



SÚŤAŽ MLADÝCH PRACOVNÍKOV DO 35 ROKOV  
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**ABSTRAKTY**

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# **FRET and Poisson probability density function model as the tools to describe the dye surface concentration in hybrid materials with smectite**

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Hybrid nanomaterials based on layered silicates and laser dyes often exhibit outstanding optical and photophysical properties. However, the photoactivity of such hybrid materials is strongly dependent on the dyes concentration on the clay surface. High dyes concentrations often lead to formation of supramolecular assemblies with reduced photoactivity. Considering high sensitivity of Förster resonance energy transfer (FRET) on the distance between the interacting particles FRET was used to obtain the main distances between dyes molecules adsorbed on the clay mineral surface. FRET could be easily determined experimentally using steady-state and time-resolved fluorescence spectroscopies. Using these techniques FRET efficiency was found to increase with the concentration of the adsorbed dye molecules. The experimental results were supplemented with the Poisson probability density function model. The model was applied to describe the characteristics of the dye molecules distribution on the Sap particles. High concentrations of dye cations on the surface of saponite led to a relatively narrow distribution of distances, whereas lower concentrations were characterized by a broader distribution of distances. The expected values of FRET efficiencies were calculated as a function of the intermolecular distances. The theoretical and experimental results of FRET efficiencies were in good agreement. The theoretical model presents a good tool to predict photophysical properties of hybrid systems based on organic dyes and inorganic nanoparticles. The statistical approach to characterize the distance distribution between dye cations adsorbed on the clay mineral surface brought a considerably higher accuracy than a simpler model using average intermolecular distances.

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## Preparation of thin layers of TiO<sub>2</sub> on organic and inorganic substrates

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This work is devoted to the preparation of thin TiO<sub>2</sub> layers and to the study of their photocatalytic properties. Compact and nanotube layers were prepared by sol-gel method and oxidative anodization, respectively, on different substrates such as silicon, titanium foil and flexible Kapton® polyimide tape. The photocatalytic properties were studied by the ability of TiO<sub>2</sub> layers to degrade an organic dye (Rhodamine B) under UV irradiation.

The prepared TiO<sub>2</sub> thin layers were characterized by XRD and SEM in order to study their crystalline phase composition, morphology and thickness, respectively. The diffractograms confirmed that all the prepared layers contained TiO<sub>2</sub> anatase phase after annealing at 450 °C. SEM observations showed that the sol-gel layers had a dense structure while TiO<sub>2</sub> nanotubes had higher active surface area. The thicknesses of sol-gel and nanotube layers were in the range of 400-500 nm and 1400-1660 nm, respectively.

The photocatalytic activity studies of thin TiO<sub>2</sub> layers showed that TiO<sub>2</sub>NTs had better efficiency in the degradation of RhB than the sol-gel layers. This can be explained by the much higher active surface area of TiO<sub>2</sub>NTs. Concerning the effects of different substrates, TiO<sub>2</sub> layers deposited on Si showed better degradation rate of RhB compared to other substrates. These differences can be explained by the properties of each substrate. Kapton® is hydrophobic, therefore, it was necessary to etch its surface with KOH solution before the sol-gel preparation of TiO<sub>2</sub> layers. Despite better adhesion of TiO<sub>2</sub> layers to the etched substrate a certain delamination was observed. When the surface of Kapton® was modified by plasma, only very thin TiO<sub>2</sub> layers with lower total surface area were successfully deposited. Although the TiO<sub>2</sub>NTs prepared by anodic oxidation of sputtered Ti layers on Kapton® were homogeneous but during annealing of tapes at 450 °C they had a tendency to roll.

Despite the observed differences in the photocatalytic activities of TiO<sub>2</sub> layers prepared by sol-gel or anodic oxidation, it can be concluded that Kapton® is a promising substrate with potential environmental and medical applications. However, further research is necessary for the deposition of TiO<sub>2</sub> layers on flexible Kapton tape to make it attractive for industrial applications.

# Processing of ZrB<sub>2</sub>-based ultra-high temperature ceramics

Zuzana Fördósová

A new diboride material for extreme applications was developed by introducing the Lu<sub>2</sub>O<sub>3</sub> sintering additive into the well-known and commonly used ZrB<sub>2</sub> – 25vol. % SiC material system, with the aim to improve mechanical properties of ZrB<sub>2</sub>-SiC ceramics, especially the high temperature properties. A variety of the ceramic powder mixture preparation routes and their effect on the densification and sintering of the ZrB<sub>2</sub>-based materials were investigated. A systematic and thorough study of the effect of ball milling parameters on the particle size was conducted. The two most promising ball milling conditions were selected with regards the appropriate particle size ( $\leq 1 \mu\text{m}$ ) and the acceptable level of WC contamination ( $\leq 3 \text{ wt.}\%$ ). The positive effect of such a powder preparation was confirmed by the sedimentation tests, as the milled powders showed significantly better stability in both isopropylalcohol and water based solutions than the as-received powder. The influence of different amounts of the Lu<sub>2</sub>O<sub>3</sub> additive on the sintering behaviour, microstructural and phase evolution of the ZrB<sub>2</sub>-SiC with two different initial particle sizes was investigated. The sintering process was optimised and all materials reached the theoretical density when sintered using a field assisted sintering technology at 2050°C / 90 MPa / 7 min/ Ar. Some of the basic mechanical properties, such as hardness, strength and fracture toughness were determined for the fully dense sintered materials. The mechanical properties of the newly-developed ZrB<sub>2</sub>-SiC-Lu<sub>2</sub>O<sub>3</sub> system were compared to the reference ZrB<sub>2</sub>-25vol.% SiC system.

# **Rheological Optimization of Water Based Silicon Nitride Tape Casting Suspensions for Biomaterial Production**

Hakan Ünsal

## **Abstract**

In this study, the water-based ceramic solutions of Si<sub>3</sub>N<sub>4</sub> material, which has a great potential as a future biomaterial, were prepared for the tape casting process and their dispersion parameters were investigated. The properties of the water-based Si<sub>3</sub>N<sub>4</sub> suspensions was optimized by investigating the effect of the parameters, such as pH value, dispersant ratio, dispersing medium, binder and plasticizer amounts, on the rheological behaviour of the suspensions. The most appropriate way of the preparation of water-based Si<sub>3</sub>N<sub>4</sub> solutions for green body tapes of Si<sub>3</sub>N<sub>4</sub> was proposed and verified.

## Modification of Si<sub>3</sub>N<sub>4</sub> surface for enhancement bioactivity

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Silicon nitride-based ceramics are characterized especially by high chemical resistance, combination of fracture toughness, hardness and tribological properties. These properties are important for applications such as cutting tools, ball bearings, and combustion engine components. Silicon nitride also attracts interest for bio-applications in the human body as a biomaterial. However, the biological applications require additional properties, as bioactivity, to enable stronger bonding to the host tissue. This work deals with possibility of surface modification of dense silicon nitride substrate with goal to achieve bioactive, continuous layer with interconnected porosity and strong adhesion to substrate on the surface of dense sample. Substrate was prepared from commercial Si<sub>3</sub>N<sub>4</sub> and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> powders. Before sintering mixture of powders (Si<sub>3</sub>N<sub>4</sub> 95 and 90 wt %, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> 5 and 10 wt %) was homogenized and sieved. Sample was prepared by hot pressing and was almost fully dense (98,3 %, 98,8 % TD). Prior a further treatment the samples were cutted and polished.

The oxidation behaviour of Si<sub>3</sub>N<sub>4</sub> ceramics is process (annealing at temperatures from 1000 to 1600°C) witch markedly changed a surface. For our purpose was used oxyacetylene torch for thermo-oxidative treatment of substrate surfaces using different temperatures and times (1350 °C 60, 120, 180 s, 1450 °C 60 s and 1550°C 60 s).

Formation of porous, continuous layer on surface of dense sample was confirmed (see. Fig. 1.)

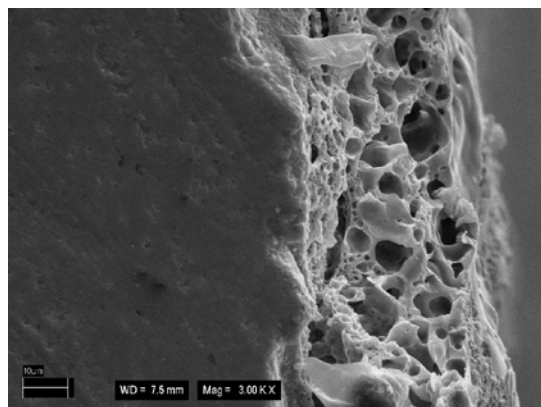


Fig. 1 Crossection of sample (90 wt % Si<sub>3</sub>N<sub>4</sub>, 10 wt % Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) after oxyacetylene torch treatment 1550°C 60 s

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# Metal-organic framework UiO-66 for organophosphate catalytic degradation in aqueous environment

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Porous coordination polymers, known as metal-organic frameworks (MOFs), are a developing class of materials with advantageous properties (e.g., high surface area, sorption of gasses, catalytic activity, etc.). These crystalline porous materials are composed of metal (oxo)clusters, which are connected by organic linkers (ligands).

Zirconium-based MOFs (Zr-MOFs) were recently investigated as catalysts for degradation of organophosphate toxic compounds such as pesticides or chemical warfare agents.[1] The most often utilized Zr-MOF for this purpose, UiO-66, is composed of  $Zr_6O_4(OH)_4^{12+}$  secondary building units connected by 12 terephthalate linkers. The detailed studies led to a conclusion that the catalytic activity of the UiO-66 is related to a number of defects in the structure. The defects, especially missing linkers, are replaced by a modulator instead of the terephthalate linker, and in aqueous environment the modulator or coordinated water is substituted by organophosphate compounds, which are hydrolyzed.

Here we report on the evolution of the UiO-66 stability in water with various pH values and we correlate it with catalytic activity towards degradation of methyl-paraoxone. In general, the number of defects is controlled by reaction conditions used for the UiO-66 synthesis and this number is believed to be related to the catalytic activity. Using HPLC, we developed a method enabling to quantify the amount of leached terephthalate linker and monocarboxylic acids modulator, indicating that UiO-66 is changing considerably in the course of the reaction. Thus, the activity of UiO-66 evolves in real environment and cannot be directly related to the initial amount of defects. Moreover, we show that UiO-66 is stable only in acidic environment (pH < 5.0). In alkaline environment with pH above 9.5, the UiO-66 structure completely collapses. The catalytic degradation of methyl-paraoxone is fastest in the pH range 7 - 8.5, corresponding to the region where a substantial amount of the terephthalate linker is released; however, the structure of UiO-66 is not substantially damaged. Thus, the stability of UiO-66, expressed by the amount of the linker released, is related to the *in situ* formation of new catalytic sites and, in turn, it is in agreement with the course of methyl-paraoxone degradation.

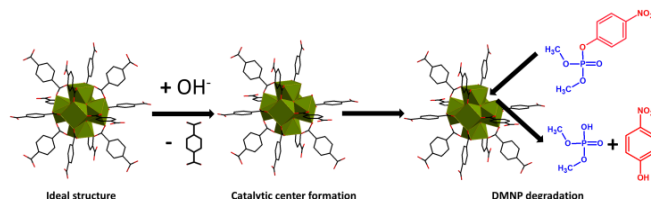


Fig. 1 Formation of the new catalytic center responsible for methyl-paraoxone degradation.

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## Corrosion of SiC in FLiNaK melt

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The molten fluoride salts are possible coolants for Gen IV. nuclear reactors due to smaller equipment size, because of the higher volumetric heat capacity of the salts, and the absence of chemical exothermal reactions between the reactor intermediate loop coolant and power cycle coolant. This concept will employ LiF-BeF (67-33 mol. %) (FLiBe) as primary coolant and either LiF-NaF-KF (46.5-11.5-42 mol. %) (FLiNaK) or KF-ZrF (58-42 mol. %) as its intermediate. Silicon carbide ceramic found wide range use as abrasive or cutting tools, bulletproof protection, brake discs in automobiles, crucibles for melting metals, electronic circuit elements or nuclear fuel in Pebble Bed Reactor. A layer of silicon carbide gives coated fuel particles structural support and is the main diffusion barrier to the release of fission products. In our work the corrosion of SiC conductive ceramic material was carried out by static corrosion tests. Experiments were performed in molten LiF-NaF-KF (46.5-11.5-42 mol. %) at 700°C for 100, 200 and 500 hours and at 1000°C for 100 hours. After the corrosion tests, the samples were analyzed by SEM-EDX, XRD and XRF. The SEM evaluation showed the increasing of the corrosion layer depth. Whereas on the sample corroded 100 hours the corrosion layer has thickness in average around 60 μm, the samples corroded 200 and 500 hours had corrosion layer in the range 150-170 μm. The samples revealed uniform intergranular character with negligible dimensional changes.

# Arrangement of the primary alkylammonium cations in the interlayers of montmorillonite

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Keywords: near-infrared spectroscopy, organoclays, conformation, alkyl chain, *gauche*, *trans*

Infrared (IR) spectroscopy is one of the most commonly used methods for characterization of organoclays. Their behaviour and properties strongly depend on the structure and arrangement of the intercalated organic cations (surfactants) in clay mineral interlayers. Most often, the arrangement/conformation of tetraalkylammonium cations has been discussed in the literature. The objective of this paper, in contrary, was to study the conformation of surfactants prepared from a series of primary amines. Such studies appear in the literature only exceptionally.

The organo-montmorillonites were prepared from a Na-saturated  $<2 \mu\text{m}$  fraction of bentonite Jelšovský Potok (JP, Slovakia) and alkylammonium ( $\text{C}_n\text{-NH}_3^+$ ) salts with increasing length of alkyl chain from C5 to C19. The X-ray diffraction analysis showed basal spacing ( $d_{001}$ ) in the range 1.35–1.95 nm (C5-JP – C19-JP) in dependence on the alkyl chain length. The basal spacing was almost the same ( $\sim 1.33 - 1.37$  nm) for montmorillonite saturated with C5 – C8 cations suggesting a monolayer arrangement. With further increase of the alkyl chain length the  $d_{001}$  values gradually increased from 1.41 nm (C9-JP) through 1.75 nm (C14-JP), 1.83 nm (C16-JP) to 1.95 nm (C19-JP), indicating consecutive transitions from monolayers to bilayers and pseudotrimolecular layer arrangement.

IR spectroscopy in the middle-IR (MIR) and near-IR (NIR) regions was further used to follow the conformation of the cations. The positions of the absorption bands related to the stretching vibrations ( $\nu\text{CH}_2$ ) and the first overtone ( $2\nu\text{CH}_2$ ) of the methylene groups were found to be very sensitive to the alkyl chain arrangements. The MIR spectra of organo-montmorillonites showed a gradual replacement of the asymmetric  $\nu_{\text{as}}\text{CH}_2$  and symmetric  $\nu_{\text{s}}\text{CH}_2$  stretching bands from 2935 to 2925  $\text{cm}^{-1}$  and from 2858 to 2851  $\text{cm}^{-1}$ , respectively. A shift towards lower wavenumber with increasing alkyl chain length confirmed a transition from disordered (*gauche*) to more ordered (all-*trans*) conformers of the surfactants. The NIR spectra of organo-montmorillonites showed a broad complex band related  $2\nu\text{CH}$  in the 6100–5600  $\text{cm}^{-1}$  and band related  $(\nu+\delta)\text{H}_2\text{O}$  in the 5300–5100  $\text{cm}^{-1}$  region. With the increasing number of  $\text{CH}_2$  groups in alkyl chain the intensity of the  $(\nu+\delta)\text{H}_2\text{O}$  band gradually decreased indicating an increase in samples hydrophobicity. The positions of the  $2\nu_{\text{as}}\text{CH}_2$  band was shifted from 5829 to 5787  $\text{cm}^{-1}$  with increasing the alkyl chain length suggesting the transition from disordered liquid-like to more ordered solid-like structures of the surfactants. The most significant shift of the bands was observed between samples C10 and C11 (10  $\text{cm}^{-1}$ ), indicating critical point of length dependent conformational change. The magnitude of the overall shift of  $2\nu_{\text{as}}\text{CH}_2$  (42  $\text{cm}^{-1}$ ) was significantly higher than those observed for  $\nu_{\text{as}}\text{CH}_2$  (10  $\text{cm}^{-1}$ ), showing the NIR spectroscopy to be very suitable for studying the conformation of surfactants in organo-clays.

# **The influence of the preparation method of Cerium oxide nanoparticles on its properties**

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Cerium oxide is a relatively widespread material with many applications in the industry, for example polishing or scouring of glass. It is also the most important heterogeneous catalysts. In recent years, its interactions with biologically relevant systems and related applications in medicine, as well as newly discovered and unexpected physical properties, such as its ferromagnetic behaviour at high (room) temperatures, have been extensively investigated. These newer applications of cerium oxide are usually based on the use of so-called nanocrystalline forms of cerium oxide (nanoceria). For these materials, which are able to mimic the effects of enzymes in living organisms, the term inorganic enzymes or nanozymes is used. Several processes for the preparation of active forms of cerium oxide have been developed at the workplaces of UJEP and UACH. Some of these forms have the ability to decompose highly toxic compounds such as organophosphorus pesticides or even structurally similar neural paralytic chemical warfare agents such as sarin, soman or VX.

A number of types of cerium oxide have been prepared and detailed characterization carried out using a wide range of physico-chemical methods such as XRD, DTA, BET and HRTEM. The aim was to find the relationship between the cerium oxide production process and its physicochemical properties. Samples of cerium oxide with defined properties was then tested for their efficacy at the mentioned application (degradation activity).

## Atrazine-Beidellite intercalates: a DFT study

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One of the most employed pesticides in the last century is an atrazine (A). It has a negative impact on the environment such as soil and ground water<sup>1</sup>. Clay minerals, e.g. montmorillonite or beidellite are suitable candidates to immobilize organic contaminant, like atrazine. These clays are highly hydrophilic and consequently show very limited adsorption capacities for hydrophobic organic contaminants. However, a higher adsorption of organic molecules/cations can be obtained by modifying of the clay surface by organic surfactants. Beidellite (Bd) is aluminosilicate with predominant substitutions in tetrahedral sheets. This charge distribution improves a stability of prepared organoclays<sup>2</sup>. This study aims the characterization of the interactions in the interlayer space of Bd, the way of keying of atrazine to Bd structure and analysis of the bands of IR spectra by means of calculated vibrational modes.

The Density Functional Theory (DFT) D3 method with involved dispersion corrections<sup>3</sup> was used for study of interactions in the atrazine-beidellite (A-Bd) structures. Three models were proposed for the study: A intercalated in the Bd (A-Bd), the tetramethylphosphonium cation (TMP) as organic surfactant intercalated in the Bd (TMP-Bd), and both, A and TMP cation, intercalated in the Bd (ATMP-Bd). The analysis of results revealed e.g. that in the optimized A-Bd and ATMP-Bd model structures the atrazine has a flatty arrangement in Bd interlayer space. The interactions that form the intercalates are mostly weak hydrogen bonds. Calculated vibrational spectra obtained from *ab initio* molecular dynamics calculations were analyzed in detail and compared with measured FTIR spectra to resolve the problematic part of measured spectra.

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# Preparation, characterization and oxidation behavior of polymer derived ceramic coatings with passive fillers

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The work is aimed at the development of an oxidation/corrosion resistant environmental barrier coating system on steel substrates. The slurry preparation as well as processing route, filler systems and microstructure of the coating system were optimised. The PDC system consists of two layers that were consecutively applied to stainless steel (AISI 441) substrates. The bond-coat was prepared from pre-ceramic polymer perhydropolysilazane (PHPS) by dip-coating of the metal sheets. The optimized composite top-coat was prepared from the ceramic matrix forming polysilazane HTT 1800 precursor, filled with YSZ and Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> powder as passive fillers, and the commercial barium silicate glass particles (G018-311, G018-385, Scott AG) as sealing agents. The resulting mixture was applied onto bond-coat by spray coating technique and the curing of the composite coatings was performed in air at the temperature of 800 °C with a holding time of 1 h. After pyrolysis in air, uniform and crack-free composite coatings on stainless steel with a thickness up to 90 µm were prepared. High temperature oxidation tests were carried out in a high temperature horizontal electric tube furnace at the temperatures of 900 °C, 950 °C and 1000 °C and the exposure times in the range of 1 – 48 hours in flowing atmosphere of synthetic air. X-Ray diffraction along with SEM/EDS analysis confirmed extensive corrosion of the uncoated stainless steel accompanied by formation of oxide layer comprised Cr<sub>2</sub>O<sub>3</sub> sub-layer and Mn-Cr spinel crystals top layer. The tested coating provides effective protection from oxidation at 900 °C and 950 °C, while no significant corrosion damage was observed.

**Keywords:** polymer-derived ceramics, passive filler, environmental barrier coating, high-temperature oxidation

# Preparation and study of microstructure of Yttria and Ceria stabilized tetragonal Zirconia polycrystals for dental applications.

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The excellent mechanical properties of zirconia-based materials combined with their superior aesthetics and biocompatibility characteristics have encouraged their application as bioceramics, particularly in the dental field. Yttria stabilized zirconia ceramics (Y-TZP) compared to other bio ceramics is characterized by its superior flexural strength and high fracture toughness, thus becoming very interesting materials for dental applications. However, this ceramic can undergo Low Temperature Degradation (LTD), which refers to a spontaneous zirconia phase transformation from the metastable tetragonal (t) phase to the stable monoclinic (m) form that can cause micro-cracking, loss of strength, roughness increase and the device destructio. For this reason, research focused on ceria-stabilized zirconia (Ce-TZP) is gaining a lot of interest. The overall aim of this work was the preparation of two different zirconia ceramics material stabilized in their tetragonal form by 3mol% of Yttria (3Y-TZP) and 12mol% of Cerria (12Ce-TZP), study the different sintering paramaters and their influence of the phase transformation, density and microstructure. 3Y-TZP and 12Ce-TZP powders after freeze granulation an freeze drying by 48h were subjected to unaxial pressing with the pressure of 50MPa and then to Cold Isostatic pressing with the pressure of 350MPa. Prepared materials were sintered at three different temperatures 1300°C, 1400°C and 1450°C with the dwell time 2h. After sintering the phase and microstructure analysis were carried out. The aim of the experiments is to select the best sintering method in order to obtain the finest microstructure of prepared Y-TZP and Ce-TZP ceramics and to evaluate their resistance to Low Temperature Degradation (LTD) and corrosion in acidic environment.

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# Montmorillonite intercalated with acetylcholine and choline – a comparison of computational and experimental results

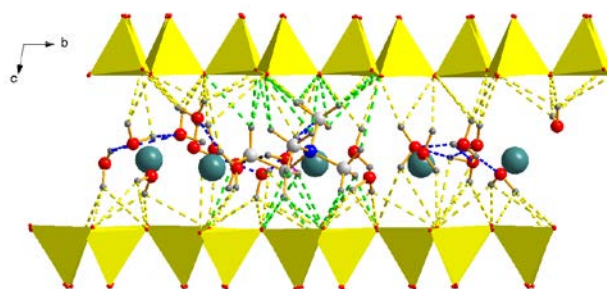
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In the last two decades, organoclays intercalated with organic cations were intensively studied on the theoretical and experimental level. Montmorillonite, representative of smectite family, is widely used to prepare organoclays because of their excellent properties and various chemical interactions (EZQUERRO et al., 2015).

This work is focused on the experimental and theoretical study of four organoclays – montmorillonite (Mt) intercalated with acetylcholine (AC) and choline (C) in hydrated (hAC-Mt and hC-Mt) and dehydrated (dAC-Mt and dC-Mt) form, respectively (as example see **Figure 1**). The models of the organoclays were studied by means of the density functional theory (DFT) method. DFT calculations were performed with involving dispersion corrections using a D3 scheme, which was taken as recommended for the PBE functional (GRIMME et al., 2010). The results from calculations were compared with measured experimental data.



**Figure 1:** Scheme of weak hydrogen bonds in the hC-Mt model.

The structural analysis of all optimized models shows that the organocations have a quasi-planar arrangement in the interlayer space of Mt. The interactions of  $[\text{Na}(\text{H}_2\text{O})_4]^+$  and AC/C cations in the interlayer space of Mt form weak hydrogen bonds for both, dehydrated and hydrated forms. The vibration modes of dAC/C-Mt were identified from calculated spectra and compared with experimental measurements.

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