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Surface fractal dimension of composites TiO_2-hydrotalcite

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ABSTRACT

Composites TiO_2-Hydrotalcite were prepared from synthesized TiO_2 using titanium i) isopropoxide, ii) titanium butoxide and hydrotalcites Mg/Al—CO_3^{2-} obtained by the sol - gel method. Adsorption-desorption isotherms from N_2 were obtained to determine BET surface area, volume and average diameter for pore. Surface fractal dimension determination has been a powerful tool to describe the roughness and irregular shape in several objects at different scales. The most common method to obtain surface fractal dimension data is calculated based on the surface area measurement by gas N_2 adsorption. This work computes fractal dimension of composites using adsorption-desorption isotherms from N_2, applying both Frenkel–Halsey–Hill and Mahnke-Mogel methodologies for this purpose. Surface fractal dimension values show minimal differences in both methodologies, and the analyzed materials were in the intermediate roughness range ($2.11 \le D \le 2.47$), which is due to the mesoporous original materials; hydrotalcite and TiO_2. Pore size distribution and hysteresis loop affects the surface fractal dimension, but it did not have a significant influence on catalyst process.

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1. Introduction

Recently, many researchers have focused on the development of materials with environment applications, particularly for photocatalytic process in wastewater treatment that are applied to degrade organic compounds. TiO_2 has a high degradation activity because it has wide band valence, low toxicity and good resistance to light chemical corrosion [1]. Nevertheless, commercial TiO_2 particles tend to be nanometric in size, which makes it difficult to recover and reuse, therefore, composite materials are needed to immobilize TiO_2 allowing it to be reused as a photocatalyst. Hydrotalcite-like compounds are suitable to immobilize TiO_2; they belong to anionic clay families [2,3,4]. Hydrotalcite is a lamellar compound. Its chemical formula is defined as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]_x(A^n)_{x/n}\bullet mH_2O$, where M^{2+} and M^{3+} are di and trivalent cations ($Mg^{2+}\cdot y\cdot Al^{3+}$). They are coordinated in octahedral positions in each sheet, resulting in an excess positive charge which is balanced by A^{n-} anion (CO_3^{2-}) and water molecules in the interlamellar space [5]. Hydrotalcites could be activated by calcination at temperatures over 500 °C, increasing properties like ion exchange capacity, surface area and pore volume [6]. Textural and surface characteristics are dependent on the preparation method and chemical reagents of material synthesis [7], meaning the photocatalytic properties could also be affected [8].

Dimension zero points, uni-dimensional lines and curves, bi-dimensional plane figures like square and circles and tri-dimensional objects like spheres and cubes all let us see and understand the world. Nevertheless, some natural phenomena are better described by a dimension whose value is not an integer but it is a fraction (fractal). Also, fractal objects have autoafinity and autosimilitude properties at variating scales. Until now, surface analysis is the only parameter that relates surface roughness to fractal dimension. For molecular sized particles, the surface of most materials is fractals. If one part of the fractal object is separated and amplified, this part will look like that of the rest of the object. Measurement capacity to fill in the space a curve or surface is the principal requirement in fractal dimension, the simplest conceptual form to reach this in a material surface. The simplest conceptual form to reach this in a material surface. Fractal dimension requires the simple concept of measurement capacity to fill in the space in a material surface, resulting in a curved absorption graph. This consists of covering the surface with a monolayer of molecules, with ratio r, repeating this method to several ratios of r. If the molecule number $N(r)$ in the monolayer grows in the r^D order, while r is decreasing, as does the D exponential, which is called effective dimension of the surface between $2 < D < 3$ [9].

The surface fractal dimension value is important for several physicochemical processes (adsorption, adhesion, surface diffusion and catalyst) because of the definition of structural heterogeneity of solids, which affects their form to interact with other substances [10]. A new viable option to determine the surface fractal dimension in a material is through the adsorption-desorption isotherms from N_2. Different mathematic models have been described in literature [11,12,13] to determine surface fractal dimension D from gas adsorption data. The aim of this work is to prepare the composites TiO_2-hydrotalcite and determine the textural parameter evaluated by the surface of the composites

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using fractal dimension analyses through Frenkel–Halsey–Hill [13] and Mahnke-Mogel [12] equations.

2. Materials and Method

2.1. TiO_2 Synthesis

Sol-gel process was applied [14] using the reagents i) titanium isopropoxide (TTIP 97%) $Ti[OCH(CH_3)_2]_4$ (Sigma), and ii) titanium butoxide (TOBT 97%) $C_{16}H_{36}O_4Ti$ (Sigma-Aldrich). In a first stage; 5.25 mL of TTIP added to 47 mL of ethanol, a mixture was stirred for 3 h and 12.25 mL of deionized water was added and stirred for 20 h at 78 °C. The product was washed by centrifugation using deionized water, the resulting solid was dried for 1 h at 80 °C and lastly it was calcined. In the second stage; 90 mL of 1-butanol $C_4H_{10}O$ (Sigma-Aldrich) were added to 120 mL of deionized water, the mixture was heated at 70 °C in a water bath with continuous stirring and reflux then 45 mL of TOBT were dropped in the solution. The final mixture was aged 24 h and the product was recovered by centrifugation which was then dried for 24 h at 100 °C and finally the solid was calcined.

2.2. Mg/Al—CO_3^{2-} Hydrotalcite Synthesis by Sol-Gel Method

0.05 mol of magnesium ethoxide $C_4H_{10}MgO_2$ (Aldrich) was dissolved in 100 mL of ethanol CH_3CH_2OH 99.5% (Civeq) and was added 8.8 mL of HCl 37.2% (Fermont), keeping it at 80 °C. A second solution was prepared with 0.017 mol of aluminum acetylacetonate $C_{15}H_{21}AlO_6$ (Aldrich) dissolved in 80 mL of ethanol, this solution was titrated into the first solution and the mixture was kept at a pH of 10 using ammonium hydroxide NH_4OH (Herschi) at 35%, finally, 1 mL of water was added. The final product was aged for 20 h. The solid was separated by centrifugation, washed with ethanol and dried at 100 °C for 24 h (Hs), finally it was calcined (HsC).

2.3. TiO_2-Hydrotalcite Composite Synthesis

The first group of composites was prepared in a 1:1 weight relation for both materials, following methodologies are shown in Fig. 1.

In the procedure for M0, 9 mL of TTIP were mixed with 0.5 g of calcined hydrotalcite, the mixture was stirred for 0.5 h in air, then immediately calcined. M1's procedure consists of TiO_2 being prepared following the sol-gel method- but dry TiO_2 was added to the hydrotalcite gel before the aging step. M2 also followed the sol-gel procedure, however TiO_2 and hydrotacite were mixed in before the aging step and at the end, the product was mixed in an ultrasonic bath for 2 h. The solid was separated by centrifugation then dried at 100 °C for 24 h and ultimately calcined. In M3's synthesis, TiO_2 gel and 2.0 g of calcined hydrotalcite were added to the gel once the aging step was complete, it stirred for 2 h using a magnetic stirrer followed by 1 h of ultrasonic stirring. The solid was separated, dried at 100 °C for 24 h and calcined. M4 was obtained using a similar procedure to M1's, the TiO_2 gel obtained by TOBT was added to the gel hydrotalcite, keeping with the methodology for hydrotalcite and at the end the solid was calcined.

All calcination processes were performed at 550 °C for 3.5 h in a muffle furnace.

The second group of composites used TiO_2, obtained by the sol-gel method, used TOBT.

In their preparation, in which calcined hydrotalcite was added four different ways. (A, B before and after added TOBT, C at the end of the aging process and D mixing both solid) as demonstrated in Fig. 2. In all cases, HsC was used and the 10:1 ratio for TiO_2–hydrotalcite was maintained.

2.4. Photocatalitic Activity Evaluation

Phenol was used as the model pollutant, 200 mL of solution was prepared using C_6H_6O (Baker) ($C_o = 10$ mg/L), each composite was added into this solution ($C_{material} = 1$ g/L). One solution was treated without material to determine photolytic reaction. At started contact between solid and solution, this was stirred and air was pumped for 20 min into solution to hydroxilate the mixed and reach adsorption equilibrium [15], after that, the mixed was irradiated using an UV lamp CS 5300 ($\lambda = 254$ nm, 4 w) for 3 h keep a stirring and air pumping. All tests were made in the absence of visible light and no pH changes. The quantity of phenol adsorbed in the composites was determined as described before without UV lamp. Remained concentration was determined as follows amine-4-antipiridine method, and it was using a UV–Vis spectrofotometer ($\lambda = 510$ nm)[16].

2.5. Textural Parameter Determination

Adsorption-desorption isotherms for preparing materials were determined by N_2 physisorption using BEL Japan INC analyzer model Belsorp Max, samples were degasified at 150 °C for 6 h. Surface area,

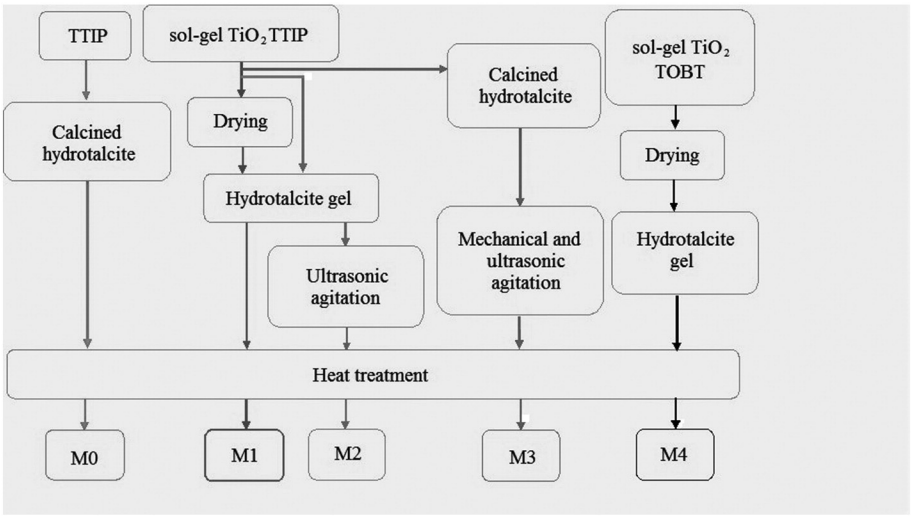

Fig. 1. Methodologies for TiO_2–hydrotalcite composites (1:1 relation).

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