Research Article

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

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The mesoporous TiO$_2$-Al$_2$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$_2$O$_3$. 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 m$^2$/g, and the average pore size decreased from 22 to 11 nm. The TiO$_2$-Al$_2$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 TiO$_2$-Al$_2$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$_2$O [15], and Ta$_2$O$_5$ [16] into the microstructure of porous TiO$_2$. Although there are reports about TiO$_2$-Al$_2$O$_3$ photocatalytic materials [17–20], these materials are the simple mixtures of TiO$_2$ and Al$_2$O$_3$ particles prepared separately. The mechanical mixture of the two oxides has only limited interaction between external surfaces.

In the present work, mesoporous TiO$_2$-Al$_2$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 TiO$_2$-Al$_2$O$_3$ binary oxides.

2. Experimental

2.1. Material Preparation. A given mass of tetrabutyl titanate, aluminum isopropoxide \([n(Ti)/n(Al) = 12]\), polyethylene glycol (PEG1000), and concentrated hydrochloric acid were added into absolute ethanol under magnetic stirring.
2.2. Characterization. The crystalline phase of the photocatalyst was measured by X-ray diffraction (XRD) with D/max-rB diffractometer using a Cu Kα 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 N₂ 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 N₂ 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 photodegradation reaction. The decoloration rate of MO on photocatalyst was measured in the suspension after adsorption-desorption equilibrium, and concentration after certain time of irradiation.

The solution of MO and photocatalyst (V = 50 mL, C_MO = 10 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 μm) to remove the catalyst. 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 filtered 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 [H–(O–CH2–CH2)n–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.

Figure 1: XRD patterns of mesoporous TiO₂-Al₂O₃ binary oxides prepared using different concentration of PEG1000.
Template PEG1000 acted as pore forming reagent in sol-gel preparation of TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{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 TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{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\textsubscript{2} in the binary oxides.

The low-frequency absorption band in the binary oxides. The aggregation of smaller crystallites was fairly flat with very slight roughness. Some particles in the size less than 1 \( \mu \)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 TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{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 TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} binary oxides prepared using different concentration of PEG1000 are shown in Figure 3. The low-frequency absorption band at 499 cm\textsuperscript{-1} is attributed to the Ti–O–Ti vibration of the samples [22, 23]. The band at 1628 cm\textsuperscript{-1} corresponds to the bending vibration of O–H, and the band around 3392 cm\textsuperscript{-1} is assigned to the surface adsorbed water and hydroxyl groups [24, 25]. The broad band between 500 cm\textsuperscript{-1} and 800 cm\textsuperscript{-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\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}.

The purpose of this paper was to prepare TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} binary oxides. Since tetrabutyl titanate and aluminum isopropanoxide 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 TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} binary oxides prepared at PEG1000 concentration of 0.030 mol/L in the sols. The binding energy peaks of Ti2p\textsubscript{1/2} and Ti2p\textsubscript{3/2} are approximately at 458.5 eV and 464.2 eV, which are attributed to the typical XPS spectra of Ti\textsuperscript{4+} [27]. The symmetrical binding energy peaks of Ti2p\textsubscript{1/2} and Ti2p\textsubscript{3/2} indicate that the titanium was in its full oxidation state and there was no reduced titanium existing in TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} oxides. The Al2p peak of the TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} composite occurring at the binding energy of 75.1 eV is expected for Al\textsuperscript{3+} in aluminum oxide [28, 29]. The O1s spectrum observed at 529.5 eV is agreed with the electronic binding of O\textsuperscript{2−} in Ti–O and Al–O [30], and the binding energy of 531.8 eV is assigned to O\textsuperscript{2−} of OH adsorbed on the surface of the sample [31]. Therefore, it can be concluded that TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} existed in the binary oxides. As indicated before in XRD patterns, there was no other species formed in the materials.

| Table 1: BET specific surface area, pore volume, and pore size of mesoporous TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} binary oxides. |
|----------------------|----------------------|----------------------|----------------------|
| \( C_{\text{PEG1000}} \)/mol·L\textsuperscript{−1} | BET specific surface area/m\textsuperscript{2}·g\textsuperscript{−1} | Pore volume/cm\textsuperscript{3}·g\textsuperscript{−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                 |

PEG1000 template during sol-gel process resulted in small pore size and large specific surface area in the materials. 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\textsubscript{2}. The aggregation of smaller crystallites is responsible for the formation of smaller pores in the materials [32]. The sample prepared using 0.060 mol/L PEG1000 had smaller surface area than the sample prepared using 0.048 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 TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} binary oxides prepared at \( C_{\text{PEG1000}} \) of 0.03 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 nm, and pore diameter mainly distributed in the range of 5–10 nm. As calculated by BET equation and BJH method, BET specific surface area, pore...
Figure 2: SEM images of mesoporous TiO$_2$-Al$_2$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 TiO$_2$-Al$_2$O$_3$ binary oxides prepared using different concentration of PEG1000.

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

The effects of $C_{\text{PEG1000}}$ on the adsorption and photocatalytic activity of mesoporous TiO$_2$-Al$_2$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 $C_{\text{PEG1000}}$ 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 $C_{\text{PEG1000}}$ 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 $C_{\text{PEG1000}} = 0.048$ mol/L were the maximum, photocatalytic activity of the sample was only 27.0%. The sample prepared at $C_{\text{PEG1000}}$ 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 $C_{\text{PEG1000}}$.

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 TiO$_2$-Al$_2$O$_3$ binary oxides prepared in this paper had high adsorption abilities due to their porous structure and the addition of Al$_2$O$_3$ into
TiO$_2$ could also contribute significantly. However, what is more valuable is the photocatalytic activity of the materials because the adsorbed dye can be fully oxidized only through photocatalytic degradation.

The effect of the concentration of mesoporous TiO$_2$-Al$_2$O$_3$ binary oxides (prepared at C$_{PEG1000}$ = 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 TiO$_2$-Al$_2$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 TiO$_2$-Al$_2$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 TiO$_2$-Al$_2$O$_3$ binary oxides, methyl orange photocatalytic degradation and

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**Figure 4:** XPS spectra of mesoporous TiO$_2$-Al$_2$O$_3$ binary oxides prepared at C$_{PEG1000}$ = 0.030 mol/L.

**Figure 5:** N$_2$ desorption isotherms (a) and pore size distribution (b) of mesoporous TiO$_2$-Al$_2$O$_3$ binary oxides prepared at C$_{PEG1000}$ = 0.03 mol/L.
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 TiO$_2$-Al$_2$O$_3$ oxides. The binary oxides were prepared at $C_{\text{PEG1000}}$ of 0.03 mol/L, and photocatalyst concentration was 600 mg/L for decoloration of the dye. The main absorption peaks near 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 TiO$_2$-Al$_2$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 TiO$_2$-Al$_2$O$_3$ oxides were larger than the sample prepared without PEG1000. The TiO$_2$-Al$_2$O$_3$ oxides prepared with $C_{\text{PEG1000}}$ 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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References


