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Tailoring surface properties and structure of layered double hydroxides using silanes with different number of functional groups



Qi Tao^{a,b}, Hongping He^{a,b,*}, Tian Li^{a,c}, Ray L. Frost^b, Dan Zhang^{a,c}, Zisen He^{a,c}

^a Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

^b Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland 4001, Australia

^c University of Chinese, Academy of Sciences, Beijing 100039, PR China

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ABSTRACT

Four silanes, trimethylchlorosilane (TMCS), dimethyldiethoxysilane (DMEDES), 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS), were adopted to graft layered double hydroxides (LDH) via an induced hydrolysis silylation method (IHS). Fourier transform infrared spectra (FTIR) and ²⁹Si MAS nuclear magnetic resonance spectra (²⁹Si MAS NMR) indicated that APTES and TEOS can be grafted onto LDH surfaces via condensation with hydroxyl groups of LDH, while TMCS and DMEDES could only be adsorbed on the LDH surface with a small quantity. A combination of X-ray diffraction patterns (XRD) and ²⁹Si MAS NMR spectra showed that silanes were exclusively present in the external surface and had little influence on the long range order of LDH. The surfactant intercalation experiment indicated that the adsorbed and/or grafted silane could not fix the interlamellar spacing of the LDH. However, they will form crosslink between the particles and affect the further surfactant intercalation in the silylated samples. The replacement of water by ethanol in the tactoids and/or aggregations and the polysiloxane oligomers formed during silylation procedure can dramatically increase the value of BET surface area (S_{BET}) and total pore volumes (V_p) of the products.

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1. Introduction

Silylation, also known as silane grafting, has been proven to be an efficient method to modify inorganic materials [1–4]. Comparing with surfactant intercalation, silylation enables a durable immobilization of the organic moieties by forming covalent bonds between silane and substrates. Therefore, the stability of the products against hydrolysis would be improved and the leaching of the organic moieties into the surrounding solutions, as surfactant modified products usually do, would be prevented [5]. More importantly, silylation provides a precise control over the surface component and pore features of the products for specific applications, such as in chromatography, antimicrobials, catalyst, immobilized enzyme and so on [6].

Burket et al. [7] initiated to synthesize silicas using a co-condensation of tetraalkoxysilanes and organo-silanes method (also known as sol–gel method). Well-ordered mesoporous silica and organo silica with tunable nanometer pores, large surface areas, and high pore volumes could be synthesized by using this method [8].

* Corresponding author at: Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China.

E-mail address: hehp@gig.ac.cn (H. He).

During this process, the hydrolysis and grafting reaction of silanes were the most critical issues to determine the structure and morphology of the product. Therefore with various kinds of silanes with different numbers of hydrolysable groups and functional groups have been widely adopted to synthesize or graft silica kinds of materials [8–11]. Ruiz-Hitzky [10] found that trimethylchlorosilane and hexamethyldisilane could easily be grafted onto the external surface of H-magadiite and the internal surface with the help of a pre-intercalation with organic polar molecules. Herrera et al. [9] investigated the grafting reaction on laponite with monofunctional (γ -MPDES) and trifunctional alkoxy silanes (γ -MPTMS). The monofunctional silane only formed a monolayer coverage on the border of the laponite plates and exhibited nearly no effect on the physicochemical properties of the laponite. However, the trifunctional silane was capable of both reactions with the clay edges and formation of complex polysiloxane oligomers in the bulk which were further deposited on the laponite surface, resulting in decreased porosity, increased interlayer distance and higher hydrophobicity. This implies that the number of functional groups in the used silane has a significant effect on the structure and property of the silylated products. More interestingly, Mochizuki et al. [12] successfully developed a novel method for constructing molecularly ordered silica nanostructures with two dimensional and three dimensional networks, involving silylation of a layered silicate octosilicate with alkoxytrichlorosilanes and subsequent reaction

within the interlayer spaces. All these cases demonstrated that silylation is a promising method for tailoring the surface frameworks and properties of layered compounds.

Layered doubled hydroxides (LDHs) are a kind of synthesized lamellar compounds, which have the same structure and properties as natural layered mineral, hydroxalites ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot m\text{H}_2\text{O}$). The Mg^{2+} in the brucite-like octahedral sheet is partly substituted by Al^{3+} , and the resultant excess positive charges are balanced by the interlayer anions. The unique positively charged layers and excellent anion exchange capacity result in wide applications such as adsorbents, ion exchangers, pharmaceuticals, catalysts or catalyst supports etc. [13–19]. Park et al. reported for the first time a covalent bonding formed between LDH and silane [20]. Shortly afterwards, Wypych et al. successfully synthesized the single-layer LDH silylated products [21]. More recently, our group developed an *in-situ* coprecipitation method and a calcination–rehydration method to graft silanes onto the LDH surfaces. The influences of surfactant content on the structures, morphologies, and thermal properties of the final products were discussed based upon the water abundant reaction system [22,23]. We also designed an induced hydrolysis silylation method (IHS) to graft water-rich LDH in ethanol. IHS is a convenient way to control the hydrolysis rate of silane by controlling the water content in LDHs [24]. However, in all the above studies, 3-aminopropyltriethoxysilane (APTES) was used as the grafting agent, the possibility for silylation of LDH with the silanes other than APTES and their effect on the structure and property of the silylated products are still unknown.

The main aim of this study is to investigate the influence of the number of hydrolysable groups in silanes on the structure and properties of the silylated products. Four silanes with 1–4 hydrolysable groups were used in this study, i.e. trimethylchlorosilane (TMCS), dimethyldiethoxysilane (DMEDES), 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS). The experiments were carried out in ethanol medium using water-rich LDH as substrate via IHS. The textural properties of the synthesized materials were characterized by X-ray diffraction (XRD), the diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), solid state ^{29}Si cross polarization magic angle spinning nuclear magnetic resonance spectroscopy (^{29}Si CP/MAS NMR) and nitrogen adsorption test.

2. Experimental

2.1. Materials

2.1.1. Synthesis of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (MgAl-LDH)

The MgAl-LDH was prepared by coprecipitation as reported previously [25]. About 9.6 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4.7 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a molar ratio of 3:1 ($\text{Mg}^{2+}/\text{Al}^{3+}$) were dissolved in 44 ml distilled water (Solution A). About 4 g NaOH was dissolved in 50 ml of distilled water (Solution B). At room temperature, Solution B and Solution A were dropped into 50 ml distilled water with vigorous stirring. The pH value of the mixture was kept at ca. 10. After filtered and washed with distilled water, the gel-like resultants were separated into two batches. One was centrifugally separated and sealed for the further experiments (denoted as Ht_w), and the other was dried at 80 °C (denoted as Ht). The mass loss of Ht_w is 88% after dried at 80 °C.

2.1.2. Silylation experiments of MgAl-LDH (H-Si_n , $n=1-4$)

About 50.0 g Ht_w was suspended into 100 ml ethanol. With stirring, 0.05 mol TMCS, DMEDES, APTES and TEOS were added dropwise into the mixture, respectively. After stirred for 6 h at room temperature, the gel-like resultant was washed by centrifuge–washing cycles with ethanol and dried at 75 °C (denoted as H-Si_n).

2.1.3. Surfactant intercalation of silylated MgAl-LDH (H-L_n)

With stirring, half amount of Ht_w and the obtained H-Si_n were dispersed into 100 ml distilled water for 2 h before the input of 2.8 g sodium dodecylsulfate (DS), respectively. After stirred for 6 h, the resultant was washed by centrifuge–washing cycles and dried at 75 °C (denoted as H-L_n).

2.2. Characterization of the materials

The diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) characterization was performed on the Praying Mantis™ diffuse reflection accessory (Harrick Scientific Products Inc.) of a Bruker Vertex-70 Fourier transform infrared spectrometer at room temperature. The DRIFTS measurement lasted 2 min (from the sample loading to the spectrum recording). The spectra were collected over the range of 4000–600 cm^{-1} with 64 scans and a resolution of 4 cm^{-1} using KBr background. Powder XRD patterns were recorded using a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.5406^\circ$), operating at 40 kV and 40 mA. The incident beam was monochromated through a 0.020 mm Ni filter then passed through a 0.04 rad. Soller slit a 1.0 mm fixed mask with 1.0° divergence slit, 0.2° anti-scatter slit, between 1 and 76° (2θ) at a scan speed of 1.5° min^{-1} with a increment of 0.01°. All the solid-state NMR experiments were carried out at $B_0=9.4$ T on a Bruker AVANCE III 400 WB spectrometer. The corresponding resonance frequency of ^{29}Si was 79.5 MHz. Samples were packed in a 7 mm ZrO_2 rotor and spun at the magic angle (54.7°), and the spin rate was 7 kHz. ^1H – ^{29}Si CP/MAS spectra were recorded with a contact time of 4.5 ms and a recycle delay of 2 s. The ^{29}Si chemical shift was referenced to tetramethylsilane (TMS). The pore structure was studied by N_2 sorption isotherms (at 77 K) on samples previously outgassed for 24 h at 373 K, using an ASAP 2020 by Micromeritics. The specific surface area of the samples was obtained on the basis of the standard Brunauer–Emmett–Teller method. The pore size distribution (PSD) was obtained by means of the Horvath-Kawazoe (HK) method and Barrett–Joyner–Halenda (BJH) method from the desorption data in the pore size range 2–20 Å and 20–500 Å, respectively.

3. Results and discussion

3.1. Diffuse reflectance Fourier transform infrared spectra (DRIFTS)

The IR spectrum of Ht (Fig. 1a) showed the vibrations related to O–H stretching mode in the range of 3735 and 3050 cm^{-1} , which included the surface –OH vibrations at ca. 3611 and 3657 cm^{-1} , water and related H-bonds between 3500 and 3300 cm^{-1} , and the bridge bond between H_2O and anions at ca. 3087 cm^{-1} [26]. The vibration corresponding to the bending mode of water was observed at ca. 1636 cm^{-1} . The strong vibration at ca. 1438 cm^{-1} is due to the ν_3 asymmetric stretching mode of interlayered CO_3^{2-} .

Generally, two main changes, corresponding to the alkyl chain and Si–O vibrations, would be recorded in the IR spectra of the silylated LDHs [25]. For H-Si_1 , H-Si_3 and H-Si_4 , the vibrations corresponding to – CH_2 , – CH_3 and Si–O–metal stretching modes clearly appeared in the region of 3000–2700 cm^{-1} and at ca. 1040 cm^{-1} , respectively, together with the vibration of Si–CH at ca. 1150 cm^{-1} (Figs. 1b, d and e). The typical Si–O–Si symmetric stretching are located at 1080 cm^{-1} (in cyclic structures) and above 1100 cm^{-1} (in linear structures). In this study, the Si–O–related peaks locate at lower wavenumbers, due to the d in electronegativity between Si and Mg or Al. The existence of these vibrations demonstrates that silane was successfully grafted [25] or chemisorbed [27] onto LDHs surface. With respect to H-Si_2 , a weak peak at 1540 cm^{-1} was recorded corresponding to – CH_2

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