Research Article

Synthesis of Mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ Binary Oxides Photocatalyst by Sol-Gel Method Using PEG1000 as Template

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The mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides were prepared by sol-gel method using PEG1000 as template. The effects of PEG1000 concentration on the properties and photocatalytic activity of the materials were investigated. The binary oxides were composed of nanocrystallite anatase TiO_2 and amorphous Al_2O_3 . The surfaces of the samples prepared with PEG1000 were rough and had many long grooves on the surfaces. When PEG1000 concentration increased from 0 to 0.048 mol/L, the BET specific surface area of the samples changed from 99 to 140 $\text{m}^2\cdot\text{g}^{-1}$, and the average pore size decreased from 22 to 11 nm. The $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared at PEG1000 concentration of 0.03 mol/L had the maximum photocatalytic activity and high adsorption capacity. Methyl orange photocatalytic degradation and adsorption rates on 600 mg/l of $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides were 36.1% and 18.6% after 30 min, respectively. Total removal of the dye was achieved after 3 h of reaction.

1. Introduction

TiO_2 is regarded as the most powerful photocatalyst in recent years because of its prospective properties such as high photocatalytic activity, inexpensive, and nontoxic to human life [1–5]. However, photocatalytic activity of TiO_2 cannot meet the demand of large-scale industrial application. Porous photocatalytic materials were used to promote photocatalytic activity and to improve the efficiency of photoelectron conversion because large surface area and porous structure are usually good for strong adsorption ability. Many microporous and mesoporous photocatalytic materials have been prepared accordingly [6–11].

In order to improve photocatalytic activity of porous TiO_2 , a popular route is to incorporate other inorganic oxides such as SiO_2 [12], ZrO_2 [13], WO_3 [14], Cu_2O [15], and Ta_2O_5 [16] into the microstructure of porous TiO_2 . Although there are reports about $\text{TiO}_2\text{-Al}_2\text{O}_3$ photocatalytic materials [17–20], these materials are the simple mixtures of TiO_2 and Al_2O_3 particles prepared separately. The mechanical mixture of the two oxides has only limited interaction between external surfaces.

In the present work, mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides were synthesized simultaneously by sol-gel method using a mixed precursor of tetrabutyl titanate and aluminum isopropoxide. Polyethylene glycol (PEG1000) was used as template. The effects of PEG1000 concentration on the physiochemical properties and photocatalytic activity of the materials were investigated. The samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), frontier transform infrared spectrophotometer (FT-IR), X-ray photoelectron spectroscopy (XPS), and N_2 -adsorption and desorption techniques. Adsorption capacity and photocatalytic degradation of methyl orange on the materials under UV-light irradiation were investigated to ascertain the enhanced activity of the mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides.

2. Experimental

2.1. Material Preparation. A given mass of tetrabutyl titanate, aluminum isopropoxide [$n(\text{Ti})/n(\text{Al}) = 12$], polyethylene glycol (PEG1000), and concentrated hydrochloric acid were added into absolute ethanol under magnetic stirring.

Another mixture of deionized water and absolute ethanol was dropped into the former solution at a constant speed. The volume ratio of constituents in the final solution was $V[\text{Ti}(\text{OC}_4\text{H}_9)_4] : V(\text{C}_2\text{H}_5\text{OH}) : V(\text{HCl}) : V(\text{H}_2\text{O}) = 1 : 5 : 0.05 : 0.5$. The solution was kept under stirring until the sol and gel formed. The gel was aged for 12 h at ambient temperature and dried at 80°C for 8 h. After that, the samples were grinded and calcinated at 500°C for 3 h. The prepared materials were grinded again before use.

2.2. Characterization. The crystalline phase of the photocatalyst was measured by X-ray diffraction (XRD) with D/max-rB diffractometer using a $\text{Cu } K\alpha$ radiation in 2θ range of 10° – 80° . The surface morphology was observed by scanning electron microscope (SEM). FT-IR spectrum of the sample was recorded using a FT-IR spectrometer in the wavenumber range of 4000 – 400 cm^{-1} . The elemental composition of the sample was investigated by X-ray photoelectron spectroscopy (XPS, Multilab 2000). The N_2 adsorption and desorption of the sample was measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. Specific surface areas and pore size distribution were calculated from the N_2 desorption isotherms, according to Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method, respectively.

2.3. Adsorption and Photocatalytic Activity. The adsorption and photocatalytic activity of the samples were investigated by measuring the decoloration rate of methyl orange (MO) in a lab-scale photocatalytic reactor. The reactor consisted of a 250 mL beaker and a UV lamp hanging over the beaker. The 20 W UV-light lamp with main irradiation wavelength at 253.7 nm was used as light source to trigger the photocatalytic reaction, and the average light intensity was about $1100\text{ }\mu\text{W}/\text{cm}^2$. The concentration of MO was calculated by Lambert-Beer law using 721E spectrophotometer and TU-1901 UV-Vis double-beam spectrophotometer. The absorbency of MO was measured at 468 nm corresponding to the maximum absorption wavelength. The decoloration rate of methyl orange was calculated by the following equation [21],

$$\begin{aligned}\omega(\text{Adsorption}) &= \frac{(C_0 - C_1)}{C_0} \times 100\%, \\ \omega(\text{Degradation}) &= \frac{(C_1 - C_2)}{C_0} \times 100\%,\end{aligned}\quad (1)$$

where C_0 is the initial dye concentration, C_1 is the concentration after adsorption-desorption equilibrium, and C_2 is the concentration after certain time of irradiation.

The solution of MO and photocatalyst ($V = 50\text{ mL}$, $C_{\text{MO}} = 10\text{ mg/L}$) was mixed in the reactor. The adsorption of MO on photocatalyst was measured in the suspension before photocatalytic reaction. The solution was allowed to reach an adsorption-desorption equilibrium under 30 min of magnetic stirring in the dark. After that, 5 mL of suspension was taken out of the reactor and was filtered through a Millipore filter (pore size $0.45\text{ }\mu\text{m}$) to remove the catalyst.

FIGURE 1: XRD patterns of mesoporous TiO_2 - Al_2O_3 binary oxides prepared using different concentration of PEG1000.

The filtrated solution was measured for its absorbency. After that, the remaining MO and photocatalyst suspension was put under UV light irradiation. After a distinct time, 5 mL of suspension solution was removed and filtrated to measure the change of MO concentration. If not indicated, the irradiation time in the subsequent experiments was set to 30 min.

3. Results and Discussion

Sol-gel method with the advantages of reacting in low temperature and easily controlled homogeneous multicomposition system has become a popular method to prepare microporous and mesoporous photocatalytic materials in a relatively large scale. In order to obtain porous structure, suitable template needs to be used to bond with precursors in sol-gel system. There are some chemical compounds that have been used as templates, such as surfactants and copolymers. Polyethylene glycol $[\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}]$ is one of nonionic templates and dissolves easily in polar solvents. In sol-gel system, three-dimensional structure of precursor is formed preferably by crosslink action among hydrolysates and PEG. Porous materials with arranged structure can be prepared by removing PEG template consequently.

XRD patterns of mesoporous TiO_2 - Al_2O_3 binary oxides prepared using different concentration of PEG1000 are shown in Figure 1. All the diffraction peaks in the patterns indicate the formation of anatase TiO_2 crystallite. The diffraction peaks turned from sharp and high to broad and low when PEG1000 concentration increased from 0 to 0.060 mol/L. The peaks relating to the characteristic peaks of Al_2O_3 were not found. It declares that Al_2O_3 was in its amorphous state in the materials. The anatase TiO_2 crystalline sizes calculated based on Scherrer's formula were 16.1, 12.8, 10.6, 8.8, and 7.6 nm along with increasing PEG1000 concentration. It indicates that the growth of TiO_2 nanocrystals was hindered by PEG1000 addition during sol-gel preparation of the materials.

Template PEG1000 acted as pore forming reagent in sol-gel preparation of $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides. The precursor molecules were attached to PEG1000 molecules in the sol and formed a three-dimensional structure. After the PEG template was burned out during thermal treatment at high temperature, the resulting material was composed of porous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides. The pores inside the oxides prohibited crystallite aggregation during calcination process. When high concentration of PEG1000 was used in the sols, more pores could form in the binary oxides, leading to small crystalline size of anatase TiO_2 in the binary oxides.

The SEM images of the samples are shown in Figure 2. The surface morphology of the $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides prepared without PEG1000 was quite smooth. The main surface was fairly flat with very slight roughness. Some particles in the size less than $1\ \mu\text{m}$ scattered on the surface. These particles might be the residues of small particles produced during grinding. The surfaces of the samples prepared with PEG1000 were comparatively rough, and there were many long grooves on the surfaces. Many small particles formed during grinding also scattered over the surfaces.

Surface morphology is quite essential for photocatalytic activity of the materials. It is believed that rough and structured surface with high surface area is capable of providing more active centers. The rough surface of porous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides clearly indicates the function of PEG template. There were no large pores existing on the surfaces of the binary oxides prepared with PEG. In other words, the surfaces were quite rough with obvious steps and grooves.

The FT-IR spectra of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared using different concentration of PEG1000 are shown in Figure 3. The low-frequency absorption band at $499\ \text{cm}^{-1}$ is attributed to the Ti-O-Ti vibration of the samples [22, 23]. The band at $1628\ \text{cm}^{-1}$ corresponds to the bending vibration of O-H, and the band around $3392\ \text{cm}^{-1}$ is assigned to the surface adsorbed water and hydroxyl groups [24, 25]. The broad band between $500\ \text{cm}^{-1}$ and $800\ \text{cm}^{-1}$ is attributed to Al-O-Al vibration of the samples [26]. No evidence of Ti-O-Al vibration is found, indicating that the samples were composed of TiO_2 and Al_2O_3 .

The purpose of this paper was to prepare $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides. Since tetrabutyl titanate and aluminum isopropoxide were mixed together as precursor in order to make the sol containing both titanium and aluminum, the oxides of titanium and aluminum were thoroughly distributed in the prepared binary oxides. The FT-IR spectra reveal that there was no chemical reaction between titanium dioxide and aluminum oxide.

Figure 4 shows XPS spectra of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared at PEG1000 concentration of $0.030\ \text{mol/L}$ in the sols. The binding energy peaks of $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ are approximately at $458.5\ \text{eV}$ and $464.2\ \text{eV}$, which are attributed to the typical XPS spectra of Ti^{4+} [27]. The symmetrical binding energy peaks of $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ indicate that the titanium was in its full oxidation state and there was no reduced titanium existing in $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides. The $\text{Al}2p$ peak of the $\text{TiO}_2\text{-Al}_2\text{O}_3$ composite occurring at the binding energy of $75.1\ \text{eV}$ is expected for

TABLE 1: BET specific surface area, pore volume, and pore size of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides.

$C_{\text{PEG1000}}/\text{mol}\cdot\text{L}^{-1}$	BET specific surface area/ $\text{m}^2\cdot\text{g}^{-1}$	Pore volume/ $\text{cm}^3\cdot\text{g}^{-1}$	Average pore size/nm
0	99.2	0.45	22.4
0.012	101.5	0.37	14.7
0.030	128.4	0.39	14.6
0.048	140.1	0.38	10.9
0.060	122.9	0.39	12.6

Al^{3+} in aluminum oxide [28, 29]. The O1s spectrum observed at $529.5\ \text{eV}$ is agreed with the electronic binding of O^{2-} in Ti-O and Al-O [30], and the binding energy of $531.8\ \text{eV}$ is assigned to O^{2-} of OH adsorbed on the surface of the sample [31]. Therefore, it can be concluded that TiO_2 and Al_2O_3 existed in the binary oxides. As indicated before in XRD patterns, there was no other species formed in the materials.

BET specific surface area, pore volume, and pore size of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides are listed in Table 1. When PEG1000 concentration increased from 0 to $0.048\ \text{mol/L}$, the BET specific surface area of the samples grew from 99.2 to $140.1\ \text{m}^2\cdot\text{g}^{-1}$, and the average pore size decreased from 22.4 to $10.9\ \text{nm}$. Further increase of PEG1000 concentration led to the reverse trend. The addition of PEG1000 template during sol-gel process resulted in small pore size and large specific surface area in the materials.

The PEG1000 molecules which were captured in the gel were consequently burnt out during calcination process, leaving pores inside the binary oxides. The pore skeleton was composed of titanium and aluminum oxides. The pores shrank at high temperature to some extent depending on stability of the pores structure during thermal treatment. As calculated from XRD results, high concentration of PEG1000 in the sols was responsible for more pores forming in the prepared binary oxides, leading to small crystalline size of anatase TiO_2 . The aggregation of smaller crystallites is responsible for the formation of smaller pores in the materials [32]. The sample prepared using $0.060\ \text{mol/L}$ PEG1000 had smaller surface area than the sample prepared using $0.048\ \text{mol/L}$ PEG1000. The PEG1000 molecules might combine and form large micelles at high concentration. As a result, the prepared sample can therefore have larger pore size and smaller surface area than the optimized one.

Figure 5 shows N_2 desorption isotherms (A) and pore size distribution (B) of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared at C_{PEG1000} of $0.03\ \text{mol/L}$. With the increase of relative pressure P/P_0 in Figure 5(a), the adsorption of N_2 on the materials amplified relevantly. When the relative pressure P/P_0 was about 0.6 to 0.8, the increment of adsorption was significant because of capillary condensation in the pores of the material. Figure 5(b) clarifies the mesoporous structures of the material. The mesopore size inside the material was below $50\ \text{nm}$, and pore diameter mainly distributed in the range of $5\text{--}10\ \text{nm}$. As calculated by BET equation and BJH method, BET specific surface area, pore

FIGURE 2: SEM images of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared using different concentration of PEG1000. (a) 0 mol/L, (b) 0.012 mol/L, (c) 0.030 mol/L, (d) 0.048 mol/L, and (e) 0.060 mol/L.

FIGURE 3: FT-IR spectra of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared using different concentration of PEG1000.

volume, and average pore size of the material prepared at C_{PEG1000} of 0.03 mol/L were $128.4 \text{ m}^2 \cdot \text{g}^{-1}$, $0.39 \text{ cm}^3 \cdot \text{g}^{-1}$, and 14.6 nm , respectively.

The effects of C_{PEG1000} on the adsorption and photocatalytic activity of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides are shown in Figure 6. Methyl orange adsorption and photocatalytic degradation rates on the material prepared without using PEG1000 were 9.9% and 35.0%, respectively. With increasing PEG1000 concentration, methyl orange adsorption on the samples climbed up to the maximum value of 24.2% at C_{PEG1000} of 0.048 mol/L. Further increase of PEG1000 concentration led to dropping off of methyl orange adsorption on the material. It indicates that adsorption ability of the samples was in accordance with the BET specific

surface area. The larger the specific surface area is, the more adsorption capacity the sample has.

Photocatalytic degradation of methyl orange was improved slightly with the increase of PEG1000 concentration up to the maximum rate of 36.1% at C_{PEG1000} of 0.03 mol/L. After that, methyl orange degradation rate declined obviously after using excessive amount of PEG1000 template in the sols. Although the specific surface area and adsorption capacity of the sample prepared at $C_{\text{PEG1000}} = 0.048 \text{ mol/L}$ were the maximum, photocatalytic activity of the sample was only 27.0%. The sample prepared at C_{PEG1000} of 0.03 mol/L had the optimal photocatalytic activity of 36.1% after 30 min of irradiation, and methyl orange adsorption rate on this material was 18.6%. Photocatalytic activity of the samples is related to several main factors. The samples can all adsorb a certain amount of methyl orange molecules, which is essential for the subsequent degradation process. The difference in surface area does not have as much effect on photocatalytic activity as that on adsorption capacity. On the other hand, the growth of TiO_2 nanocrystals was hindered by PEG1000 addition, leading to lowered degradation activity for the samples prepared at high C_{PEG1000} .

Although adsorption and photocatalytic degradation of methyl orange can all be regarded as decoloration of the dye in the water, the mechanisms are quite different. After physical adsorption on the materials, the dye remains on the surface of the materials in its initial form. On the other hand, photogenerated electrons and holes and the subsequently produced oxidizing species such as hydroxyl radicals contact with the adsorbed organic substances and initiate deep oxidation of the dye. The $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared in this paper had high adsorption abilities due to their porous structure and the addition of Al_2O_3 into

FIGURE 4: XPS spectra of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared at $C_{\text{PEG1000}} = 0.030$ mol/L.

TiO_2 could also contribute significantly. However, what is more valuable is the photocatalytic activity of the materials

FIGURE 5: N_2 desorption isotherms (a) and pore size distribution (b) of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides prepared at $C_{\text{PEG1000}} = 0.03$ mol/L.

because the adsorbed dye can be fully oxidized only through photocatalytic degradation.

The effect of the concentration of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides (prepared at $C_{\text{PEG1000}} = 0.03$ mol/L) used for methyl orange decoloration was investigated, as shown in Figure 7. Both of adsorption and photocatalytic degradations of methyl orange on $\text{TiO}_2\text{-Al}_2\text{O}_3$ increased sharply along with increasing photocatalyst concentration. The degradation rate increased much faster at low photocatalyst concentration. The photocatalyst particles might aggregate at high concentration. In spite of the constant increase of adsorption at higher $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides concentration, the enhancement rate of degradation was slowed down when photocatalyst concentration was higher than 600 mg/L. When using 600 mg/L of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides, methyl orange photocatalytic degradation and

FIGURE 6: Effect of C_{PEG1000} on the photocatalytic activity and adsorption of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides.

FIGURE 7: The effect of concentration of mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides (prepared at $C_{\text{PEG1000}} = 0.03 \text{ mol/L}$) on methyl orange decoloration.

adsorption rates were 36.1% and 18.6%, respectively. As indicated before, the degradation rate was achieved in 30 min, and deep oxidation of the dye can be expected with prolonged irradiation time.

Figure 8 shows the UV-Vis spectra of methyl orange solution during photocatalytic degradation on $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides. The binary oxides were prepared at C_{PEG1000} of 0.03 mol/L, and photocatalyst concentration was 600 mg/L for decoloration of the dye. The main absorption peaks near

FIGURE 8: The UV-Vis spectra of MO during photocatalytic degradation on $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides prepared at $C_{\text{PEG1000}} = 0.03 \text{ mol/L}$. Photocatalyst concentration was 600 mg/L.

468 nm and 270 nm are assigned to benzene ring and azo-structure of methyl orange molecule. The absorption peaks shrank sharply under UV-light irradiation. Fully degradation of the dye was achieved after 3 h of reaction. The main absorption peaks of methyl orange disappeared after methyl orange molecules broke into small parts during photocatalytic degradation. The high adsorption and photocatalytic activity of the material are attributed to large surface area, mesoporous structure, and small crystallite size.

4. Conclusions

Mesoporous $\text{TiO}_2\text{-Al}_2\text{O}_3$ binary oxides were synthesized by sol-gel method using PEG1000 as template agent. The effects of PEG1000 concentration on the physicochemical properties of the materials were investigated. The specific surface area and adsorption capacity of the $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides were larger than the sample prepared without PEG1000. The $\text{TiO}_2\text{-Al}_2\text{O}_3$ oxides prepared with C_{PEG1000} of 0.03 mol/L had optimal photocatalytic activity and high adsorption capacity, which are contributed to large surface area, mesoporous structure, and small crystallite size.

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