



Physicochemical characterization of organosilylated halloysite clay nanotubes



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ABSTRACT

Halloysite nanotubes (HNTs) were functionalized with several organosilanes with different functional groups, by a post-grafting methodology, in aprotic and anhydrous conditions: 3-aminopropyltriethoxysilane (APTES), *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS), (3-mercaptopropyl)trimethoxysilane (MPTMS), (3-bromopropyl)-trimethoxysilane (BrTMS), vinyltrimethoxysilane (VTMS) and phenyltriethoxysilane (PhTES).

The pristine and silylated clay minerals were characterized by transmission and scanning electron microscopy, energy-dispersive X-ray spectroscopy, powder X-ray diffraction, nitrogen adsorption-desorption isotherms at $-196\text{ }^{\circ}\text{C}$, bulk elemental analysis, X-ray photoelectron spectroscopy, thermogravimetry, Fourier transform infrared spectroscopy-attenuated total reflectance and ^{13}C , ^{29}Si and ^{27}Al solid-state nuclear magnetic resonance.

The techniques identified pristine HNTs as halloysite-7Å (dehydrated form) and proved their successful silylation without the disruption of the nanotubes structure. The silylated HNTs showed bulk Si and C contents up to 7.30 and 1.92 mmol/g, respectively, with the APTES functionalized material containing the highest bulk and surface Si and C loadings, confirming its highest silylation efficiency. Some insights into the silylation reaction and mechanism were also provided by the techniques used. Combination of ^{29}Si and ^{27}Al MAS NMR and XRD data suggested that silylation reaction occurred at Al–OH groups from the inner lumen surface, as well as the Al–OH and Si–OH groups at the edges or external surface defects; no evidence was found for the existence of functionalization in the interlayer Al–OH groups. The silylation mechanism was found to proceed through reaction of the alkoxy moieties from the organosilane with the referred surface groups from the HNTs in a 3-fold (for VTMS and BrTMS), or 2-fold covalent grafting (for MPTMS) or a mixture of both approaches (for APTES, AEAPTMS and PhTES); in the case of APTES- and AEAPTMS-functionalized HNTs, a polymerization side-reaction was also evidenced, as a parallel functionalization pathway.

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1. Introduction

Halloysite nanotubes (HNTs) with $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ composition is a naturally occurring two-layered (1:1) aluminosilicate, chemically similar to kaolinite, with a predominantly hollow tubular structure in the submicrometer range [1]. Halloysite occurs mainly as two types of polymorphs: the anhydrous form, with an

interlayer spacing of 7 Å, and the hydrated form, with expanded interlayer spacing of 10 Å, as a result of the incorporation of water in the interlamellar space. Halloysite is a cost-effective material that can be mined from deposits as a raw mineral and its nanosized dimensions and tubular arrangement depend on the region deposits: the tubes length typically varies from 500 to 1000 nm and the inner diameter is in the range of 15–100 nm [2–4]. Hydroxyl groups are present as Al–OH groups at the inner surface, wall interlayers and edges, and as Si–OH groups at the edges and external surface defects of the material. Alumina innermost and silica outermost surfaces allow for HNTs inner/outer chemical modification, resulting in halloysite-based materials with enhanced

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properties for applications as nanosized supports for chemical species [5–7] as adsorbents [3,8], as drug-delivery systems [9,10], as nanofillers for polymers [11], as control release agents [12] and as corrosion inhibitors [13,14]. In fact, despite the considerable interest in a range of other synthetic nanotubular materials such as carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs), recent works have highlighted the importance of the use of HNTs in catalysis, either as support of active phases or as an intrinsic catalyst.

Organosilylation is a well-known method to selectively modify clay mineral surfaces efficiently and has already been used in the functionalization of pristine halloysite, but using a limited number of bifunctional organosilanes (typically containing amine and thiol groups) [4,15]. The covalent bonding between the organic functionalities of the organosilane and the hydroxyl groups of the clay mineral not only allows fine tuning the clay surface chemistry, but also enables a robust immobilization of the organic moieties, preventing their leaching [16].

Yuan et al. investigated the surface modification of different types of natural HNTs with 3-aminopropyltriethoxysilane (APTES) and concluded that the extension of amino-functionalization was strongly affected by the morphological parameters of the pristine halloysite (nanotubes length, outer and inner diameters and wall thickness), since they lead to differences on the amount of available hydroxyl groups; afterwards, the authors used the functionalized HNTs in the fabrication of nanocomposites, enzyme immobilization and controlled release of guest molecules [4,17]. The same organosilane APTES was also used to chemically modify HNTs with *N*-2-pyridylsuccinamic acid (PSA) to produce a nano-adsorbent for the selective solid-phase extraction of Pb(II) [18]. An APTES-functionalized halloysite was also tested as host material for model dye (acid orange II) loading and controlled release: the study showed that the HNTs functionalization occurred at the internal lumen surface and that the pH acted as external trigger for controlling the guest upload and subsequent controlled release [17]. In a distinct work, the organosilane *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS) was used in the functionalization of HNTs to allow immobilizing Au nanoparticles to be subsequently used as a surface-enhanced Raman scattering substrate, showing a remarkable enhancement effect due to the synergy between the Au nanoparticles and the HNTs [19]. In another application, HNTs functionalized with bis(triethoxysilylpropyl)-tetrasulphide (TESPT) were used to improve the dispersion and physical properties of a natural rubber matrix [1]. Functionalized HNTs have also been used as supports for catalytic active species (metal complexes and metallic nanoparticles), although not in so great extent as other clay minerals, such as K10-montmorillonite [20]. Calcined kaolinite and halloysite were used as supports for an anionic iron(III) porphyrin, which were subsequently used as heterogeneous catalysts in the oxidation of cyclooctene, cyclohexane and *n*-heptane using iodosylbenzene as oxidant, giving expressive product yields for all the substrates [21]. The complex CuBr-AEAPTMS supported in HNTs proved to mediate the living polymerization of methylmethacrylate showing increased conversion, relative low poly-dispersion and linear first-order rate plots [22]. Ag nanoparticles were immobilized into AEAPTMS-functionalized HNTs and the resulting material showed high adsorption capability and photocatalytic activity towards methylene blue degradation [6]. Pt nanoparticles were uniformly immobilized into APTES functionalized HNTs and were subsequently tested in the catalytic hydrogenation of styrene to ethylbenzene with 100% substrate conversion after 180 min; however, the catalytic activity slowly decreased with the increasing number of reaction cycles because of the low recovery of the catalyst [23]. Finally, raw HNTs were used as intrinsic acid catalysts in methylic and ethylic

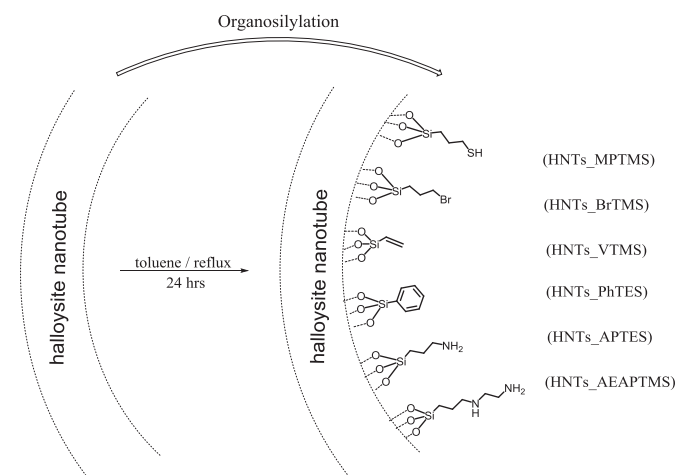
esterifications of lauric acid with substrate conversions of 95.0% and 87.1% for the methylic and ethylic esterifications, respectively [24].

In the present work, pristine HNTs were functionalized with several organosilanes with different functional groups ($-\text{NH}_2$, $-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$, $-\text{SH}$, $-\text{Br}$, $-\text{C}_6\text{H}_5$, $-\text{C}=\text{CH}_2$) in aprotic and anhydrous media, Scheme 1, with the ultimate goal of being used as linkers or reactive groups for the immobilization of metal complexes/other active phases (metal and metal oxide nanoparticles) with catalytic activity. Furthermore, some of the introduced groups can be chemically modified in a subsequent step in order to impart intrinsic catalytic properties to HNTs; the catalytic applications of the silylated HNTs will be the subject of a forthcoming paper. The influence of the type of organosilane on the silylation efficiency, amount of anchored organosilane, type of chemical bond and textural properties of the resulting functionalized HNTs were evaluated. Finally, with the selected group of organosilanes, we endeavor to get insights into the silylation reaction of HNTs and corresponding mechanism in order to establish correlations between HNTs structure/organosilane properties/organosilane loading/functionalization mechanism. To the best of our knowledge, a complete study of the silylation of this type of clay material with different types of organosilanes and the establishment of the aforementioned relations is lacking. In this context, this work provides relevant insights that will allow tuning the surface chemistry of HNTs and broadening the spectrum of applications through the selection of the most suitable organosilane.

2. Experimental section

2.1. Materials

All of the reagents and solvents were used without further purification. HNTs were commercially obtained from Sigma–Aldrich



Organosilane names and abbreviations:

3-Mercaptopropyltrimethoxysilane: MPTMS

(3-Bromopropyl)trimethoxysilane: BrTMS

Vinyltrimethoxysilane: VTMS

Phenyltriethoxysilane: PhTES

3-Aminopropyltriethoxysilane: APTES

N-2-aminoethyl-3-aminopropyltrimethoxysilane: AEAPTMS

Scheme 1. Schematic representation of HNTs functionalization with organosilanes, and organosilanes abbreviations.

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