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Chemically modified smectites

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ABSTRACT: This paper summarizes recent results obtained on chemical modifications of smectites. These include replacement of exchangeable cations with protons, a process connected with smectite autotransformation – attack of protons on the layers and liberation of central atoms from the octahedral and tetrahedral sheets, causing modification of the acid sites on the particles. More severe modifications occur during dissolution in inorganic acids, when the layers are dissolved and three-dimensional amorphous silica is formed. The negative charge on the smectite layers can be increased via reduction of structural Fe(III) to Fe(II) or decreased via fixation of small exchangeable cations, such as Li^+, upon treatment at elevated temperatures. Heating for 24 h at different temperatures between 100 and 300°C leads to a series of chemically similar materials of different charge, prepared from the same parent mineral. Such series are suitable for investigation of the effect of the layer charge on selected properties of smectites. Fe(II) can be partly stabilized in reduced smectites by Li fixation upon heating.

KEYWORDS: H-smectites, acid dissolution, charge modification, Li fixation, reduction.

Bentonites are abundant clay ores. Most of their properties, such as fine particle size, high surface area and cation exchange capacity (CEC), surface acidity, etc., are typical properties of smectites, the dominant clay minerals in bentonites. Chemical modifications of smectites, such as acid activation, Fe(III) reduction, fixation of cations, or their combination, affect substantially the layers of smectite, together with their most important properties and applications. This has been our reason for extensive investigation of fine fractions of various bentonites and effects of different chemical modifications. The most common alteration of smectites is the substitution of exchangeable cations. It is abundant in the nature as well as in the laboratories. Many papers report that pure homoionic forms were prepared via repeated ion exchange and subsequent washing of the solid phase obtained. However, detailed quantitative analyses of exchangeable cations rarely appear and if performed correctly, usually prove that the product is not a true homoionic smectite (e.g. Low, 1980).

H-smectites

H-smectites differ from other forms due to their instability; the surface and interlayer protons attack the layers in a similar fashion to protons from strong inorganic acids (Barshad, 1969). This instability has probably contributed to the lack of appeal of these materials for extensive investigation. On the other hand, acid sites are very important, mainly for catalytic and sorption properties, and H-smectites are usually a component of bleaching earths and other acid-activated materials. Therefore we have investigated them in detail. Dioctahedral smectites differ substantially in their

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swelling ability (Low, 1980). H-smectites, like Na- and Li-forms, are good swelling materials (Norrish, 1954), some capable of forming voluminous sediments (Komadel & Číčel, 1987, 1988; Komadel & Schomburg, 1993). This property decreases with ageing but can be stabilized by treatments with Na salt solutions (Komadel & Číčel, 1991). These assays suggested that substantial changes in surface acidity of H-smectites occur upon ageing.

The greatest proton saturation of the <2 µm fractions of bentonites were obtained by first saturating with Na^+ ions using 1 M NaCl solution, then dispersions were prepared and treated with a solution of 1 M NaCl + 0.1 M $Na_2C_2O_4$ + 0.1 M HCl to remove easily soluble iron and aluminium oxide/hydroxides. The dispersions of Na-smectites were passed through a train of three columns under applied suction. The first and third columns were filled with Amberlit IR-120 resin in the H^+ form, and the second with Wofatit SBW resin in the OH^- form to ensure maximal saturation with protons (Barshad, 1969; Janek *et al.*, 1997; Janek & Komadel, 1993, 1999).

Potentiometric titrations of fresh and aged proton-saturated forms were used to characterize the acid centres at the smectite-water interface of dioctahedral smectites. The ageing of the dispersions occurred at 90°C and finished within 4 days. This sample preparation procedure ensured maximal saturation with protons for the very beginning of the experiment with their molar amount equal to the CEC of smectite. After the protons had replaced the original exchangeable cations, they were consumed in the process of autotransformation. Titration data were entered into the thermodynamic calculation of proton affinity distribution using the SAIEUS program (Jagiełło, 1994). Numerical solving of an integral adsorption equation provided the continuous distribution of proton interacting sites for the smectites investigated. The proton affinity distributions identified up to five different proton interacting sites in all the proton-saturated smectite/water systems, within the accessible experimental range of pHs between 2 and 12. The isotherms of freshly prepared H-forms showed titration of both strong and weak acid sites (Fig. 1). The number of the strongest acid sites, i.e. those with the lowest pK values, decreased on ageing, while the number of all weaker acid sites increased with autotransformation. The number of strong acid sites varied among samples and accounted for 60–95% of the total acidity in the freshly prepared H-forms. The strongest acid sites were connected with free protons present in the dispersion, while the weaker acid sites were connected with the titration of Al^{3+}, Fe^{3+} and Mg^{2+} cations released from the structure and/or their hydrolysed species, together with the deprotonation of functional SiOH groups (Janek & Komadel, 1999).

The layer-charge distributions of all smectites investigated were heterogeneous. Oxalate pretreatment of the samples resulted in changes in the layer-charge distribution due to the removal of readily soluble phases which may have blocked exchange sites. After autotransformation, the alkylammonium exchange method revealed heterogeneous charge-density distributions wherein the fraction of layers of the highest charge was decreased. Comparison of total CEC, obtained from potentiometric curves, and interlamellar CEC, calculated from the mean layer charge confirmed the attack of protons in the particle edges. However, for several samples the structural attack may also occur in the interlayer space. Autotransformation of the H-smectites decreased the mean layer charge, suggesting that protons attack preferentially the $Mg(O,OH)_6$ octahedra during the autotransformation (Janek *et al.*, 1997).

Acid activation

Though dissolution of smectites in inorganic acids of different concentrations is a very common chemical treatment, several questions remain to be answered. Dissolution occurs in nature through the attack of acid mine waters or weathering and it is also used in industry. Acid activation, i.e. partial dissolution of smectites in inorganic acids, is a common treatment applied to produce sorbents (bleaching earths), catalysts or catalyst supports, carbonless copying papers, etc. (Siddiqui, 1968; Adams, 1987; Brown, 1994; Fahn & Fenderl, 1983). As might be expected, the process of acid dissolution of smectites is affected by the temperature, acid concentration, acid/clay ratio and stirring, with significant differences occurring between reactions in closed and open systems. Closed systems, with no addition or removal of any substance in the course of reaction, are more common for experiments performed in laboratories, while open systems are typical for processes occurring in nature. Continuous addition

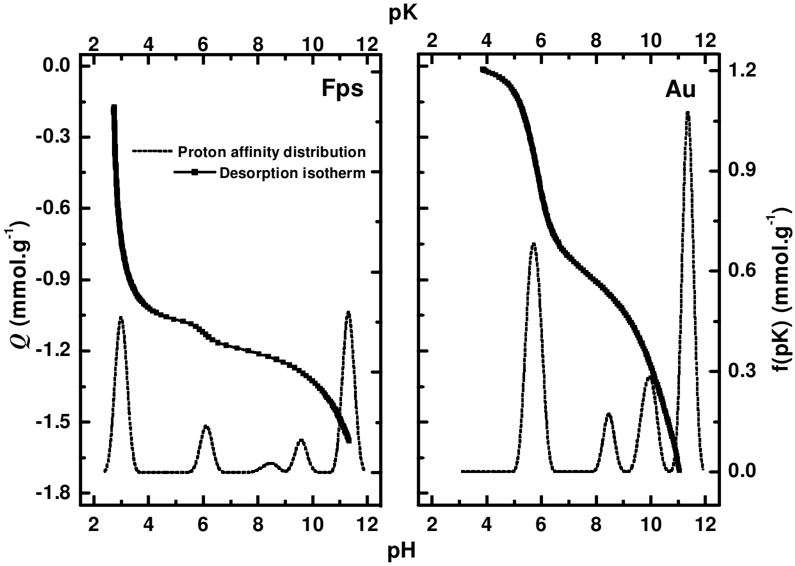

FIG. 1. Recalculated proton adsorption isotherms of SAz-1 montmorillonite and revealed proton affinity distributions. Fps – fresh prepared sample, Au-after autotransformation. Data from Janek & Lagaly (2001).

of fresh acid, though usually of much lower concentration than in most laboratory experiments, causes substantial dissolution of relatively resistant layer silicates, such as pyrophyllite (Lintnerová *et al.*, 1999). Direct comparison of results obtained for closed and open systems can lead to erroneous conclusions.

Several methods have been used to follow the extent of smectite dissolution in acids, including chemical analysis (CA) of the liquid and/or solid reaction products, X-ray diffraction, infrared (IR) spectroscopy, magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, thermal analysis, surface area measurements, etc. Comparison of the sensitivity of these techniques, their availability in the laboratories and time needed per analysis favour IR spectroscopy, since the spectra are very sensitive to modifications of the mineral structure upon acid treatment. As protons penetrate into the clay layers and attack the OH groups, the resulting dehydroxylation connected with successive dissolution of the octahedral sheet can be readily followed by intensity decreases in the hydroxyl-bending vibrations of Al_2OH and AlMgOH at 915 and 842 cm^{-1}, respectively (Farmer, 1974). The Si-O-Al bending vibration near 520 cm^{-1} is the most sensitive band to the presence of residual Al in the octahedral sheet (Fig. 2). A gradual transformation of the tetrahedral sheet to a three-dimensional framework of protonated amorphous silica can be observed in the region of the stretching vibrations of Si-O groups. Changes in the Si environment with prolonged acid treatment are reflected in both the position and the shape of the Si-O-stretching band near 1050 cm^{-1}. The component near 1100 cm^{-1}, assigned to Si-O vibrations of amorphous silica with a three-dimensional framework, appeared and increased in

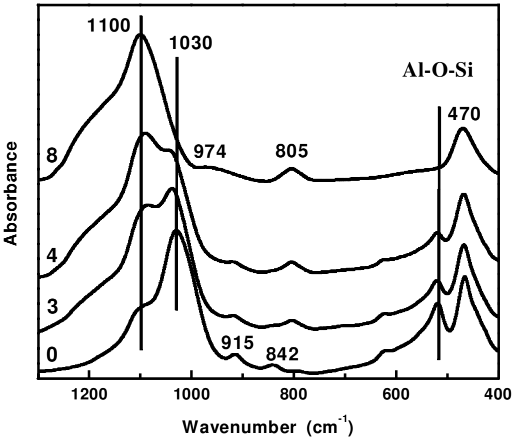

FIG. 2. IR spectra of montmorillonite SAz-1 treated in 6 M HCl at 80°C for 0, 3, 4 and 8 h. Data from Madejová *et al.* (1998).

intensity with increasing severity of acid treatment. The characteristic smectite absorption bands are absent from the spectrum of the sample treated for 8 h and only the bands of amorphous silica at 1100, 805 and 470 cm^{-1} are observed. The broad band near 974 cm^{-1} is due to the Si-O-stretching vibration of SiOH groups (Moenke, 1974), which are present in the three-dimensional product formed as the octahedral sheet in the smectite layer becomes substantially depleted (Madejová *et al.*, 1998).

Chemical analysis of leaching solutions and IR and MAS NMR spectroscopy of the prepared solids were used for analysis of acid-treated hectorite (Komadel *et al.*, 1996b). ^{27}Al MAS NMR spectra proved that the small amount of Al present in hectorite occurred in both tetrahedral and octahedral sheets and both forms were released to the solution upon acid treatment. Solution analysis showed that Li dissolved slightly faster than Mg at weaker acid concentrations, thus indicating that protons preferentially attacked the more negative Li octahedra compared to Mg-octahedra. The difference diminished at higher acid concentrations. Relative intensities of the Si-O-stretching bands of hectorite near 1015 cm^{-1} and of free silica near 1100 cm^{-1} provided direct information on the dissolution of the mineral. Progressive increases in the content of amorphous silica in the samples was reflected in the increasing intensities of the Si-O bands near 1100 and 800 cm^{-1} and in the decreasing absorption of the Si-O vibration of the tetrahedral sheets near 1015 cm^{-1}. The IR spectra of the acid dissolution product obtained from hectorite did not exhibit an absorption band near 1015 cm^{-1}, but did show intense bands near 1100 and 800 cm^{-1} and a broad absorption band near 965 cm^{-1}, attributed to Si-O stretching vibrations of SiOH groups. As much as 37% of total Si atoms, identified by ^{29}Si MAS NMR as Si in $Si(OSi)_3OH$ and $Si(OSi)_2(OH)_2$ environments, contributed to the absorption near 965 cm^{-1}. Analysis of relative peak intensities of the components in the ^{29}Si MAS NMR spectra (Gates *et al.*, 1996) provided direct dissolution data, concordant with the Mg contents in the leaching solutions (Fig. 3). The changes in the environment of Si atoms in the tetrahedra upon acid treatment occurred at a rate similar to the dissolution of octahedral Mg. The progressive changes in IR and ^{29}Si MAS NMR spectra of hectorite and montmorillonite due to acid dissolution are alike. A combination of these spectroscopies is extremely useful to probe structural changes occurring during acid dissolution of smectites (Breen *et al.*, 1995a,b; Gates *et al.*, 1996; Komadel *et al.*, 1996b; Madejová *et al.*, 1998; Tkáč *et al.* (1994).

Substitution of the exchangeable cations by hydrated protons is much faster than dissolution of the mineral layers and the effect of structural composition on the acid dissolution of smectites is significant. Trioctahedral smectites dissolve much faster than their dioctahedral counterparts (Madejová *et al.*, 1998). Novák & Číčel (1978) showed that the rate of dissolution of dioctahedral smectites in HCl increases with the substitution of Fe and Mg for Al in the octahedral sheet. A smaller amount of octahedral substitution is one of the reasons for the slower dissolution rate of pyrophyllite compared to montmorillonite. Moreover, the effect of swelling interlayers on the dissolution rate has been experimentally proven only recently (Komadel *et al.*, 1996a). It was postulated that different rates of dissolution of tetrahedral and octahedral Al(III) and Fe(III) in acids would serve as an experimental basis to distinguish between portions of these atoms bound in the tetrahedral and octahedral sheets (Ostahaus, 1956; Novák & Číčel, 1978). Later, the Mössbauer study of Luca & MacLachlan (1992) and the MAS NMR assay of Tkáč *et al.* (1994) confirmed that acid treatment removes Fe(III) and Al(III), respectively, from the tetrahedral and octahedral sheets of dioctahedral

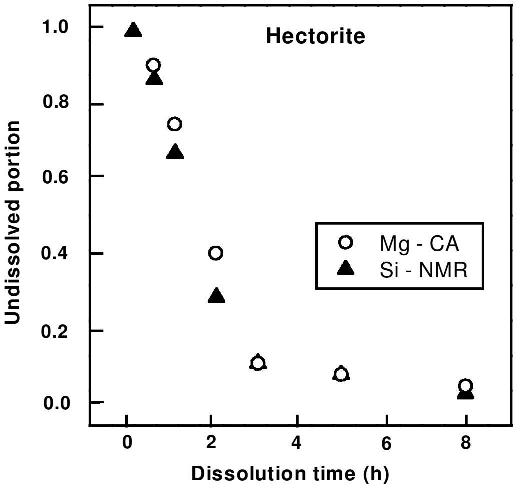

FIG. 3. Dissolution of hectorite in 1 M HCl at 20°C. Mg data were obtained from solution analysis, Si data from the ^{29}Si MAS NMR spectra. Data from Gates *et al.* (1996).

smectite layers at similar rates. Readily soluble, octahedral + tetrahedral and 'insoluble' portions of constituent atoms can be calculated from the dissolution curves, thus providing information on the distribution of atoms in the sample. Readily soluble portions include exchangeable cations and easily soluble admixtures such as goethite. Common 'insoluble' phases found in the fine fractions of bentonites are kaolinite, quartz, anatase and volcanic glass (Komadel *et al.*, 1993; Čičel & Komadel, 1994).

Catalytic activity of acid-treated smectites was tested using the reaction of 2,3-dihydropyran with methanol yielding the tetrahydropyranyl ether. Both Mg-rich and Al-rich montmorillonites, treated under the same conditions, were partially decomposed, but Mg-rich Cheto montmorillonite proved more susceptible to acid attack. The test reaction was a sensitive indicator of changes in clay acidity. Mild acid treatments exhibited high Brønsted acidities comparable with the CECs of the parent minerals and this was reflected in their high catalytic activity. Longer acid treatments caused a reduction of both acidity and catalytic activity due to the presence of fewer exchange sites resulting from the depopulation of the octahedral sheets (Breen *et al.*, 1995a,b).

Four dioctahedral smectites of various chemical compositions, including a Mg-rich and an Al-rich montmorillonite, an Fe-beidellite and a ferruginous smectite, together with a hectorite were leached using treatment conditions selected to produce catalysts in which the octahedral sheet was depopulated in a controlled manner. The Brønsted acidity and catalytic activity of the resulting materials were highest for the samples prepared with the mildest acid treatments and decreased with increasing depletion of the octahedral sheets. The hectorite exhibited no catalytic activity, though cyclohexylamine desorption profiles suggested presence of Brønsted acid sites (Breen *et al.*, 1997b). The recent study of cyclohexylamine desorption from Ni^{2+}- and Al^{3+}-exchanged bentonite showed that this method need not distinguish Brønsted and Lewis acid sites unambiguously (Breen *et al.*, 2000). The chemical composition of the starting material had no significant effect on the catalytic activity for the chosen test reaction. On the other hand, it plays a key role in determining the severity of the activation conditions required for the optimization of catalytic activity. FTIR and ^{29}Si MAS NMR spectroscopies provided evidence regarding the extent of the octahedral depletion, which correlated well with the acidity determined from thermal desorption of cyclohexylamine (Breen *et al.*, 1997b). The number of acid sites obtained from cyclohexylamine desorption from a series of mildly acid-treated Cheto montmorillonite and hectorite samples agreed with the CEC data. No evidence of any free protons was found in the potentiometric titration curves, which proved that complete autotransformation of the acid-treated samples had occurred over a short period. Acid sites associated with Al^{3+} or Fe^{3+} released from the Cheto montmorillonite layers during acid treatment and subsequent autotransformation catalysed the test reaction and produced the tetrahydropyranyl ether from 2,3-dihydropyran and methanol in 80% yield. The complete absence of catalytic activity in the acid-treated hectorite samples confirmed that acid sites associated with interlayer Mg^{2+} and Li^{+} were unable to catalyse this test reaction (Komadel *et al.*, 1997).

The catalytic activity of acid-activated organoclays was tested for the conversion of α-pinene to camphene (Breen *et al.*, 1997a). The catalysts included a range of organosmectites containing tetramethylammonium, dodecyltrimethylammonium or octadecyltrimethylammonium cations at the 25, 50 or 100% exchange level and subjected to selected acid-leaching procedures. The organic cation content and extent of acid dissolution was controlled by IR spectroscopy. The conditions used for acid leaching seldom removed extensive amounts of organocation and the yields (40% conversion to camphene) compared favourably with those reported for pillared clays. Acid-leached tetramethylammonium clays were the most active with yields four times higher than the corresponding parent clay. Acid-leached dodecyltrimethylammonium and octadecyltrimethylammonium clays were only active when the organocations occupied no more than 25% of the exchange sites (Breen *et al.*, 1997a).

Acid catalysts were prepared by heating of NH_4-saturated montmorillonite at 200–600°C for 24 h via decomposition of the cation, $NH_4^+ \rightarrow NH_3\uparrow + H^+$, and their catalytic activity was tested in acetylation of 3,4,5-trimethoxybenzaldehyde with acetic anhydride. This reaction was sufficiently sensitive to the different catalyst modifications making it a suitable test for catalytic activity of modified montmorillonites. Most of the prepared catalysts were able to catalyse the test reaction and produce diacetate in yields >50%. The most active catalyst, obtained upon heating at 300°C, was only slightly less effective than the commercially available acid-activated K10 catalyst (Jankovič & Komadel, 2000).

Reduction of structural Fe(III)

Less common than acid activation are chemical treatments leading to a modification of the negative layer charge in smectites. The layer charge is perhaps the most important characteristic of smectites, connected with many properties of these minerals; therefore its increase via Fe(III) reduction and the decrease via Li-fixation upon heating has been intensively investigated in our laboratories. At least some Fe(III) occurs in various dioctahedral smectites including most montmorillonites, beidellites and illites, and Fe(III) is the dominant central atom in octahedral sheets of nontronites. Reduction of structural Fe(III) to Fe(II) in smectites profoundly affects many fundamental properties of the mineral, including layer charge, CEC, cation fixation, swelling pressure and water-holding capacity, specific surface area, hydraulic conductivity, colour, magnetic exchange interactions, etc. The ability to manipulate the oxidation state to modify clay properties *in situ* could be of great benefit to agriculture, industry and the environment. In many situations, however, such benefits depend on the stability of the reduced oxidation state (Stucki, 1988).

The most effective method currently used to reduce structural Fe(III) and prepare reduced smectites is reduction by sodium dithionite added to a smectite dispersion in the presence of a citrate and bicarbonate buffer while the vessel is being purged with N_2. This treatment led to >90% reduction in ferruginous smectite and nontronite (Komadel *et al.*, 1990, 1995) but to only ~60% reduction in griffithite, which is an Fe-rich trioctahedral smectite with dioctahedral domains, in which a negative charge is located on the tetrahedral sheets and a positive charge on the octahedral sheets. The lower reducibility of Fe(III) in griffithite relative to nontronites may be due to the differences in structure between griffithite and nontronites (Komadel *et al.*, 2000). Reduced dioctahedral Fe-rich smectites are unstable materials in air, undergoing rapid and complete reoxidation with oxygen in water dispersions. The structural OH content of reduced-reoxidized nontronite is ~15–20% less than in the original sample, indicating that the structure remains partially dehydroxylated even after reoxidation. Mössbauer spectra of reoxidized samples exhibited Fe(III) doublets of larger quadrupole splitting compared with those in the unaltered sample, suggesting that Fe(III) is in a more distorted environment after the reduction-reoxidation treatment (Komadel *et al.*, 1995). Manceau *et al.*, (2000) showed that migration of Fe from *cis*- to *trans*-sites occurred during the reduction process. Some of the Fe atoms occupy *trans*-sites in the reduced state, forming small trioctahedral domains within the structure of reduced nontronite.

Li fixation

Heating of Li-saturated montmorillonites at 250–300°C for several hours is known to cause their loss of expandability and CEC (Hofmann & Klemen, 1950). Li fixation and resultant changes in swelling have served to distinguish between different smectites in that the irreversible collapse of the layers of Li-montmorillonite after heating was proposed to be the criterion to distinguish montmorillonite from beidellite (Greene-Kelly, 1953). Calvet & Prost (1971) reported fixation of different amounts of Li^+ in Camp Berteaux montmorillonite upon heating for 24 h at 108–220°C. Indeed, a series of reduced-charge montmorillonites (RCM) were prepared from different minerals by heating at various temperatures in the 105–300°C range (Madejová *et al.*, 1996, 2000a; Hrobáriková *et al.*, 2001). The amount of fixed Li(I) increased with the temperature, confirming the successful preparation of a set of samples of variable layer charge from the same parent Li-montmorillonite by varying only preparation temperature. Heating for different periods of time at 135 or 150°C showed that the extent of Li fixation increased with the duration of the treatment (Bujdák *et al.*, 1991).

The effect of heating temperature on the CEC of Li-saturated smectites is presented in Fig. 4. The CEC values for all three montmorillonites decreased gradually with increasing temperature up to 200°C, with final CEC values of 12 to 22% of that for the unheated sample. These data show that a substantial portion of Li^+ ions was fixed in the layers of all three montmorillonites investigated, upon heating at 200°C for 24 h, similar to that observed for other montmorillonites (Komadel *et al.*, 1996a; Hrobáriková *et al.*, 2001). On the other hand, a much smaller decrease in the layer charge with heating temperature was observed for Stebno Fe-beidellite and SWa-1 ferruginous smectite, i.e. the minerals with prevailing tetrahedral charge. The CECs of ST200 and SWa200 (the number indicates the preparation temperature of 200°C) were only reduced to 67 and 83%, respectively, of their original values. Clearly, some Li fixation occurred in all smectites upon heating at 200°C; however, the extent of fixation decreased with decreasing proportion of octahedral charge (Madejová *et al.*, 2000a,b). This is in agreement with previous studies (e.g. Jaynes & Bigham, 1987).

Series of RCM with gradually decreasing layer charge were prepared from montmorillonites of varying chemical composition. Heating the samples at temperatures up to 120°C caused some Li fixation but initiated only minor changes in the sorption properties. The biggest changes in the properties were observed among the samples prepared at 130–200°C (Fig. 5), while using higher temperatures had much less effect (Bujdák *et al.*, 1992; Hrobáriková & Komadel, 2002). The most extensive reduction in CEC in these experiments, by 81% after heating at 300°C, was obtained with Otay montmorillonite, the mineral of the highest octahedral and the smallest tetrahedral charge studied.

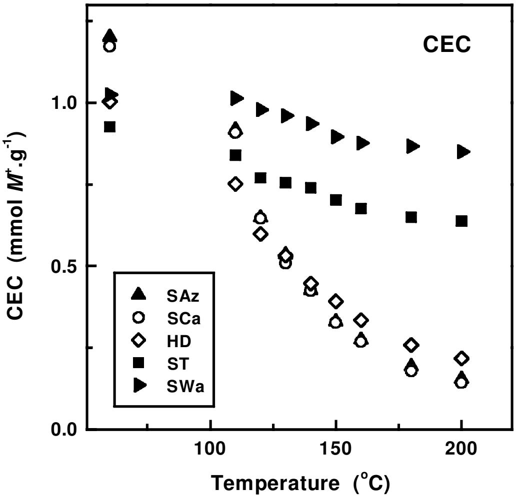

FIG. 4. Cation exchange capacities for SAz-1 (Cheto, Arizona), SCa-2 (Otay, California) and Horní Dunajovice (HD) (Czech Republic) montmorillonites, Stebno (ST) Fe-beidellite (Czech Republic) and SWa-1 ferruginous smectite (Grant County, Washington) heated at various temperatures for 24 h. Figure from Madejová *et al.* (2000a).

The parent Kriva Palanka montmorillonite and the samples KP110 and KP130 retained similar amounts of water under the same conditions, thus showing that the decreased negative charge on the layers had only a minor influence on the water uptake at all relative humidities (RHs) investigated. A significantly decreased amount of water was retained by KP160 while KP300 adsorbed only 8% water at 100% RH. The basal spacings, obtained by *in situ* XRD at different RHs, of the parent montmorillonite and the samples KP110 and KP130 increased with RH, while those of KP160 and KP300 were independent of RH and were stable within experimental error at ~10.4 and ~9.6 Å, respectively (Komadel *et al.*, 2002).

Fixation of Li^+ ions in the structure upon heating at a temperature 120°C or higher caused the appearance of a new OH-stretching band near 3670 cm^{-1} in the spectra of all the montmorillonites investigated, confirming the formation of local trioctahedral domains containing Li(I) in the previously vacant octahedral positions. No similar band was observed in the spectra of heated ferruginous smectites with prevailing tetrahedral charge. A gradual upward frequency shift and decrease in intensity of the AlAlOH-bending band showed that Li(I) present in the layers caused pronounced perturbation of this OH-bending mode;

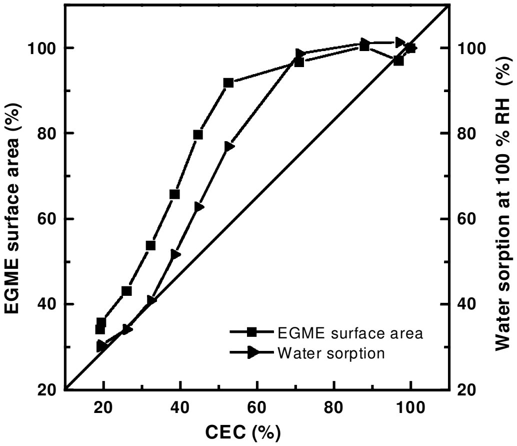

FIG. 5. Comparison of relative CECs and relative specific surface areas determined by ethylene glycol monoethyl ether adsorption for a series of reduced-charge Otay montmorillonite. Data from Hrobáriková & Komadel (2002).

whilst it only caused a small perturbation of the OH-bending mode near 850 cm^{-1} but it does activate a new OH-bending mode near 803 cm^{-1}. Reversible changes in the positions of the stretching Si-O and bending OH bands in the spectra of Fe-beidellite and a ferruginous smectite proved that lithium was present in these minerals primarily in the hexagonal holes of the tetrahedral sheets (Madejová *et al.*, 2000a).

Diffuse reflectance spectra in the near-infrared (NIR) region provided further evidence of substantial differences in the fixation of Li^+ in montmorillonites and in other dioctahedral smectites. Unheated samples showed a complex band near 7060 cm^{-1} assigned to the first overtone of the OH-stretching mode of structural hydroxyl groups and bound H_2O. The OH combination bands appeared in the 4600–4300 cm^{-1} region. Spectra of heated montmorillonites showed an upward shift and splitting of the OH-overtone band into two components near 7170 and 7110 cm^{-1}. The presence of a band near 7170 cm^{-1}, assigned to the overtone of the AlMgLiOH-stretching vibration, implied that local trioctahedral domains were created upon Li fixation in the previously vacant octahedral positions of montmorillonites. The OH-combination bands were shifted to higher frequencies and a new band appeared near 4472 cm^{-1} in the spectra of montmorillonites heated above 130°C. No feature indicating Li(I) in the structure of Fe-beidellite or ferruginous smectite was observed in the NIR spectra (Madejová *et al.*, 2000b).

The gradual decrease of the layer charge due to Li fixation led to a shift of the Si-O-stretching band to higher frequencies and to the appearance of new, weak, pyrophyllite-like bands near 1120 and 420 cm^{-1} (Madejová *et al.*, 1996; Hrobáriková *et al.*, 2001). A series of RCM was treated with 6 M HCl at 95°C for periods up to 30 h. Reaction solutions obtained were analysed for Al (Fig. 6), Fe, Mg and Li and the solid reaction products were investigated using FTIR spectroscopy. Both analyses provided evidence that the extent of dissolution decreased with increased amounts of Li(I) fixed within the montmorillonite structure, i.e. with increased preparation temperature. Differences in the acid dissolution process reflected the fact that structural changes occurred within the samples presumably due to differing positions of the fixed Li. The EGME surface areas and XRD and HRTEM analyses of the series revealed an increased number of non-swelling interlayers in the samples prepared at 160 and 210°C, which caused a substantially slower decomposition of these samples in HCl. The calculated XRD patterns of samples prepared at 135 and 160°C confirmed the presence of 20% and 45% pyrophyllite-like layers, respectively, in these samples. Mixed-layer pyrophyllite-like/smectite and pyrophyllite-like crystals, containing only non-swelling interlayers, were found in the sample prepared at 210°C. The results confirmed that the number of swelling interlayers in RCM substantially affects their dissolution rate in HCl (Komadel *et al.*, 1996a). This is direct experimental evidence that protons do not attack the smectite particles from their edges only.

^{29}Si MAS NMR spectra revealed a consistent chemical shift to more negative values and increased line-width of the main Si resonance with increasing levels of fixed Li(I) (Gates *et al.*, 2000). The ^{29}Si chemical shift of −95.4 ppm obtained for the sample prepared at 210°C agrees well with the value reported for pyrophyllite (Sanchez-Soto *et al.*, 1993). This is consistent with the formation of pyrophyllite-like layers in RCM, as was observed in the IR spectra (Madejová *et al.*, 1996), in increased numbers of non-swelling, pyrophyllite-like layers and in decreased specific surface area (Komadel *et al.*, 1996a) for the same series of samples.

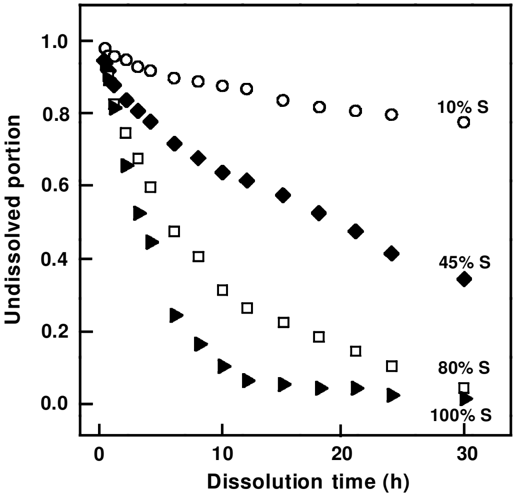

FIG. 6. Effect of non-swelling interlayers on dissolution of Al from reduced-charge montmorillonite in 6 M HCl at 95°C. The percentage data indicate the content of swelling layers in the samples. Data from Komadel *et al.* (1996a).

Absorption and specular reflectance FTIR and electron spin resonance spectroscopies were employed for analysis of sites of Li(I), Cu(II) and Cd(II) fixed in the structure of montmorillonite from Jelšový Potok (Slovakia) upon heating. The CEC values showed that the layer charge of the mineral decreased with increasing temperature of heating and that the amount of fixed cations was in the order Li(I) > Cu(II) > Cd(II). Analysis of the OH-stretching region in the FTIR absorption spectra revealed that most of Li^+ ions migrated into the octahedral vacancies upon heating, thus creating local trioctahedral AlMgLiOH groupings. Cu(II) were trapped in the hexagonal cavities of the tetrahedral sheet, whereas Cd^{2+} ions are too large to enter deep enough into the hexagonal cavities to become fixed. While both Cu^{2+} and Cd^{2+} ions have the same charge, the ionic radius of Cd^{2+} is too large to penetrate close to the OH groups. Even though Cu^{2+} and Li^+ ions are of similar size and therefore expected to enter vacant octahedral sites, IR spectroscopy indicated that only Li^+ ions would migrate into the previously vacant octahedra. It appears that both the size and the charge of interlayer cations affect their final position after fixation upon heating (Madejová *et al.*, 1999). After preparation at 300°C, Li(I) were predominantly trapped in the previously vacant octahedra. Cu(II) were fixed deep in the hexagonal holes, where they substantially affected the vibration modes of Si-O bonds in the specular reflectance IR spectra. Cu(II) were partially coordinated by oxygen atoms from the mineral layers and by nitrogen atoms from pyridine molecules if present in the interlayers. The bigger Cd^{2+} ions were prevented from going as deep into the hexagonal holes as Cu(II) and their effect on Si–O bonds was less pronounced (Karakassides *et al.*, 1999).

The Fe(II) in chemically reduced smectite is normally readily reoxidized in air, but it can be partially stabilized by Li fixation upon heating. More than 80% of total Fe in ferruginous smectite SWa-1 was reduced to Fe(II), then Li^+ saturated, washed free of excess ions, freeze-dried, and heated in a N_2 atmosphere at 260°C for 24 h to evoke Li fixation. This treatment caused partial stabilization of Fe(II) in the clay mineral structure. Chemical analysis, Mössbauer spectroscopy and IR spectroscopy proved that >20% of total Fe was Fe(II) after reoxidation with oxygen in a water dispersion, a treatment which normally causes complete reoxidation of Fe(II) in reduced Na-smectites. Spectral fitting of the OH-stretching band evident in the IR spectra indicated migration of Li^+ into the vacant octahedra. Some of the OH groups in the reoxidized smectite were found in local trioctahedral configurations, associated with the AlFe(II)Li or Fe(III)Fe(II)Li groupings of central atoms in the octahedral sheet (Komadel *et al.*, 1999).

Interactions with methylene blue

Methylene blue (MB) is a cationic dye readily soluble in water. In aqueous solutions of low concentrations, MB cations partially associate as cationic dimers. The surfaces of clay minerals exhibit a strong affinity for MB cations. A partial protonation of MB cations may also take place at clay surfaces. MB-clay interaction is extremely sensitive for probing the surface properties of smectites in water suspensions. The cations are adsorbed via ion exchange, frequently accompanied by agglomeration. The agglomeration of MB, at low loadings of MB, is very sensitive to the layer charge of smectites. Hence, visible absorption spectroscopy (VIS) of MB-smectite dispersions is a simple, but extremely sensitive method to probe layer charge density of natural and/or chemically modified smectites. This was the reason for investigating the effect of layer charge on MB-montmorillonite interactions in suspension using different montmorillonites. The nearly perpendicular orientation of MB cations at the clay mineral basal surface, recently proved for micas (Hähner *et al.*, 1996), facilitates the formation of large, multi-cation dye agglomerates that keep the basal spacing of MB-clay complexes at ~1.75 nm. If the orientation of MB cations was parallel to the surface such an agglomeration would not occur. Since each form of MB (monomer, dimer, higher agglomerate) absorbs visible light at a different wavelength, surfaces of different layer-charge densities exhibit different absorption spectra for the resulting clay mineral-dye dispersion. The VIS spectra of MB with Na- and H-smectite dispersions provided information about the formation of protonated dye cations, dimers, and higher agglomerates on the clay surface. The different amounts of the various dye forms were compared with negative layer charge distributions of the clay minerals used, obtained by the alkylammonium method. The formation of MB dimers and higher agglomerates reflected sensitively the layer-charge density of the smectites. Methylene blue cations formed predominantly larger agglomerates at the surface of the smectites with high charge density, whereas much less dye agglomeration was observed for the samples of lower layer-charge density, presumably because of the greater distances between the adsorbed MB cations (Bujdák *et al.*, 1998).

The layer-charge decrease, induced by Li fixation, was correlated with the trends in the VIS spectra of MB-RCM dispersions. Apparently, the distribution of the negative surface charge on the clay minerals controls the distance between the adsorbed MB cations and thus affects the formation of MB dimers and larger agglomerates. Both the CEC values and the spectra of MB-smectite dispersions clearly correlated with the extensive reduction of the layer-charge density of the RCM upon Li fixation and were in accord with the effect of treatment temperature and locus of charge described above. The CEC data and MB spectra were sensitive to the lesser charge reduction in the Fe-rich beidellite and ferruginous smectite, which is related to the low octahedral charge of these minerals. Following heating at higher temperatures (120–160°C), slightly higher Li fixation was indicated by CEC values; however, no charge reduction was confirmed by MB spectra. The spectra of protonated MB is very distinctive and the release of protons accompanying Li fixation in Fe-rich smectites heated at 180 or 200°C was detected in the spectra of MB-clay dispersions and confirmed by potentiometric titrations (Bujdák & Komadel, 1997; Bujdák *et al.*, 2001).

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