semi-conductors, for example, TiO₂, ZnO, ZrO₂, CdS, MoS₂, Fe₂O₃, and WO₃ have been studied and modified to use in photocatalysis degradation of organic and inorganic contaminants. Many researchers have highlighted on TiO₂ as a potential photocatalyst in wastewater treatment due to several factors [1]. TiO₂ is non-toxic, highly chemical and mechanical stability. It has outstanding potential in degradation of contaminants in wastewater, applied in completely oxidization of the organic pollutants to environmentally friendly products, which are H₂O and CO₂. However, titanium dioxide has major drawback in that its bandgap energy is equal to 3.2 eV, which is not only required UV to activate but also can be absorbs only 5% of visible light. Therefore, the improvement of the light absorption wavelength of TiO₂ into visible light region has been widely interested among researchers, in order to use under sunlight. To achieve this goal, the narrowing bandgap energy of TiO₂ by using various metals loading has been established as a possible option for TiO₂ modification. It has been noticed that doping metals such as Fe, Cu, V, Pt, Au, Ag, Mn, Mo, Cr, and Ni could improve the photocatalytic activity [2-13]. Among these metals, Fe and Zn seem to be considerable potential photocatalyst promoters [14-19]. However, until now there was no research studying the effect of co-doping of Fe and Zn as promoter on TiO₂. In this study, flame spray pyrolysis was selected as a method to synthesize doped TiO₂. Flame spray

pyrolysis (FSP) is an effective technique to synthesize high performance nanoparticle catalysts, which produces high purity nanoparticles with controlled particle size by adjusting the process conditions such as the concentration and flow rate of precursors, and fuel flow rate. Therefore, the purposes of this study are to synthesize Fe/Zn-doped TiO₂ catalysts using FSP, to characterize their physical and chemical properties, to find out any synergistic effect between Fe and Zn, and to measure their photocatalytic activity in phenol degradation under visible light.

2 Materials and method

2.1 Preparation of the Fe/Zn doped TiO₂

Titanium (IV) tetra isopropoxide (TTIP) (Sigma-Aldrich, United States 97%), ferrous nitrate (III) nonahydrate (Sigma-Aldrich, United States 99.95%) and zinc chloride (Ajax Finechem, Australia 95%) were dissolved in ethanol (CT Chemical, Thailand 99.9%) to a 0.4 M solution and used as a precursor feed for flame spray pyrolysis. The mixture was injected through the center capillary of the FSP nozzle with oxidizing gas into flame zone by syringe pump at the flow rate of 5 ml/min. The liquid spray was ignited by methane (at the flow rate of 1.5 l/min) and oxygen (at the flow rate of 3 l/min). After combustion, the metal precursor sprayed in FSP was then converted into nanoparticles. The product nanoparticles were collected on a glass fiber filter (Whatman GF/D, 15 cm diameter).

2.2 Characterization of catalysts

Pure synthesized TiO₂ and Fe/Zn doped TiO₂ were analyzed with a number of characterization techniques. XRD using CuK_α radiation with Ni filter in the 2θ range of 20-80 degree with resolution 2°/min was carried out to detect the phase identification and to measure the phase composition. The light absorption property of each

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catalyst sample was measured using UV-Vis under an ultra violet and visible wavelength (200-800 nm). BET surface area analysis (N₂ adsorption) was carried out with firstly pretreated in helium gas flow of 50 ml/min at 180°C for 4 hr. SEM at 5000X magnification, and EDS were performed to study the variation of the morphology and to analyze elemental compositions of doped photocatalysts.

2.3 Photocatalytic activity measurement

100 ppm of phenol aqueous solution was used as a stock solution of organic compound. The photocatalytic degradation was carried out with 150 ml of phenol solution using 0.6 g of catalyst. 30 minutes starting up procedure under dark adsorption (no irradiation source) of TiO₂ was carried out before running through the photocatalytic degradation of phenol. The mixture was stirred at 300 rpm for an hour under visible light irradiation (Phillips, mercury lamp 16 watt) with the distance of 100 mm above the solution surface. Then, the tested solution after using photocatalyst sample was collected at the end of an hour to monitor the remaining concentration of phenol using GC-FID. The product distributions from photocatalytic degradation of phenol were observed using GC-MS. The type of GC column was reverse phase fused silica capillary using helium as a carrier gas, at the column temperature of 220 °C with column flow rate of 0.81 ml/min.

3 Results and discussion

3.1 X-Ray diffraction

XRD spectra of the pure synthesized TiO₂ and doped TiO₂ are shown in the Figure 1. In case of the pure synthesized TiO₂, the strongest peak representing anatase TiO₂ occurred at $2\theta = 25.2^\circ$. On the other hand, XRD patterns exhibited the strongest diffraction peaks of the rutile phase at $2\theta = 27.4^\circ$. However, the results indicated no any characteristic peaks of Fe and Zn which implied that they were well dispersed on the surface or because of low doping amount.

Figure 1 XRD patterns of various doped-TiO₂ comparing with the pure synthesized TiO₂

In addition, Table 1 lists the crystalline size associated with $2\theta = 25.2^\circ$ and $2\theta = 27.4^\circ$ which were the sharpest peak that indicated anatase and rutile phases in all samples, respectively. By using Debye-Scherrer equation [13], the crystallite size of anatase was 41.1 nm, and 39 nm for 2% Fe-TiO₂ and 4% Fe-TiO₂, respectively. Therefore, the crystalline size of the anatase TiO₂ diminished while increasing doping amount of Fe. Similarly, in case of Zn doping, it reduced the grain size of anatase TiO₂. The anatase crystallite size of 2%Zn-TiO₂ (41.1 nm) and 4% Zn-TiO₂ (41nm) were smaller than that of the pure synthesized TiO₂ (45.4 nm). The results of anatase phase show the identical trend with rutile phase in that Fe and/or Zn doping on TiO₂ lead to smaller crystalline size.

The percentages of rutile and anatase phase in synthesized and doped TiO₂ were calculated using the Spurr-Myers equation [20];

$$\%Anatase = \frac{1}{\left(1 + 1.265 \frac{I_r}{I_a}\right)} \times 100 \quad (1)$$

$$\%Rutile = 100 - \%Anatase \quad (2)$$

Where I_r = intensity of the diffraction peak of rutile, and I_a = intensity of the diffraction peak of anatase.

Table 1 The crystalline size of anatase and rutile phases of all synthesized TiO₂ determined from XRD patterns in Figure1.

Catalyst samples	Crystalline size (nm)	
	Anatase	Rutile
Pure TiO ₂	45.4	45.9
2%Fe-TiO ₂	41.1	35.8
4%Fe-TiO ₂	39	37.3
2%Zn-TiO ₂	41.1	35.8
4%Zn-TiO ₂	41	38.9
1+1%Fe/Zn-TiO ₂	41	36.4
2+2%Fe/Zn-TiO ₂	41.1	35.7

After this calculation, 2% Fe-doped TiO₂ has approximately 67.02% anatase and 32.98% rutile which is more anatase-to-rutile than pure synthesized TiO₂ (65.2% anatase and 34.8% rutile). This revealed the fact that adding Fe and Zn into TiO₂ photocatalyst inhibits the phase transformation from anatase to rutile which results in more anatase content, corresponding to the prior study [21].

3.2 BET surface area and pore distributions

In Table 2, BET surface area of Fe and Zn doped TiO₂ are larger than that of the pure synthesized TiO₂ and range between 34.86 m²/g and 64 m²/g. After comparison among doped TiO₂, 4% Fe-doped TiO₂ has the largest surface area which is equal to 64 m²/g.

Table 2 BET surface area measurement of Fe and Zn doped TiO₂ catalysts.

Catalyst samples	BET surface area (m ² /g)
P-25	20.4
pure TiO ₂	50.5
2%Fe-TiO ₂	52.2
4%Fe-TiO ₂	64
2%Zn-TiO ₂	37.7
4%Zn-TiO ₂	48.5
1+1%Fe/Zn-TiO ₂	34.9
2+2%Fe/Zn-TiO ₂	41.7

3.3 UV-Vis spectroscopy

The bandgap energy calculated from Kubelka-Munk relationship [22] using UV-Vis results shown in Table 3, is the sufficient required energy of photons that is used to active electron and hole in the photocatalytic process. In this theory, the graph was plot between transform reflectance spectra $(F(R_{\infty})/hv)^{1/2}$ versus $h\nu$. According to Kubelka-Munk equation;

$$F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} \quad (1)$$

Transformation of absorbent unit into reflectance

$$A = \log I_0(1/R) \quad (2)$$

$$R_{\infty} = 10^{-A} \quad (3)$$

Where A = absorbent unit

h = Plank constant (6.624×10^{-34} Joules sec)

v = velocity of light (3.0×10^8 meter/sec)

R_{∞} = reflectance unit

Table 3 Calculated bandgap energy (E_g) of various doped TiO₂ compared with the pure synthesized TiO₂

Catalyst samples	E_g (eV)
P-25	3.42
Pure-TiO ₂	3.39
2%Fe-TiO ₂	3.2
4%Fe-TiO ₂	2.87
2%Zn-TiO ₂	3.26
4%Zn-TiO ₂	3.16
1+1%Fe/Zn-TiO ₂	3.08
2+2%Fe/Zn-TiO ₂	3.05

The less bandgap energy of the photocatalyst, the greater probability for photocatalytic reaction. Doping Fe and/or Zn on TiO₂ are able to narrow the bandgap energy and shift light absorption region to longer wavelength which lead to higher photocatalytic efficiency for organic removal application under visible light when compared to the pure synthesized TiO₂. Among all doped TiO₂, 4%Fe-doped TiO₂ achieves the maximum amount of light adsorption at the visible region. This was related to the calculation of bandgap energy from Kubelka-Munk relationship in that 4%Fe-doped TiO₂ has lower bandgap energy (2.87 eV) than that of 4%Zn-doped TiO₂ (3.16 eV) and 2+2% Fe/Zn co-doped TiO₂ (3.05 eV).

3.4 Photocatalytic activity

The photocatalytic degradation activities of phenol of the various catalysts under visible light irradiation are shown in Figure 2. According to the percentage remaining of phenol from Gas Chromatography (GC), the percentage of phenol conversion (X) can be determined from the following equation [23];

$$X(\%) = \left(1 - \frac{C_A}{C_{A0}}\right) \times 100 \quad (3)$$

While C_A is equal to remaining concentration of phenol in an aqueous solution measured by GC-FID, and C_{A0} is equal to an initial concentration of phenol in an aqueous solution. With the dark adsorption experiment, the adsorbed concentration of phenol was 8.2% using pure synthesized TiO₂. However, after 1 hr photocatalytic degradation under visible light irradiation, the percentage conversion of phenol was 14.3% for the pure synthesized TiO₂. With Fe and/or Zn doping, the photocatalytic activities increased according to calculated phenol conversion. After consideration all doped TiO₂, both metal types and metal loading show remarkable influence on photocatalytic activity. The results showed that 4%Fe doping on TiO₂ has the most efficiency on phenol degradation with 95.72% of phenol conversion, which is higher than that of 4% Zn doping and 2+2% Fe/Zn co-doping (73.36% and 79.34% phenol conversion, respectively).

Figure 2 The comparison of photo-degradation activity of different photocatalysts measured by %phenol conversion after 1 hr degradation under visible light irradiation

These results are corresponding with UV-Vis spectra that Fe-loading has lower bandgap energy than that of Zn- loading and shows better adsorption performance at longer wavelength which leads to the higher photocatalytic efficiency under visible light irradiation. The influence of Fe-doping on the photocatalytic activity reflects on the narrowing of the bandgap energy and leading to exhibit superior visible-light-driven photocatalytic activity and increasing BET surface area (S_{BET}). The reasons of why Zn improves photocatalytic activity of TiO₂ was that it decreases the grain size, shifts the light absorption to higher wavelength which

was confirmed by UV-Vis and XRD results in the former section. This was corresponding to the prior study that it enhances charge separation of electron-hole pairs which results in increase in oxidation and reduction reaction [19,24]. However, co-doping of Fe and Zn on TiO₂ leads to less conversion than Fe single metal-doping. Though Fe and Zn have prominently potential in improving TiO₂ photocatalytic activity, it was presumably surprising that there was rarely synergistic effect between them. Moreover, it can also be noticed that there are two factors which influence on photocatalytic activity: the bandgap energy and the specific surface area. The most potential photocatalyst should have combination of two characteristics as narrower the bandgap energy and larger the specific surface area. For example, 4% mol Zn loading provides the wider the bandgap energy than co-doped 1%Fe and 1%Zn but the larger the specific surface area, leading to the better photocatalytic performance in phenol photodegradation. Considering at all different doping amounts of Fe or Zn onto TiO₂, using 4%mol Fe loading is accomplish the highest of photocatalytic activity in phenol degradation.

4. Conclusions

This research proved the influences of doping level and doping type on photocatalytic activity, which was corresponding with some previous studies. Based on Fe and Zn modification, they help improving TiO₂ for photocatalytic degradation under visible light. There was apparent evidence that Fe and Zn doping on TiO₂ can narrow the bandgap energy. Hence, doping metal on TiO₂ supports the photocatalytic activity in the range of visible light which can be activated by using solar energy. Among the different doping levels and between Zn or Fe doping metals on TiO₂, Fe-doped TiO₂ shows the best photocatalytic performance, and the optimal amount of Fe doping was 4% mol. Unfortunately, there was no sign of synergistic effect between Fe and Zn because co-doping of Fe and Zn on TiO₂ had lower photo-activity than Fe single-doped TiO₂.

Abbreviations

AOP: Advanced Oxidation Process
FSP: Flame Spray Pyrolysis
XRD: X-Ray Diffraction
UV-Vis: Ultraviolet Visible Spectroscopy
BET: Brunauer-Emmett-Teller
SEM: Scanning Electron Microscopy
EDS: Energy Dispersive X-Ray Spectroscopy
GC-FID: Gas Chromatography-Flame Ionization Detector
GC-MS: Gas Chromatography-Mass Spectroscopy
X: percentage of phenol conversion
C_A: remaining concentration of phenol in aqueous solution
C_{A0}: initial concentration of phenol in aqueous solution
S_{BET}: Surface area from BET analysis (m²/g)
E_g: bandgap energy (eV)
A.U.: Arbitrary Unit
cps: counts per second

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