



Near-infrared study of the interaction of pyridine with acid-treated montmorillonite



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ABSTRACT

The effect of acid treatment of montmorillonite on the creation of acid sites was investigated by near infrared (NIR) spectroscopy using pyridine as a probe molecule. Na-form of SAz-1 montmorillonite was treated in HCl for 2–8 h. Gradual decrease of the intensities of the bands related to structural OH groups reflected the release of the octahedral atoms from Na-SAz upon protons attack. A new band near 7315 cm^{-1} due to SiOH overtone confirmed the formation of protonated silica. After exposure of the Na-SAz to pyridine vapors the intensity of the $(\nu + \delta)_{\text{H}_2\text{O}}$ band diminished indicating the partial replacement of water molecules by pyridine. Disappearance of the SiOH band in the spectra of acid-treated samples revealed that silanol groups as weak Brønsted acid sites formed H-bonds with pyridine-nitrogen. After pyridine adsorption, its CH overtone band ($2\nu_{\text{CH}}$) appeared near 6000 cm^{-1} . For examining the strength of the pyridine bonding, samples were heated up to $230\text{ }^\circ\text{C}$. The re-appearance of the 7315 cm^{-1} band and decreased intensity of the $2\nu_{\text{CH}}$ overtone confirmed the release of the H-bonded pyridine molecules. Almost complete loss of pyridine band was observed for Na-SAz-py and for the 8 h treated sample heated above $170\text{ }^\circ\text{C}$, while a well-resolved $2\nu_{\text{CH}}$ band, but shifted to higher wavenumbers, was still present in the spectra of the samples dissolved in HCl for 2 and 4 h. Partly leached acid-montmorillonite provided protons for generation of pyridinium cations. The bands at 6096 and 6065 cm^{-1} observed in the spectra of SAz-2 h-py and SAz-4 h-py heated at $230\text{ }^\circ\text{C}$ were assigned to the C–H vibrations of pyridinium cations. The results showed that NIR spectroscopy can distinguish between different pyridine species on montmorillonite surface.

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1. Introduction

Montmorillonite is a nano-sized clay mineral with a layered structure consisting of two tetrahedral sheets linked to an octahedral sheet. Due to the high surface area, cation-exchange capacity and surface acidity montmorillonites are widely used as adsorbents, catalytic supports or catalysts [1–6]. The surface of montmorillonite can be populated by Brønsted acid (BA) and/or Lewis acid (LA) sites. Contributors to Brønsted acidity are water molecules coordinated to exchangeable cations and hydroxyl groups at crystal edges, the Lewis acid sites are associated with unsaturated central atoms at crystal edges or with bare exchangeable cations themselves (especially transition metal ions). The main acidity in montmorillonites, however, comes from water molecules (proton donors) polarized more or less by exchangeable cations [7–11].

The interaction of montmorillonite with inorganic acids, often called acid activation, significantly changes its properties including surface area, porosity and acidity [12–21]. Upon acid treatment protons substitute the exchangeable cations and attack the structural OH groups. The resulting dehydroxylation is connected with successive depopulation of the octahedral sheets and transformation of the tetrahedral sheets into a three-dimensional framework. The final reaction product contains mainly protonated amorphous silica [22]. The surface acidity of montmorillonites largely depends on the extent of the structural modifications; therefore, it is important to monitor the nature of acid sites formed during this process. A combination of different techniques such as potentiometric titration, adsorption of base molecules followed by gravimetric or volumetric methods, temperature programmed desorption of nitrogen-containing bases including ammonia, butylamine or pyridine, or catalytic test reactions have been used to characterize the acidity of montmorillonite surface [23–30].

Another powerful technique allowing studying the surface acidity of clay minerals is infrared spectroscopy in the mid-IR (MIR) region capable to distinguish vibrational modes of base

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molecules adsorbed on different acid sites. Among the probe molecules routinely used, pyridine has certainly been the most employed [7,17,31–36]. Pyridine as a base of moderate strength can be physically and/or chemically adsorbed on the montmorillonite surface. Chemisorbed pyridine can either form hydrogen bonds between pyridine nitrogen atom and OH groups of clay minerals, can accept proton and create pyridinium cation at strong Brønsted acid sites (i.e., from polarized water molecules), or can be coordinately bound through pair of electrons on nitrogen atom to Lewis acid center (e.g., Al^{3+} cations). These various species are easily identified and distinguished by examination of the 1700–1400 cm^{-1} region, where the absorption bands related to ring stretching vibrations (skeletal modes) of pyridine are located. In the spectrum of liquid pyridine, bands near 1600, 1580, 1480 and 1440 cm^{-1} were identified. As a result of H-bonds between pyridine and weak BA sites, the ring vibrations are slightly shifted and diagnostic bands appear near 1445 and 1590 cm^{-1} . When pyridine is protonated, a diagnostic N^+H deformation band of pyridinium cation appears near 1545 cm^{-1} ; otherwise, when it coordinates LA sites, characteristic bands are observed near 1455, 1490, 1580 and 1620 cm^{-1} [6,37–40].

MIR spectroscopy and pyridine as a probe molecule were used to investigate the formation of different active sites on the HCl-treated Na-SAZ montmorillonite [41]. The diffuse reflectance spectra of acid-untreated montmorillonite and an 8 h treated sample, i.e., a sample containing mainly amorphous silica, showed only bands characteristic for skeletal modes of physically adsorbed and H-bonded pyridine. In contrast, the IR band near 1540 cm^{-1} observed for 2 and 4 h treated samples, i.e., samples with partially decomposed structure, confirmed the presence of strong Brønsted acid sites. Strongly bonded pyridine was able to bear up heating even at 230 °C.

The investigations of the interaction between pyridine and montmorillonite have been limited to mid-infrared spectroscopy so far. However, over the last years near IR (NIR) spectroscopy has proved to be a convenient, fast, efficient, and non-destructive method for the investigation of chemical composition and structure of clay minerals [42–45], their modification during acid treatment [46–49] or their interactions with organic species [50–53]. On the other hand, the interaction of pyridine with acid-treated clay minerals has not been studied by NIR spectroscopy. To our best knowledge, only the paper [54] reports the utilization of NIR spectra for characterization of pyridine adsorption on Laponite (trioctahedral clay mineral) and Laponite-derived porous clay heterostructures (PCH). The experiments, aimed mainly on the differentiation of silanol groups in PCH, showed modification of the SiOH band intensity as a result of pyridine bonding on these sites.

The objective of this work was to extend our previous study [41] and to analyze the NIR spectra of pyridine adsorbed on untreated and acid-treated SAZ montmorillonite. The main intention was to examine the potential of NIR spectroscopy to distinguish different pyridine species adsorbed on the montmorillonite surface. The effect of the mineral structure modification on the formation of acid sites was discussed together with the strength of the pyridine bonding on the montmorillonite surface.

2. Material and methods

2.1. Samples preparation

The samples used in this study were prepared by the same procedure as reported in Ref. [41]. Montmorillonite was separated from the SAZ-1 bentonite from Cheto (AZ, 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 fraction with particles $<2 \mu\text{m}$ was collected.

The excess ions were removed by washing with distilled water. The Na-SAZ sample was dried at 60 °C and ground to pass a 0.2 mm sieve.

Na-SAZ was treated in 6 M HCl at 80 °C for 2, 4, and 8 h. Afterwards, the solid products were filtered, washed with distilled water and dried. Acid treated samples are denoted as SAZ-2 h, SAZ-4 h and SAZ-8 h.

In addition, Na-SAZ montmorillonite was saturated with pyridinium salt prepared by the reaction of anhydrous hydrogen chloride gas with pyridine dissolved in cyclohexane. For the preparation of pyridinium-montmorillonite ($\text{Py}^+\text{-SAZ}$), the solvent intercalation process was used. Sodium montmorillonite (1 g) was added to 100 cm^3 of distilled water and the suspension was kept under stirring for 24 h at a room temperature to ensure the Na-SAZ was adequately exfoliated. Consequently, the calculated volume (1.2 mmol corresponding to 100% cation exchange capacity (CEC)) of 1% aqueous solution of above mentioned pyridinium chloride was slowly added by a flowrate of 1 $\text{cm}^3 \text{min}^{-1}$ to the suspension at laboratory temperature (25 °C), and the mixture was vigorously stirred for 24 h. After the reaction, the suspension was centrifuged, and the final product was washed five times with 250 cm^3 of distilled water to remove excessive water-soluble pyridinium and inorganic (NaCl) salts. Saturation with pyridinium chloride was repeated three times in order to achieve a highest possible loading. The carbon elemental analysis of washed $\text{Py}^+\text{-SAZ}$ sample confirmed almost quantitative replacement (98% of CEC of SAZ) of Na^+ by Py^+ in the SAZ montmorillonite.

2.2. Pyridine vapor adsorption

For the pyridine adsorption experiments all samples were dried overnight at 100 °C and then placed in a glass chamber with pyridine vapors for 48 h at 25 °C. The samples are denoted as Na-SAZ-py, SAZ-2 h-py, SAZ-4 h-py, SAZ-8 h-py and $\text{Py}^+\text{-SAZ-py}$. Desorption of pyridine was achieved by heating of the samples for 1 h at 110, 170, 230 °C.

2.3. Infrared spectroscopy

The infrared spectra in the mid-IR and near-IR regions were obtained by a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer from Thermo Scientific. The KBr pressed disc technique (1 mg of the sample + 200 mg KBr) was used to obtain spectra of untreated and acid-treated samples in the 1400–400 cm^{-1} region. The smart diffuse reflectance accessory (DRIFT) from Thermo Scientific was utilized to acquire all spectra of the samples with adsorbed pyridine. The spectra of the samples with adsorbed pyridine were measured immediately after their removal from the pyridine vapor chamber or after heating at temperatures at 110, 170, 230 °C.

Spectra were obtained by co-addition of 64 scans at a resolution of 4 cm^{-1} . Spectral manipulations were performed using the Thermo Scientific OMNIC™ software package. The second derivatives using a Norris derivative filter with OMNIC default parameters (segment length 5, gap between segments 5) were used to find the location of the bands appearing in the spectra as shoulders. The band component analysis of the $\nu_{\text{Si-O}}$ and $2\nu_{\text{CH}}$ regions was undertaken by the Jandel PeakFit™ software package using Gauss–Lorentz functions ($R^2 < 0.9995$).

3. Results and discussion

3.1. MIR region: acid treatment

Upon HCl treatment the layered structure of Na-SAZ montmorillonite was gradually decomposed and protonated amorphous

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