JOURNALOF

Ceramic Processing Research

Synthesis and characterization of TiO₂, CeO₂, and TiO₂-CeO₂ particles for application in the treatment of phenol

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In this work, titanium oxide particles were synthesized (TiO_2) by the sol-gel technique, yielding spherical particles with an average diameter of 55 nm and surface area of 50.6 m²/g. The material's major crystallographic phase is rutile. The CeO₂ particles synthesized in this work present a spherical morphology of 40 nm with a specific surface area of 43.6 m²/g and represent the cerianite crystalline phase. In addition, by means of this synthesis technique, particles composed of TiO₂ and ceria CeO₂ that have an average diameter were not affected by the presence of CeO₂. However, the specific area (81 m²/g) significantly increased. Strangely, in the composite material, the predominant phase occurred due to the presence of CeO₂, which prevents the growth of rutile crystals. The phenol degradation tests showed that at an initial concentration of 30 mg/L, TiO₂ degrades in approximately 20% of phenol after 120 minutes, but at an initial concentration of 50 mg/L, degrades at approximately 15% after 180 minutes. The other synthesized materials reach degradation of only around 3% in both phenol concentrations.

Key words: Photodegradation, Phenol, TiO₂, CeO₂, Photocatalysis.

Introduction

The manufacturing of products for human consumption has led to the generation of organic contaminants in their aqueous phase, which have generated environmental and health problems, so at present, studies have been conducted to optimize the traditional separation processes used in environmental remediation. However, because some contaminants are resistant to conventional treatment methods, effective treatments have been developed in recent years [1], as in the case of advanced oxidation processes (AOP), which have the advantage of completely destroying the pollutant in most cases [2,3], Heterogeneous photocatalysis occurs within these processes. The mechanism of heterogeneous photocatalysis consists of irradiating a semiconductor-like material with energy photons, generating an electron-hollow pair $(e^{-}h^{+})$. Photogenerated electron-hole pairs can migrate toward the surface of the semiconductor material and react with pre-adsorbed species to form the hydroxyl radical (•OH) and the superoxide radical $(O_2 \bullet^-)$ [4], which interact with the organic pollutant until its complete disintegration.

Among the semiconductor materials used in the photocatalysis process is TiO_2 due to its chemical,

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physical, optical, and electrical properties [5]. Cerium oxide (CeO₂) has attracted attention in recent years as a doping agent for TiO_2 particles because it is a non-toxic, chemically stable material [6, 7], promoting the storage and release of oxygen to form surface vacancies and improve the system's redox properties.

On the other hand, with the development of nanotechnology, one of the studied synthesis methods to obtain TiO_2 particles of nanometric size and improve the material's photocatalytic properties [8], is synthesis by sol-gel, which offers the advantage of creating a low-cost homogeneous material [9]. Furthermore, by this synthesis method, it is possible to obtain mixtures of oxides; therefore, the purpose of this work is to obtain TiO_2 -CeO₂ particles by sol-gel synthesis and test its photocatalytic capacity using an organic contaminant of phenol. The US Environmental Protection Agency considers it a major pollutant due to its carcinogenic nature.

Experimental

Synthesis of materials

For the synthesis of the TiO₂ particles, titanium propoxide ($C_{12}H_{28}O_4Ti$) was dissolved in ethanol and stirred at 80 °C for 1 hr after being shaken vigorously. Then, 10mL of deionized water were added dropwise and stirred it for 1 hr, after which the solution was centrifuged and allowed to dry at 60 °C for calcination

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at 550 °C for 4 hrs.

To obtain the particles of CeO₂, ammonium nitrate serum $((NH_4)_2Ce(NO_3)_6)$ was dissolved in deionized water and added dropwise to a solution of ammonium hydroxide (NH₄OH). This solution was stirred for 1 hr at 80 °C, after which the solid was recovered by centrifugation. The material obtained was allowed to dry and calcined at 550 °C.

To obtain the particles of titania-ceria, $C_{12}H_{28}O_4Ti$ was dissolved in ethanol and stirred at a temperature of 35 °C for 15 minutes. Then, 10mL of the precursor solution of CeO₂ particles dropwise were added (as previously described) and stirred for 1 hr at 80 °C. After, the solution was centrifuged and allowed to dry at 60 °C, it was calcined for 4 hrs at 550 °C.

Characterization

The surface morphology analyses of the materials were performed by scanning electron microscopy using a JEOL, 6610 LV scanning electron microscopy (SEM) microscope. The crystal phases of composites were analyzed by XRD patterns with a D8 DISCOVER.

The functional groups of the materials were analyzed by FT-IR spectroscopy using a VARIAN 640-IR spectroscope; the spectra were recorded between 4000 cm^{-1} and 500 cm⁻¹ with 40 scans.

The BET-specific surface areas were measured by nitrogen adsorption-desorption using a Belsorp Max III apparatus. Prior to these physisorption measurements, the samples were degassed at 200 °C for 2 hrs.

Photocatalytic Test

Photocatalytic degradation of phenol in the presence of the material was conducted in a cylindrical glass reactor containing a suspension of 100mL of aqueous phenol (50 mgL⁻¹ and 30 mgL⁻¹) and 100mg of the materials. The suspension was stirred for 30 minutes in dark conditions at room temperature to reach equilibrium. The suspension was irradiated for 240 minutes with a UV black light lamp, and 5-mL aliquots were collected at regular intervals; the samples were filtered using a 0.45-µm membrane filter to remove any suspended solids. The experiments were performed at concentrations of 30 mgL and 50 mg/L of phenol, and the remaining phenol was determined using the 4-aminoantipyrine spectrophotometric method [10], in a LAMBDA 35 and a Perkin Elmer UV-Vis spectrophotometer.

Results and Discussion

Fig. 1(a) shows the SEM image of the TiO_2 particles obtained at 40,000 X, in which agglomerated spherical particles with an average size of 55 nm were observed (Fig. 1(d)). These particles were mainly composed of 78% oxygen and 22% titanium according to the EDS analysis.

The morphology of the CeO₂ particles is presented in Fig. 1(b), which shows agglomerates of spherical particles with an average diameter of 40 nm (Fig. 1(c) composed of 24% Ce and 73% O. Fig. 1(c) shows particles composed of 79% O, 20% Ti, and 1% Ce, corresponding to the mixture of oxides (TiO₂-CeO₂). These particles have the same morphology when materials were obtained separately, and have an average size of 55 nm (Fig. 1(f)).

The percentage of the anatase-rutile phase in TiO₂ varied according to the calcination temperature. The higher the temperature, the higher the percentage of the rutile and brookite phase [11, 12]. Fig. 2(a), which corresponds to the diffractogram of TiO₂ particles, shows that the material is highly crystalline, presenting the anatase and rutile phases according to the cards JCP 01-089-4921 and JCP 00-021-1276, respectively. Using the Spurr-Myers equation, [13] were determined the percentage of anatase present in the material's structure, deteremining that its crystalline structure contains a higher percentage of rutile (75%), and the remainder corresponds to the anatase phase. Fig. 2(b) shows the diffractogram of CeO₂ particles, which shows the cerianite crystalline phase according to the card PDF 43-1002. It also shows that it is not a totally crystalline material because it has amorphous phases.

The diffractogram of TiO_2 -CeO₂ particles is shown in Fig. 2(c), which shows a greater proportion in the anatase phase with 85% and a proportion of 14% in the rutile phase. The stability of this material's anatase phase can be attributed to the formation of small



Fig. 1. SEM images of (a) TiO_2 , (b) CeO_2 , and (c) TiO_2 -CeO₂ obtained at 40,000X. Particle size distribution: (d) TiO_2 , (e) CeO_2 , and (f) TiO_2 -CeO₂.



Fig. 2. Diffractograms: a) TiO₂, b) CeO₂, and c) TiO₂-CeO₂.

crystals or the fact that the presence of cerium prevents the transition from the anatase to the rutile phase and the formation of Ti-Ce, Ti-O-Ce bonds [14].

Fig. 3 shows the FTIR spectra of the obtained materials, where the band associated with hydroxyl groups (OH) is located at 3283 cm^{-1} , 3220 cm^{-1} , and 3252 cm^{-1} for the materials TiO₂ (Fig. 3(a)), CeO₂ (Fig. 3(b)), and TiO₂-CeO₂ (Fig. 3(c)), respectively, due to the presence of water. The bands located at 2341 cm^{-1} ,

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2331 cm⁻¹, and 2322 cm⁻¹ formed due to the O=C=O bonds, which suggests the presence of CO₂ occluded in the material's pores due to heat treatment. The bands located at 1973 cm⁻¹, 1972 cm⁻¹, and 1967 cm⁻¹ formed due to the presence of the C=C bond. The bands located at 1637 cm⁻¹, 1640 cm⁻¹, and 1634 cm⁻¹ are related COO⁻ due to the presence of the metal cations of Ti and Ce [15]. The two bands located at 1333 cm⁻¹ and 1062 cm⁻¹ are attributed to the O-Ce-O bonds and the presence of nitrates (NO₃⁻) due to the precursor agent used and can be observed in the CeO₂ spectrum.

An approach in the region between 600cm^{-1} and 520 cm^{-1} allowed us to observe the bonds between the oxygen and the metal (Ti or Ce). In the FTIR spectrum of the TiO₂ particles (Fig. 3(d)), the O-Ti-O bonds and the Ti-O bonds were located at 585 cm⁻¹ and 528 cm⁻¹, respectively, and a band was located at 576 cm⁻¹ due to the presence of TiO₆ [16]. Among the CeO₂ particles (Fig. 3(e)), bands were located at 548cm⁻¹ and 524 cm⁻¹, which are related to the Ce-O bond and observed for the TiO₂-CeO₂ particles (Fig. 3(f)). However, the O-Ti-O bonds undergo drift at 571 cm⁻¹.

Fig. 4 shows the N₂ sorption-desorption isotherms of the materials synthesized during the development of this work, which shows that the TiO₂ particles (Fig. 4(a)) have a tendency of a type II isotherm and do not practically present hysteresis, a quality that is usually associated with non-porous adsorbents [17], This figure also shows that the CeO_2 (Fig. 4(b)) and TiO_2 -CeO₂ (Fig. 4(c)) particles present a type IV isotherm according to the IUPAC classification, which refers to mesoporous materials (i.e., materials having an average pore size of 2 nm-50 nm). The types of hysteresis loops that these materials present are II (H2) and I (H1), respectively. The first is characteristic of inorganic oxides [18], but the qualities of materials exhibiting the H1 are characteristic of materials with agglomerates of spherical particles of approximately uniform sizes and distributions.

Table 1 shows the specific surface areas of the synthesized particles obtained by the BET method. It also shows that when the TiO_2 and CeO_2 particles are in the same system (TiO_2 -CeO₂), their specific surface areas increase due to the crystal size, which is reduced in the anatase phase by stabilizing and improving the material's porous network [19].

However, it can be observed that the TiO_2 -CeO₂ particle's volume and pore size decrease with respect to the TiO_2 particles, which could be attributed to the smaller particles of CeO₂ deposited in the pores of TiO_2 or the pores of the latter material, which are blocked by CeO₂ particles.

Table 2 shows the material's phenol sorption capacity, where it is observed that the TiO_2 particles present a 10-mg/L sorption capacity of phenol, whose initial concentration is 30 mg/L, and CeO₂ and TiO₂-



Fig. 3. FTIR spectra: a) TiO₂, b) CeO₂, and c) TiO₂-CeO₂.

Table 1. Specific areas of TiO₂, CeO₂, and TiO₂-CeO₂.

Material	Specific Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
TiO ₂	50.6	0.358	28.3
CeO ₂	43.6	0.003	2.8
TiO ₂ -CeO ₂	80.9	0.219	10.8

CeO₂ particles have a sorption capacity of about 1 mg/ L. However, when these materials are in contact with the phenol solution at an initial concentration of 50 mg/ L, the TiO₂ particles reduce their sorption capacity due to the material's rapid saturation, and CeO₂ and TiO₂-CeO₂ maintain their sorption capacity of approximately 3 mg/L.

Fig. 5(a) shows the phenol photodegradation process, in which the TiO_2 particles present a phenol photodegradation yield at the 120 minutes of 20% (6 mg/

Table 2. Sorption capacities of TiO₂, CeO₂, and TiO₂-CeO₂.

Material	30 mg/L	50 mg/L
TiO ₂	10.9 mg/L	3 mg/L
CeO ₂	1.2 mg/L	3 mg/L
TiO ₂ -CeO ₂	1.5 mg/L	3.4 mg/L

L). The CeO₂ degrades only by 4% (1.2 mg/L), but on the other hand, TiO₂-CeO₂ particles showed a photodegradation of only 2% (0.6 mg/L). This detrimental effect of CeO₂ on the photocatalytic activity of TiO₂ is probably due to the shielding effect of CeO₂, which reduces the number of photons that the titania can absorb [20]. In Fig. 5b, the phenol photodegradation results are presented with an initial concentration of 50 mg/L in contact with prepared materials, where it is observed that at the 120 minutes, TiO₂ and CeO₂ present a degradation of 3% and TiO₂-CeO₂ presents a degradation of 6%.

Fig. 5(b) also shows that when the phenol



Fig. 4. Sorption-desorption isotherm: (a) TiO_2 , (b) CeO_2 , and (c) TiO_2 -CeO₂ particles.

concentration increases, the degradation rate decreases due to the material surface's saturation [21] TiO_2 particles achieve a photodegradation performance of 15% at the 180 minutes, and CeO₂ and TiO₂-CeO can be photographed at approximately 4% and 7%, respectively, because the hydroxyl groups on the materials' surfaces exist in various proportions, which inhibits the formation of hydroxyl radicals.

Conclusions

By means of the sol-gel method, it was possible to



Fig. 5. Photodegradation of phenol: (a) $C_0 = 30 \text{ mg/L}$ and (b) $C_0 = 50 \text{ mg/L}$.

synthesize spherical particles of nanometric size of TiO₂, CeO₂, and TiO₂-CeO₂ through XRD, and it was observed that TiO_2 is only present in the rutile phase. However, in the presence of CeO₂, it comprises a greater proportion in the anatase phase, which indicates that the CeO_2 prevents the growth of rutile crystals, which according to the classification of the IUPAC are mesoporous materials. The TiO2 particles exhibit a higher capacity for absorption and degradation of phenol with initial concentrations of 30mg/L and 50mg/L than the CeO₂ and TiO₂-CeO₂ particles because their pore sizes and volumes are smaller than those of TiO₂, which would cause an early saturation. In addition, CeO₂ could be causing a screen effect, which would not allow an adequate amount of UV light to be absorbed by the TiO₂ present in the material $(TiO_2 - CeO_2).$

Acknowledgments

The authors thank the Instituto Tecnológico de Toluca (DGEST 5894.16-P) and Lara-López. They also thank CONACYT for support during the preparation of this work and the Instituto Nacional de Investigaciones Nucleares (ININ, Project CB-504) for support during its development.

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