Preparation of ZrO₂-C₆₀ Nanocomposites Using Heat Treatment and Photocatalytic Degradation of Organic Dyes

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The ZrO₂ nanoparticles were synthesized by zirconia solution which is dissolved zirconyl chloride with distilled water and NH₄OH solution under microwave irradiation. The ZrO₂ and C₆₀ nanocomposites were synthesized in an electric furnace at 700 °C for 2 h. The heated ZrO₂-C₆₀ nanocomposites were characterized by XRD, SEM and TEM. In addition, by using UV-visible spectroscopy, the heated ZrO₂-C₆₀ nanocomposites were determinable as a catalyst in the photocatalytic degradation of organic dyes. The photocatalytic effect of the heated ZrO₂-C₆₀ nanocomposites was confirmed as being compared with that of ZrO₂ nanoparticles after synthesis, heated ZrO₂ nanoparticles, unheated ZrO₂-C₆₀ nanocomposites in various organic dyes such as methylene blue, methyl orange and rhodamine B under ultraviolet light at 254 nm.

Key Words: ZrO₂ nanoparticles, Fullerene[C₆₀], Methylene blue, Methyl orange, Rhodamine-B, ZrO₂-C₆₀ nanocomposites, Photocatalytic degradation.

INTRODUCTION

Due to its unique properties, zirconia is one of the important ceramics. Zirconia has the excellent combination of electrical, mechanical, optical and thermal properties and is able to be a good choice for applications such as structural material, thermal barrier coating, solid oxide fuel cell electrolytes and semiconductor material¹⁻⁴. In addition, zirconia has stable photochemical properties so it is directly applicable to photonics^{1,5}. Moreover, because of unique amphoteric characteristics and redox properties, zirconia can be appropriate for a catalyst or a catalyst support^{1,6}.

In the past decade, numerous techniques have been developed for the synthesis of nano-sized ZrO₂, whereas the polyol process has been largely studied and well adopted⁷⁻¹⁰. Zirconia shows several crystalline variations depending on temperature; at the temperatures below 1172 °C, monoclinic is stable; at the temperature range 1172-2347 °C, tetragonal is stable; above 2347 °C, cubic is stable; and rhombic is stable at a high pressure. However, at low temperatures between 550 and 750 °C, tetragonal and cubic zirconia is able to be arranged in the forms of highly dispersed metastable phases. In area of ceramic and catalytic applications of zirconia, the martensitic conversion from the tetragonal to the monoclinic structure has huge importance. Generally, the tetragonal phase of zirconia is favorably formed corresponding to the monoclinic phase

during the crystallization temperature, most of amorphous hydrous zirconia. For that reason, upon increasing calcination temperature, most of amorphous zirconia precursors transform to the tetragonal phase firstly and then convert to the monoclinic phase at higher temperature up to 600 °C. Above approximately 800 °C, conversion is completed¹¹⁻¹⁴.

C₆₀ Fullerene is a promising material. It is a well-established singlet oxygen sensitizer used in the outline of organic synthesis photooxidations¹⁵⁻¹⁹ and absorbs strongly in the ultraviolet and moderately in the visible region of the spectrum^{15,20-23}. As C₆₀ is irradiated with UV-visible radiation, it is excited from the ground state to a short-lived singlet excited state (*ca.* 1.2 ns)^{15,24} which go through rapid intersystem crossing at a rate of $5.0 \times 10^8 \text{ s}^{-1}$ to a lower lying triplet state (³C₆₀*) with a long left time (> 40 μs)^{15,25,26}. More significantly, photoexcited fullerenes are also excellent electron acceptors capable of accepting six electrons^{15,27,28}.

Nanosized metal particles, semiconductors and oxides have attracted a great deal of attention in materials science because of their specific physical and chemical properties based on quantum size effects²⁹⁻³². Transition metal oxides, such as copper, iron, nickel, cobalt and zinc, ranging from micrometer to nanometer particle sizes have been widely studied for applications in photonics, piezoelectrics, magnetic storage media, solar energy transformation, electronics, semiconductors, varistors, electrical and optical switching devices, batteries,

sensors, catalysis, drug delivery systems and separation techniques^{29,33-40}.

Photocatalytic materials take part in a very essential role for selective organic transformations in a cost-effectively and environmentally friendly. Many of these catalytic systems are operated in aromatic or halogenated hydrocarbon solvents, which are environmentally detrimental. Moreover, most of them suffer from several restrictions; being usually only effective with reactive alcohols or involving high pressures and/or temperature and high catalyst loading⁴¹⁻⁴⁴.

In particular, heterogeneous photocatalysis is an efficient technique to remove organic contaminants in water⁴⁵⁻⁴⁸.

EXPERIMENTAL

C₆₀ was purchased from Tokyo Chemical Industry Co., Ltd. Tetrahydrofuran, NH₄OH and ethanol were obtained from Samchun Chemicals. The zirconyl chloride octahydrate and organic dyes (methylene blue, methyl orange and rhodamine-B) were supplied by Sigma-Aldrich.

An electric furnace (Ajeon Heating Industry Co., Ltd.) was used to heat the sample. A UV lamp (8 W, 365 nm, 77202 Marne La Vallee-cedex 1 France) was used as the ultraviolet light irradiation source.

The surfaces of the unheated ZrO₂ particles, heated ZrO₂ particles, unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites were observed by SEM (Hitachi S4700) at an accelerating voltage of 0.5-15 kV. The morphology and crystallite size of the samples were examined by TEM (JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV. The structures of the nanomaterials were examined by XRD (Rigaku, Rigaku DMAX PSPC MDG 2000). UV-visible spectra of the samples were performed using a UV-visible spectrophotometer (Shimadzu UV -1601PC).

Microwave irradiation was carried out in multimode with continuous heating at full power in a domestic oven (2450 MHz, 700W).

Synthesis

Synthesis of ZrO₂ nanoparticles: 0.1 M zirconyl chloride was dissolved in distilled water, then adding NH₄OH until the pH was reached from 7 to 11. During on stirring, it was changed solution to gel. The gel state sample was washed by ethanol for 5 times with centrifuge. After drying at the room temperature, the sample was heated under the microwave condition for 3-5 min.

Synthesis of ZrO₂-C₆₀ nanocomposites: In a typical experiment, the prepared ZrO₂ and prepared C₆₀ nanoparticles were mixed as the molar ratio of 5:1. The mixture was dissolved in 10 mL of THF with stirring to produce the ZrO₂-C₆₀ nanocomposites. The mixture was then dried at room temperature. After drying the nanocomposites, they were heated in an electric furnace at 700 °C for 2 h.

Degradation of organic dyes with nanocomposites: To examine the photocatalytic activity of unheated ZrO₂ nanoparticles, heated ZrO₂ nanoparticles, unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites were examined using some organic dyes, methylene blue (MB), methyl orange (MO) and rhodamine-B (RhB). 10 mg of each nanomaterial was dispersed in 10 mL of water containing 0.01

mM of each organic dye solution. All the mixture solutions were irradiated with ultra-violet light at 254 nm for 20 min. The organic dyes degraded by each nanomaterial under ultra-violet light were characterized by UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Fig. 1 showed SEM images of unheated ZrO₂ nanoparticles, heated ZrO₂ nanoparticles, unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites. Fig. 1(a-b) showed SEM images of unheated ZrO₂ nanoparticles and heated ZrO₂ nanoparticles, respectively. Compared unheated ZrO₂ nanoparticles with heated ZrO₂ nanoparticles, the shape of heated ZrO₂ nanoparticles was more agglomerated figure than the shape of unheated ZrO₂ nanoparticles (Fig. 1(a-b)). Fig. 1(c-d) showed SEM images of unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites, orderly. ZrO₂ nanoparticles of both unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites were located above C₆₀ nanoparticles. After heat treatment, C₆₀ nanoparticles were broken into small parts in heated ZrO₂-C₆₀ nanocomposites and also the shape of heated ZrO₂-C₆₀ nanocomposites had a porous surface.

Fig. 1. SEM images of (a) unheated ZrO₂ nanoparticles, (b) heated ZrO₂ nanoparticles, (c) unheated ZrO₂-C₆₀ nanocomposites, and (d) heated ZrO₂-C₆₀ nanocomposites

Fig. 2 showed TEM images of the unheated ZrO₂ nanoparticles, heated ZrO₂ nanoparticles, unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites. Above all, compared unheated ZrO₂ nanoparticles [Fig. 2(a)] with heated ZrO₂ nanoparticles [Fig. 2(b)], heated ZrO₂ nanoparticles showed more crystallinity than unheated ZrO₂ nanoparticles because heated ZrO₂ nanoparticles were undergone by heat treatment. In addition, heated ZrO₂ nanoparticles had porous surfaces. After that, contrasted unheated ZrO₂-C₆₀ nanocomposites [Fig. 2(c)] to heated ZrO₂-C₆₀ nanocomposites [Fig. 2(d)], because of the heat treatment, C₆₀ in heated ZrO₂-C₆₀ nanocomposites was broken into smaller particles. As a consequence, heated ZrO₂-C₆₀ nanocomposites had higher surface area than unheated ZrO₂-C₆₀ nanocomposites. As a result, heated nanomaterials which heated ZrO₂ nanoparticles and

Fig. 2. TEM images of (a) unheated ZrO_2 nanoparticles, (b) heated ZrO_2 nanoparticles, (c) unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites, and (d) heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites

$\text{ZrO}_2\text{-C}_{60}$ nanocomposites, showed more photocatalytic effect than unheated nanomaterials in the degradation of organic dyes *i.e.*, methylene blue, methyl orange and rhodamine-B.

Fig. 3 showed XRD patterns of the unheated ZrO_2 nanoparticles, heated ZrO_2 nanoparticles, unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites and heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites. Unheated ZrO_2 nanoparticles showed no particular peaks because of their amorphous states [Fig. 3(a)]. After heat treatment, heated ZrO_2 nanoparticles showed their significant peaks. The locations of heated ZrO_2 nanoparticles peaks were at approximately 28.32, 34.43, 50.21 and 60.08 as a 2θ shown in Fig. 3(b). The locations of the peaks were similar in the unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites and heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites. On the other hand, the intensity of some peaks were changed; when we observed at the peak of C_{60} , the unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites have higher peaks than the heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites due to crush C_{60} nanoparticles after the heat treatment at 700°C for 2 h. The XRD patterns due to the C_{60} species in the unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites showed peaks at approximately 10.80, 17.73, 20.78, 21.71, 27.50, 28.15, 32.77 and 33.56 as a 2θ shown in Fig. 3(c). In addition, the peak of C_{60} in the heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites showed peaks at approximately 10.83, 17.77, 20.82, 21.69, 27.45, 28.15, 32.88 and 35.06 as a 2θ shown in Fig. 3(d).

Fig. 4 showed UV-visible spectra of the degraded organic dyes (MB, MO and RhB) with unheated ZrO_2 nanoparticles, heated ZrO_2 nanoparticles, unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites and heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites under ultra-violet irradiation at 254 nm for 20 min. Figs. 4.1-4.4. showed the UV-visible spectra of the degradation of (a) methylene blue, (b) methyl orange and (c) rhodamine-B on the unheated ZrO_2 nanoparticles, heated ZrO_2 nanoparticles, unheated $\text{ZrO}_2\text{-C}_{60}$

(a)

(b)

(c)

(d)

Fig. 3. XRD images of (a) unheated ZrO_2 nanoparticles, (b) heated ZrO_2 nanoparticles, (c) unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites, and (d) heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites

(a)

(b)

Fig. 4.2. UV-visible spectra of the degradation in (a) methylene blue, (b) methyl orange, and (c) rhodamine-B with heated ZrO_2 nanoparticles

(b)

(a)

(c)

Fig. 4.1. UV-visible spectra of the degradation in (a) methylene blue, (b) methyl orange, and (c) rhodamine-B with unheated ZrO_2 nanoparticles

(b)

(a)

(b)

(c)

Fig. 4.3. UV-visible spectra of the degradation in (a) methylene blue, (b) methyl orange, and (c) rhodamine-B with unheated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites

nanocomposites and heated $\text{ZrO}_2\text{-C}_{60}$ nanocomposites, respectively. Fig. 4.1(a) and 4.2(a) showed unheated ZrO_2 and heated ZrO_2 nanoparticles had similar efficiencies to degrade in methylene blue. Compared unheated ZrO_2 with heated ZrO_2 nanoparticles, the unheated ZrO_2 nanoparticles showed in Fig. 4.1(b) had rapidly dropped its peak line after 20 min because

Fig. 4.4. UV-visible spectra of the degradation in (a) methylene blue, (b) methyl orange and (c) rhodamine-B with heated ZrO₂-C₆₀ nanocomposites

the unheated ZrO₂ nanoparticles absorbed the methyl orange but the heated ZrO₂ nanoparticles did not absorb in Fig. 4.2(b). In addition, showed in Fig. 4.1(c) and Fig. 4.2(c), heated ZrO₂ nanoparticles had more effective than unheated ZrO₂ nanoparticles in rhodamine-B. Compared unheated ZrO₂-C₆₀ nanocomposites with heated ZrO₂-C₆₀ nanocomposites showed in Fig. 4.3. and 4.4, heated ZrO₂-C₆₀ nanocomposites were more efficient than unheated ZrO₂-C₆₀ nanocomposites in organic dyes which we have considered. Overall, heated ZrO₂-C₆₀ nanocomposites showed the most degraded efficiencies for organic dyes such as methylene blue, methyl orange and rhodamine-B.

Conclusion

Unheated ZrO₂ nanoparticles, heated ZrO₂ nanoparticles, unheated ZrO₂-C₆₀ nanocomposites and heated ZrO₂-C₆₀ nanocomposites were synthesized as a catalyst for the degradation of methylene blue, methyl orange and rhodamine-B under ultra-violet irradiation at 254 nm for 20 min. Unheated

ZrO₂ nanoparticles and heated ZrO₂ nanoparticles showed similar agglomerated morphologies but the heated ZrO₂ nanoparticles had smaller particle size than unheated ZrO₂ nanoparticles. C₆₀ nanoparticles were broken into small parts in heated ZrO₂-C₆₀ nanocomposites and also the shape of heated ZrO₂-C₆₀ nanocomposites had a porous surface after heating at 700 °C for 2 h. Since the heated nanomaterials showed increased surface areas because their nanoparticles had decomposed at high temperatures, the heated ZrO₂ nanoparticles and heated ZrO₂-C₆₀ nanocomposites were more effective in degrading the organic dyes. Overall, heated ZrO₂-C₆₀ nanocomposites had better photocatalytic effects in the degradation of organic dyes such as methylene blue, methyl orange and rhodamine B under ultra-violet irradiation at 254 nm than the other nanomaterials.

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