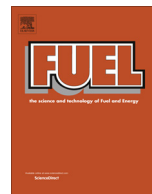




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Full Length Article

Calcium-containing materials as alternative catalysts in advanced oxidation process

Manuel Sánchez-Cantú^{a,*}, Ma. de Lourdes Ruiz Peralta^{a,**}, Alejandra B. Galindo-Rodríguez^a, Edgar Puente-López^a, Efraín Rubio-Rosas^a, Claudia M. Gómez^b, Francisco Tzompantzi^c

^a Benemérita Universidad Autónoma de Puebla, Facultad de Ingeniería Química, Avenida San Claudio y 18 Sur, C.P. 72570 Puebla, Puebla, Mexico

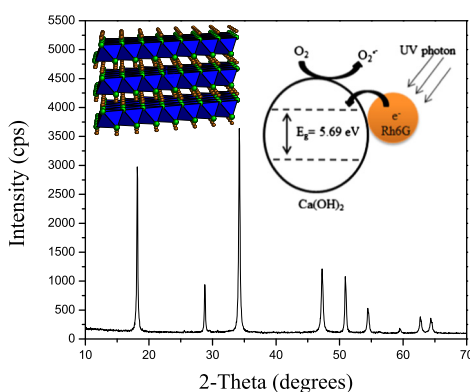
^b Universidad de Guanajuato, Col. Noria Alta SIN, C.P. 36050 Guanajuato, Gto., Mexico

^c UAM-Iztapalapa, Departamento de Química, Av. San Rafael Atlixco # 186, C.P. 09340 México, DF, Mexico

HIGHLIGHTS

- Four calcium-containing materials were evaluated in Rhodamine 6G photodegradation.
- Pure calcium hydroxide was identified as the most active photocatalyst.
- More than 60% mineralization was achieved within four hours.
- Ca(OH)₂ photocatalytic activity was attributed to an indirect dye sensitization.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, four calcium-containing materials (calcium hydroxide, commercial hydrated lime, calcium oxide and calcium carbonate) were evaluated as catalysts in the photodegradation of Rhodamine 6G (Rh6G) under UV radiation. The effect of catalyst concentration, reaction time and pH were evaluated. Materials were characterized by X-ray powder diffraction, thermogravimetric analysis, Scanning Electron Microscopy and Diffuse Reflectance Spectroscopy. The X-ray powder patterns showed that Ca(OH)₂, CaO and CaCO₃ samples presented pure crystalline phases while commercial hydrated lime consisted of a mixture of calcite and calcium hydroxide. Materials evaluation indicated that among the calcium-containing catalysts Ca(OH)₂ was the most active material showing a degradation and mineralization percentages of 50 and 61, respectively. Since Ca(OH)₂ band gap value was 5.69 eV, characteristic of an insulator material, the photocatalytic activity was attributed to an indirect dye sensitization.

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1. Introduction

In general, semiconductor materials have been reported in the literature as effective photocatalysts and among them TiO₂, in its

* Corresponding author.

** Corresponding author.

E-mail addresses: manuel.sanchez@correo.buap.mx (M. Sánchez-Cantú), lourdes.ruiz@correo.buap.mx (Ma. de Lourdes Ruiz Peralta).

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anatase phase, is the most frequently used semiconductor. This and other semiconductor materials have been doped [1] or dye-sensitized [2] to improve their photocatalytic behavior. However, these methods increase their cost restricting their industrial application. Thus, the search for novel, cheap and available photocatalysts is of paramount importance.

Recently, materials not considered as potential photocatalysts due to their dielectrical nature have been evaluated successfully

in the photodegradation of distinct organic molecules. Such materials include Al_2O_3 [3,4], layered double hydroxides [5] and spinel [6]. It is worth mentioning that among these non-semiconductor compounds the calcium-containing catalysts have attracted special attention due to their low cost, availability and their photoactivity. For instance, Zhang [7] evaluated $\text{Ca}(\text{OH})_2$ as photocatalyst against methylene blue (MB) aqueous solution under visible light radiation. It was proposed that reaction was conducted by indirect dye photosensitization. In this sense, also CaO has been used in the photodegradation of methylene blue [8], Violet GL2B [9], indigo carmine [10] and Rhodamine B [11].

It is worth mentioning that despite some works have been published with either $\text{Ca}(\text{OH})_2$ or CaO there are still some uncertainties regarding the reaction mechanisms of these materials and although their insulator nature is well known in some works they have been considered as semiconductors. Besides, some reaction mechanisms consider that CaO phase remained after their contact with water without considering the possibility of its hydration or reaction with atmospheric CO_2 producing calcium carbonate.

Thus, in this work, CaCO_3 , CaO, $\text{Ca}(\text{OH})_2$ and commercial hydrated lime were evaluated in the photodegradation of Rhodamine 6G (Rh6G). The effect of the catalyst nature, amount, reaction time and pH was studied.

2. Experimental

2.1. Materials' synthesis

Commercial hydrated lime (CHL) purchased from Cales Santa Emilia located at Perote, Veracruz, México, sold in 25 kg paper sacks, was used without further purification.

CaO was obtained from CHL annealing at 800 °C. The annealing temperature was determined from the thermogravimetric analysis (see Section 3).

Pure $\text{Ca}(\text{OH})_2$ was prepared as follows: 2 g of CHL was calcined at 800 °C for two hours. Then, the resulting material was hydrated at room temperature with 200 mL of decarbonated water under a static nitrogen atmosphere and vigorous stirring for one hour. Then, the suspension was filtered and dried at 120 °C for 20 min.

Calcium carbonate was synthesized by precipitation as follows: 13.8 g of K_2CO_3 and 11.8 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved by separate in 100 mL of deionized water. Then both solutions were added to a reaction vessel maintaining a constant pH of 11. Then, the slurry was aged at 60 °C for 17 h under vigorous stirring. Afterwards, the solid was washed with hot deionized water and dried at 120 °C for one hour.

2.2. Analytical methods

2.2.1. X-ray powder diffraction

The X-ray diffraction patterns of the solid samples were acquired in a D8 Bruker Discover Series 2 diffractometer with $\text{Cu K}\alpha$ radiation. The samples were measured between 5 and 70°, with a 2 θ step of 0.04° and a counting time of 0.6 s per point. Average crystal sizes were determined by the Scherrer equation from the most intense reflection: $L_{(hkl)} = K\lambda / (B(\theta)\cos\theta)$ where K is the shape factor (a value of 0.9 was used), L is the average crystal size, λ is the wavelength of $\text{Cu K}\alpha$ radiation, $B(\theta)$ is the Full Width at Half Maximum (FWHM), θ is the diffraction angle and hkl are the Miller indices. The crystalline phases were identified by means of the JCPDS (Joint Committee of Powder Diffraction Standards) database.

2.2.2. Thermogravimetric analysis

Thermogravimetric analyses (TGA) were carried out using a TGAi 1000 series system which was operated under an air flow

(20 mL min⁻¹) at a heating rate of 20 °C min⁻¹ from room temperature to 1000 °C. In the determination, ~40 mg of finely powdered dried sample was used.

2.2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) analysis was carried out in a JEOL JSM-6610 LV with an acceleration voltage of 20 keV. Images of the uncovered samples were taken using secondary electrons signals.

2.2.4. Diffuse reflectance spectroscopy

Diffuse reflectance spectra of the different samples were recorded on a Cary-5000 Varian (Agilent) spectrophotometer equipped with an integration sphere; polytetrafluoroethylene (Halon material) was used as reference standard. The band gap value was calculated using the Kubelka-Munk formalism [12].

2.3. Photocatalytic experiments

In order to evaluate the photocatalytic activity of the samples, Rhodamine 6G, hereafter called Rh6G ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$; ~99%, Aldrich) was chosen as a representative dye pollutant. For a typical procedure a specific amount of the catalyst was dispersed in 150 mL of a 5 ppm Rh6G aqueous solution. The ultraviolet light was provided by a 15 W Hg-lamp UVP-XX-15S (254 nm short wavelength; ~5.3 W m⁻²).

Prior to photoreaction, air was pumped into the reactor and the catalyst was magnetically stirred in the dark for 30 min to reach an adsorption/desorption equilibrium. After the mixture was irradiated for a given time an aliquot was collected at regular intervals and centrifuged to separate the solid from solution; the quantitative determination of Rh6G was performed measuring its UV-vis absorption spectrum using a Varian Cary100 UV-vis spectrophotometer. The photodegradation of Rh6G dye was followed analyzing the evolution of the optical absorbance at $\lambda = 526$ nm.

The degradation efficiency was calculated using the following Eq. (1):

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of the dye and C is the concentration at certain time. The photocatalytic variables were catalyst nature, amount, reaction time and pH.

The amount of organic carbon present in the solution after reaction was determined with a TOC-V CSH/CSN Shimadzu Analyzer.

3. Results and discussion

3.1. Catalyst characterization

The X-ray powder diffraction patterns of the samples are presented in Fig. 1. JCPDS files #88-1807, 84-1263, 78-0649 were used for calcium carbonate (asterisk), calcium oxide (letter x) and calcium hydroxide (circle) identification, respectively. It was evidenced that these samples presented pure crystalline phases. On the other hand, commercial hydrated lime (CHL) exhibited the characteristic reflections of calcium hydroxide and calcite as the main and secondary crystalline phases. Calcite presence in CHL was attributed to CO_2 contamination during storage or in the course of CaO rehydration process [13].

Cell parameters and average crystal sizes are presented in Table 1. Cell parameters values of CaCO_3 identified in pure calcite and that found in CHL were very close to the reported ones in the JCPDS file ($a = 4.988$ Å, $c = 17.061$ Å). In the same way, CaO showed a cell parameter value $a = 4.805$ Å which is identical to

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