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Full Length Article

Characterization of selectively etched halloysite nanotubes by acid treatment

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ABSTRACT

Halloysite nanotubes (HNTs) are a type of naturally occurring inorganic nanotubes that are characterized by a different composition between their external and internal walls. The internal walls are mainly composed of alumina whilst external walls are composed of silica. This particular structure offers a dual surface chemistry that allows different selective surface treatments which can be focused on increasing the lumen, increasing porosity, etc. In this work, HNTs were chemically treated with different acids (sulphuric, acetic and acrylic acid), for 72 h at a constant temperature of 50 °C. As per the obtained results, the treatment with sulphuric acid is highly aggressive and the particular shape of HNTs is almost lost, with a remarkable increase in porosity. The BET surface area increases from 52.9 (untreated HNTs) up to 132.4 $m^2 g^{-1}$ with sulphuric acid treatment, thus showing an interesting potential in the field of catalysis. On the other hand, the treatment with acetic acid led to milder effects with a noticeable increase in the lumen diameter that changed from 13.8 nm (untreated HNTs) up to 18.4 nm which the subsequent increase in the loading capacity by 77.8%. The aluminium content was measured by X-ray fluorescence (XRF) and laser induced breakdown spectroscopy (LIBS). The final results using two systems, suggest a good correlation between the acid strength and the aluminium reduction. Consequently, is possible to conclude that new applications for HNTs can be derived from selective etching with acids. Sulphuric acid widens the potential of HNTs in the field of catalysis while weak acids such as acetic and acrylic acids give a controlled and homogeneous lumen increase with the corresponding increase in the loading capacity.

1. Introduction

One of the main features of nanomaterials is their high surface to volume ratio which gives an exponential increase in the reactivity of the molecules thus leading to a remarkable change in their electronic, optical, chemical or mechanical properties with regard to their bulk counterpart materials. For this reason, nanomaterials offer a great potential in a wide range of research areas such as biomedicine, cosmetics, food and food packaging, coatings, electronics, catalysis or materials sciences [1]. A wide variety of metal oxides, nanoclays, carbon nanomaterials, organometallic nanocomposites (MOFs) have been successfully introduced in new materials [2], with the particular feature that nanoparticles offer a strong different behavior than their counterpart micro/macro particles. Nanoclays have been widely studied as support for different catalysts [3]. In particular, the petroleum industry is leading the introduction of nanoparticles as supports for catalysts in several reactions. It has been reported the potential of activated carbon and carbon nanotubes (CNTs) as support for ethanol oxidation [4], aluminosilicates, cordierites [5], zeolites [6], other feldspars, kaolinite derivate such sespiolites [7], HNTs, etc., which allow the conversion of crude oil in a wide range of products. Nanomaterials are continuously acquiring new features in the catalysis industry. Abbasov et al. [8] reported the positive effects of a previous acid treatment on HNTs with HCl to improve the efficiency as support for NiO and CoO for fuel production from heavy crude oil. Zhang et al. [9] used a silane treatment with aminopropyltriethoxysilane as a previous treatment to increase Pd adsorption on HNTs as catalytic system for the conversion of styrene to ethylbenzene. In a parallel way, CNTs are also being investigated as support for different catalysts [10]. Nevertheless, the use of CNTs is restricted in the medicine field due to their potential health risks. On the other hand, their high cost is a key disadvantage for a wide use in the field of composites.

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Other important application of nanoparticles is hydrogen storage on micro/nanoporous materials [11]. Many of the abovementioned materials are intrinsically porous of can be modified to increase the overall porosity and surface area. Another feature of porous nanoparticles is related to their potential use as container for controlled drug release [12]. Despite it is true that a wide variety of encapsulated structures for controlled delivery are currently used, aluminosilicates own a privileged position due to their low cost and health safety. Aluminosilicates are currently being used for controlled delivery of antimicrobials in the cosmetic industry [13], non-foaming oxygen nanocontainer [14], support of compatibilizer agents in immiscible polymer blends [15], flame retardant containers [16,17], heavy metal nanoadsorbers [18], with a remarkable effect on the prolonged effect with time [19]. In addition, aluminosilicates can be loaded with active additives such as thermal stabilizers, antioxidants, UV light stabilizers, etc. to protect polymers for prolonged exposure to environment. The use of aluminosilicates HNTs has been widely reported in polymer formulations to improve mechanical properties [20,21]; also, their use in the food-contact products is increasing as HNTs can provide controlled delivery of preservatives, antibacterials and others [22].

HNTs have been also used in pharmacology, prosthesis [23], bone repairing and therapy against cancer [24]. HNTs are characterized by extremely high biocompatibility [25]. They are good drug carriers for controlled drug release [26,27]. Qi et al. [28] manufactured nanofiber mats with poly(lactide-*co*-glycolide) with HNTs previously loaded with tetracycline hydrochloride antibiotic. Other aluminosilicates nanotubes, i.e. imogolite nanotubes, were successfully used as scaffolds for cell growth [29].

The particular aluminosilicate structure of HNTs with an internal alumina layer and an external silicate layer allows a wide variety of chemical modifications such as acid [30–32], alkali [33] and other [34] to selectively change porosity, lumen size, surface activity, etc. Acid treatments promote the removal of Al_2O_3 while an alkaline treatment preferably attacks the silica layer. Both the acid and the alkali treatments lead to electrically charged structures which play a key role in substance absorption. Different research works have been done in the last years, focused on HNTs modification. Abdullayev et al. [35] used sulphuric acid at different concentrations and treatment-times with the main aim of increasing the average diameter of the HNTs lumen. They reported an increase in the load capacity by 2–3 times higher regarding the initial capacity. Wang et al. [36] studied the effect of several concentration of hydrochloric acid (HCl) on the morphology, the crystalline structure and the porous texture of HNTs. They concluded that very slight changes in the crystalline structure and the hollow shape were obtained with this treatment. Nevertheless, to our knowledge, an in depth comparative study of the effects of different acids (including sulphuric acid which is the most used for this treatments) on chemical and morphological changes of HNTs has not been carried out.

The present work explores the effect of the strength of different acids (sulphuric, acrylic and acetic acids) on the morphology of chemically modified HNTs to define their possibilities in the field of catalysis and/or container for controlled delivery. The novelty of the present work is focused on the use of weak acids, i.e. acetic and acrylic acids, to treat HNTs and study their effect on the chemical changes and morphology, compared to the effects of a widely used acid for this type of treatments, sulphuric acid. The work covers the use of different techniques: transmission electron microscopy (TEM), X-ray fluorescence (XRF), X-ray diffraction spectroscopy (XRD), laser induced breakdown spectroscopy (LIBS), thermogravimetric analysis (TGA) and specific surface area (BET) to give new insights on the chemical changes produced by acid treatment on HNTs.

2. Materials and methods

2.1. Materials

Halloysite nanotubes were supplied by Sigma Aldrich (Madrid, Spain). Sulphuric acid (95% H_2SO_4) and acetic acid (99.7% CH_3COOH) were supplied by PanReac Applichem (Barcelona, Spain) and acrylic acid (99% $CH_2=CHCOOH$) was obtained from Sigma Aldrich (Madrid, Spain). All reagents were used without any other purification.

2.2. Selective etching of HNT by acid treatment

An acid treatment was carried out on HNTs which allows a selective etching of the alumina located in the interior parts of HNTs with a similar procedure as that described by Abdullayev et al. [35]. In summary, HNTs were previously dried overnight at 100 °C. Then, 5 g of HNTs were poured into 500 mL of the corresponding acid solutions with a constant concentration of 1 mol L^{-1}. The obtained suspension was maintained with magnetic stirring for 72 h on a hot plate at 50 °C. After this stage, chemically modified HNTs were collected by centrifugation and washed with distilled water until the obtained pH was in the 6–7 range. Finally, HNTs were dried at 50 °C for 24 h prior to further characterizations.

2.3. Characterization techniques

2.3.1. Transmission electron microscopy (TEM)

The morphology and size distribution of raw HNTs and the etched-HNTs were studied by transmission electron microscopy (TEM) in a Philips mod. CM10 (Eindhoven, the Netherlands) using an acceleration voltage of 100 kV. Prior to TEM observation, a small amount of the corresponding HNTs samples was dispersed in acetone immersed in an ultrasound bath; subsequently, a drop of this dispersion was poured onto a carbon grid and subjected to solvent evaporation at room temperature. The lumen size of HNTs was obtained from the collected TEM images and a minimum of 50 measurements were done to obtain the size distribution.

2.3.2. X-ray fluorescence spectroscopy (XRF)

The chemical composition of HNTs before and after the corresponding acid treatments was obtained by X-ray fluorescence spectroscopy in a sequential X-ray spectrometer PHILIPS MAGIX PRO PW2400 (Panalytical B.V., The Netherlands) equipped with a rhodium tube and a beryllium window. Results of the chemical compositions were analysed by using the SuperQ analytical software. Each treated-sample was subjected to three different analyses and the average values were calculated.

2.3.3. Laser induced breakdown spectroscopy (LIBS)

LIBS analysis of raw and chemically etched HNTs was performed by a μ-LIBS system based on a MODI' LIBS equipment (Mobile Dual-Pulse Instrument) [37]. The system is equipped with a double-pulse Nd:YAG laser, emitting at 1064 nm with pulse energy up to 60 mJ (20 ns FWHM pulse width). Laser radiation was focused through an optical microscope model Axio Scope A1 (Zeiss, Germany) on the sample to analyse. The microscope is equipped with a 10 x objective having a focal distance of 10 mm. For LIBS analysis, the sample was placed on a motorized stage which develops a 2D scanning of the sample surface. The optical signal from the laser-induced plasmas was collected by an optical fibre, placed at an angle of about 45 ° and at a distance of 10 mm from the laser spot, and then sent to a broadband spectrometer model AvaSpec-2048-2 from Avantes (Eerbeek, The Netherlands) covering the spectral range comprised between 180 and 900 nm. The synchronization between the laser firing, data acquisition and x-y movement of the motorized stage