



## The effect of acid treatment on the structure and surface acidity of tetraalkylammonium-montmorillonites

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### ARTICLE INFO

#### Article history:

Received 6 November 2012

Accepted 11 December 2012

Available online 19 December 2012

#### Keywords:

Clay mineral  
Organic surfactant  
Alkylammonium cation  
Acid-treatment  
MAS NMR spectroscopy  
Pyridine adsorption  
Infrared spectroscopy  
Acidity

### ABSTRACT

The effect of tetrabutylammonium ( $\text{Bu}_4\text{N}^+$ ) and tetrapentylammonium ( $\text{Pe}_4\text{N}^+$ ) cations on the modification of the organo-montmorillonite structure upon acid-treatment was investigated. Samples were treated with HCl for various times (2–12 h). Structural changes were followed by MAS NMR spectroscopy. The  $^{29}\text{Si}$  MAS NMR spectra of initial Na-saturated form (Na-SAz) showed gradual decrease of the intensity of the resonance assigned to  $\text{SiO}_4$  cross-linked in the tetrahedral sheets  $\text{Q}^3(\text{OAl})$  while signals arising from the reaction product  $\text{Q}^3\text{IOH}$  and  $\text{Q}^4(\text{OAl})$  became more pronounced upon acid treatment. The  $\text{Q}^3(\text{OAl})$  signal almost completely disappeared for Na-SAz treated for 8 h on contrary to  $\text{Bu}_4\text{N-SAz}$  and  $\text{Pe}_4\text{N-SAz}$  showing signal of relatively high intensity even after 12 h. The  $^{27}\text{Al}$  MAS NMR measurement proved that more than one half of Al remained in the reaction product of  $\text{Bu}_4\text{N-SAz}$  and  $\text{Pe}_4\text{N-SAz}$  after 8 h treatment, while Al content dropped below 5% for Na-SAz. Formation of acid sites was investigated via pyridine adsorption. Only physically adsorbed and H-bonded pyridine was detected for acid-untreated samples. In contrast, the IR spectra of the samples partially decomposed in HCl revealed bands of pyridine adsorbed on Brønsted acid sites. Strongly bonded pyridine was able to bear up heating even at 230 °C.

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### 1. Introduction

Clay minerals modified with organic compounds have continuously attracted the attention of researchers due to their utilization as components in functionalized organic/inorganic hybrid materials. These natural layered nanomaterials often act as inorganic counterparts for the association to molecular organic species. Among them a montmorillonite, mineral from the smectite group, is the most often studied. Layered structure of montmorillonite consists of one octahedral sheet sandwiched between two tetrahedral sheets. The tetrahedra contain mainly Si(IV) as the central atom with some Al(III) substitution, while central positions in the octahedral sheets are occupied by Al(III) partly replaced with Fe(III) and Mg(II). Non-equivalent substitution generates a negative charge on the layers balanced by hydrated exchangeable cations (mostly  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ ) present in the interlayers and on the particles edges. Naturally occurring inorganic cations can be replaced with different organic cationic surfactants, most often alkylammonium cations, by simple ion-exchange process. The organic components expand the inter-layer spacing of montmorillonite, leaving to the layers a well-defined and consistent spatial relationship to each other [1,2]. Moreover, such treatment changes

the surface properties of montmorillonites from naturally hydrophilic to more hydrophobic [3,4]. Resulting hybrid materials can be used as adsorbents for environmental applications or as precursors for polymer-clay nanocomposites (reviewed in e.g. [5–7]).

The combination of surfactant intercalation with acid activation, another method often used to modify the properties of smectites, may further extend their application potential. Acid activation of smectites consists of their treatment with a mineral acid solution, usually HCl or  $\text{H}_2\text{SO}_4$ . The main task is to obtain partly dissolved material of increased specific surface area, porosity [8–10] and surface acidity [11–13]. The extent of decomposition reaction depends on the mineral type and reaction conditions, such as the acid/clay mineral ratio, acid concentration, time and temperature of the reaction. The reaction product is amorphous partly protonated silica [14–17]. The acidifying process results in a proton rich environment which influences the uptake of organic cations to the smectite. Kooli et al. in his studies [18,19] showed that alkylammonium cations uptake to acid activated montmorillonite was related to the acid activation extent. The basal spacing upon loading of hexadecyltrimethylammonium cations to acid treated clays increased as the acid/clay ratio increased showing modification in the orientation (packing) of alkyl chains within clay layers. The  $^{13}\text{C}$  CP/MAS NMR spectra indicated that conformation of alkyl chains changed in acid treated samples from more ordered all-trans to dominant gauche disordered conformation.

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Up to date only few papers describe a reverse approach of previously mentioned treatments, i.e. acid-dissolution of organo-clays [20–27]. Breen et al. [20] in his earlier work demonstrated that a size of organic cation was very important parameter in acid treatment process. Smectites modified with large dodecyltrimethylammonium (DDTMA<sup>+</sup>) and octadecyltrimethylammonium (ODTMA<sup>+</sup>) cations showed higher stability in HCl than un-modified smectites or those exchanged with small tetramethylammonium (TMA<sup>+</sup>). Acid-activated TMA<sup>+</sup>-clays, however, showed higher activity in selected catalytic reaction not only compared to ODTMA- and DDTMA-samples but also to corresponding parent clay minerals. Further report [21] was focused on synthesis of hybrid inorganic/organic catalyst based on one organic cation TMA<sup>+</sup> and four different acid activated smectites. Smectites were simultaneously treated in the solution with TMA<sup>+</sup> and selected volumes of 12 M HCl. The ability of TMA<sup>+</sup> to compete with H<sup>+</sup> for exchange sites was assessed. Such preparation resulted in highly active catalyst TMA/H due to synergistic effect between adsorbed H<sup>+</sup> and TMA<sup>+</sup> cations. Moronta et al. [22] compared both methods i.e. samples fully exchanged with fixed amount of TMA<sup>+</sup> and displaced from the clay surface using acid treatment with method of acid and TMA<sup>+</sup> in simultaneous competition. The activity in selected reaction depended on the nature of the parent clay used and on content of TMA<sup>+</sup> and H<sup>+</sup>.

Another example of applying of acid treatment to organo-inorganic clay based hybrid materials was published by Ishii et al. [28]. Acid treatment was used for selective leaching of cationic organic surfactant together with organic part of alkoxy silanes in order to prepare porous nanocomposites. Arising products possessed high surface areas with relatively wide pore size distribution and due to presence of Si–OH group products had hydrophilic character.

In our recent studies [25,26] the acid treatment of Mg-rich montmorillonite saturated with tetraalkylammonium cations (tetramethyl-, tetraethyl-, tetrapropyl-, tetrabutyl- and tetrapentyl-) was systematically investigated using different analytical methods. The attention was paid to morphological and surface area changes [25] as well as to the structural modifications [26]. The montmorillonite containing smaller organic cations was more accessible to the acid attack than that with bulkier tetrabutyl- and tetrapentyl-ammonium cations. As indicated XRD patterns, these samples preserved their ordered layered structure even after treatment for 8 h in 6 M HCl. The specific surface area of all samples increased with progressing time of treatment and pore network was generated, although this increase was significantly hindered by the bulkier tetraalkylammonium cations. Using infrared (IR) spectroscopy in both, middle (MIR) and near (NIR) regions the release of organic cations, the alteration of the montmorillonite structure and creation of reaction product were followed. A magnitude of the shift of SiO stretching band to higher positions and the intensity increase of the band at 7315 cm<sup>-1</sup> assigned to SiOH overtone reflected the extent of organo-montmorillonite decomposition and creation of reaction product, protonated amorphous silica. Despite the valuable results obtained in previous works, further deeper insight into the structural changes of montmorillonite upon its decomposition in HCl and on the stability or disintegration of longer alkyl-chains in alkylammonium cations would be of importance mainly with respect to the preparation of tailored hybrid materials based on clay minerals. Moreover, the SiOH groups are supposed to be active sites for adsorption or other processes therefore their better characterization could bring new information on the activity of prepared materials.

To fulfill such objectives the <sup>29</sup>Si, <sup>27</sup>Al, and <sup>13</sup>C MAS NMR spectroscopies were used to characterize in detail the structural alteration of the tetrabutylammonium and tetrapentylammonium montmorillonite by acid attack. The FTIR spectroscopy was used to characterize the possible acidity of materials through the adsorption of pyridine.

## 2. Experimental

### 2.1. Materials

All chemicals i.e., sodium chloride, pyridine, tetrabutylammonium (Bu<sub>4</sub>N) and tetrapentylammonium (Pe<sub>4</sub>N) bromide were used as received.

Montmorillonite (SAz) was separated from the bentonite SAz-1 (Cheto, Arizona, USA), obtained from the Source Clays Repository of The Clay Minerals Society. The clay was suspended in distilled water, Na-saturated by repeated treatment with 1 M NaCl, and the <2 μm fractions were collected. The excess ions were removed by washing with distilled water. The sample (Na-SAz) was dried at 60 °C and ground to pass a 0.2 mm sieve.

To prepare organoclays 1 M solution of organic salt was directly added into the prepared suspension of Na-montmorillonite. The molar amount of organic salt was equal to the three fold excess of montmorillonite's cation exchange capacity (CEC). The suspension of montmorillonite and organic salt was stirred overnight at 70 °C. The excess of the alkylammonium salt was removed by repetitive washing with distilled water until an AgNO<sub>3</sub> test indicated the absence of halide anions. The samples were dried at 60 °C.

The Na-SAz and organo-modified samples were treated in 6 M HCl at 80 °C using different reaction times (2–12 h). Due to very fast decomposition of Na-SAz the 8 h was selected as the longest treatment time, while for organo-montmorillonites 12 h decomposition was also performed. Acid treated samples are denoted as e.g. Na-SAz-8h or Bu<sub>4</sub>N-SAz-8h. After acid treatment, the solid products were filtered, washed with distilled water and dried.

#### 2.1.1. Pyridine adsorption experiments

The pyridine adsorption experiments were performed on selected samples from Na-SAz and Bu<sub>4</sub>N-SAz series. Samples were dried overnight at mild temperature (50 °C) prior pyridine adsorption. Afterwards they were placed in desiccator and exposed to pyridine vapor for 48 h. To determine the presence of acid sites DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra were measured. Later, the samples were heated at temperature 110, 170, 230 °C and the IR spectra were again collected. While DRIFT technique is not designed for quantitative measurements, only positions (not intensities) of the bands were evaluated. Samples after pyridine adsorption were subjected also to the thermal analysis measurements.

### 2.2. Methods and techniques

The high-resolution solid-state NMR measurements were carried out on a 400 MHz Varian solid-state NMR spectrometer (Palo Alto, CA, USA).

The <sup>29</sup>Si NMR spectra were recorded at the resonance frequency of 79.43 MHz with the use of 4 mm rotors and magic angle spinning frequency of 10 kHz. In magic-angle-spinning (MAS) measurements (without <sup>1</sup>H-decoupling) the time of π/2 pulse was 4.5 μs, recycling times 30 s, acquisition time 20 ms.

In <sup>29</sup>Si CP MAS NMR (CP = cross polarization) experiments the Hartmann–Hahn condition was obtained with the radio frequency field strength of 70 kHz, at 5 ms contact time and relaxation delay between two consecutive scans 3 s. The high power proton-decoupling field of 93 kHz was applied during data acquisition. Tetrakis (trimethylsilyl) silane was used as an external reference and chemical shifts of <sup>29</sup>Si are referred to TMS.

The <sup>27</sup>Al MAS NMR spectra were recorded at the resonance frequency of 104.19 MHz and sample spinning frequency of 12 kHz. Time of π/2 pulse was 2.1 μs, recycling times 0.3 s and acquisition

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