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Synthesis and acid-base properties of Mg-saponite

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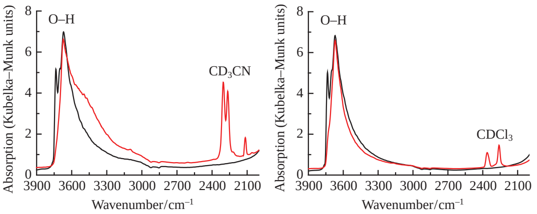
Magnesium aluminosilicate was prepared and characterized by XRD analysis, Fourier transform spectroscopy (DRIFTS) and thermodesorption measurements. Compared to H-forms of zeolites, Mg-saponite contains Brønsted acid sites of a lower acidity and fairly strong Lewis acid sites. On the contrary, basic sites turned out to be weak, whereas proton-donor ability can be easily recognized.



Layered magnesium aluminosilicates are described as a type of clay consisting of alternating layers of octahedral coordinated magnesium atoms and tetrahedral coordinated silicon and/or aluminum atoms. The clay sheets are negatively charged when lower valence cations completely or partially substitute higher valence cations in the structure. For instance, tetravalent metal ions such as Si^{4+} in the tetrahedral layer may be completely or partially replaced by trivalent metal ions like Al^{3+}. In the case of clay with a trioctahedral layered structure, substitution will give a mesoporous structure of saponite or vermiculite.

The synthesis of clay minerals under hydrothermal conditions is well documented in the literature. Such hydrothermal synthesis can involve a long hydrothermal treatment at relatively high temperatures and pressures. The application of this technology on the industrial scale can be difficult and costly due to the reaction conditions employed. Other known methods for producing clay materials such as metallo-aluminosilicates involve the formation of a silica–alumina gel prior to addition of the metal-containing component.[1]

Clay science experiences nowadays a Renaissance period because the synthetic clays are not inferior to many oxide carriers in terms of the surface areas and pore volumes, and scalable methods of production of synthetic clays developed. Saponite is one of the most promising mesoporous structures that may find application in industrial processes due to its well-defined acidity and stability. One of the recent examples is the use of synthetic saponites as hydro processing catalyst components in refining as described in a patent by Chevron Corp.[2]

The aim of this study was the characterization of textural and physicochemical properties of synthesized Mg-saponite[†] by the surface and bulk sensitive methods.

According to the XRD pattern (Figure 1),[‡] the sample under study possesses the basal reflections of Mg-saponite as a layered material consisted of the alternating tetrahedral sheets containing Si (and partially Al) atoms and the octahedral sheets containing Mg atoms.[3–6]

Estimating the crystallite dimensions *via* the Scherrer equation indicated 50 Å as an average size of crystallites that form the Mg-saponite specimen.

Figure 2 represents the DRIFT spectra of Mg-saponite measured after its treatment *in vacuo* at 350 °C for 2 h. The DRIFTS region of OH stretching vibrations of Mg-saponite displayed clear peaks at 3734 and 3669 cm^{-1}, a shoulder at 3704 cm^{-1}, and a set of peaks with frequencies lower than 2000 cm^{-1}. As reported,[7–10] the region below 2000 cm^{-1} is characteristic of the Mg-saponite lattice vibrations. The band of stretching vibrations at 3734 cm^{-1} and the band of combination vibrations (stretching + out-of-plane bending vibrations) at 4557 cm^{-1} are characteristic of terminal isolated hydroxyl silanol (Si–OH) or/and Mg–OH groups. The bands at 3704 and 4492 cm^{-1} are attributed to vicinal (involved in hydrogen bonding) Si–OH groups, and those at 3669 and 4458 cm^{-1} are assigned to the bridged OH groups [Si(OH)Al

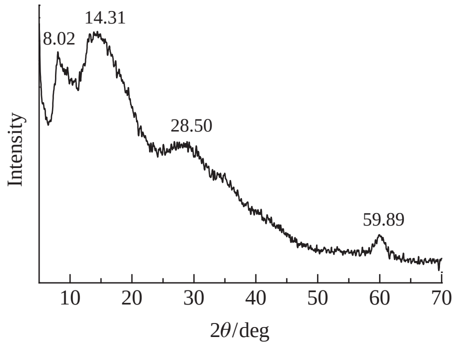


Figure 1 XRD pattern of Mg-saponite.

[†] A magnesium aluminosilicate $Mg_{5.7}[Si_{6.4}Al_{1.6}]O_{20}(OH)_4$ of the saponite type with a Si:Al ratio of 4:1 was prepared as follows. Water glass (sodium silicate) (27 wt% SiO_2) was mixed with aluminum nitrate at room temperature to form a silica–alumina gel. Then the mixture was filtered and added to a solution of magnesium nitrate; and the pH was adjusted with NaOH to ~8.8. The reaction was carried out at 90 °C for 40 h, then the reaction mixture was filtered and washed. The magnesium aluminosilicate clay was added to a 0.1 M solution of ammonium nitrate to replace the sodium cations by ammonium ones. The ammonium substituted magnesium aluminosilicate clay was collected by filtration and washed with water, then calcined at 450 °C for 12 h to convert to the protonated form.

[‡] For details, see Online Supplementary Materials.

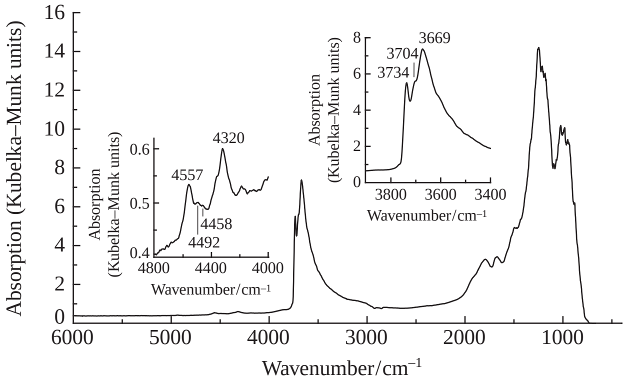


Figure 2 DRIFT spectrum of the Mg-saponite treated *in vacuo* at 350 °C for 2 h. Inserts: OH stretching vibration and OH combination vibration regions.

or/and Si(OH)Mg]. The band at 3669 cm^{-1} may also be attributed to admixtures of Mg(OH)$_2$.[8] The wide absorption bands of stretching vibrations and combination vibrations centered at about 3500 and 4320 cm^{-1}, respectively, are characteristic of a set of hydrogen-bonded OH groups.

After adsorption of CD$_3$CN, the band at 3734 cm^{-1} in the OH region (Figure 3) disappeared and a broad band at about 3470 cm^{-1} appeared. This process was reversible and the initial spectrum restored after evaporation *in vacuo* at 20–350 °C.

The red shift of stretching vibrations of silanol hydroxyl groups was about 264 cm^{-1}. The comparison of this shift with that observed for strong acid bridged OH groups in H-forms of zeolites[11] (about 1000 cm^{-1}) allowed us to conclude that the synthesized Mg-saponite contains surface Brønsted acid sites (BAS) of a lower acidity or shows proton-donor ability. The absence of a band shift at 3669 cm^{-1} in the presence of a strong base clearly indicates that this band belongs to magnesium hydroxide.

Three bands at 2303, 2265, and 2115 cm^{-1} are observed in the spectrum of Mg-saponite after CD$_3$CN adsorption [Figure 4(*a*)]. The band of C≡N stretching vibrations at 2303 cm^{-1} was characteristic of CD$_3$CN adsorption on low-coordinated (coordinative unsaturated) metal ions,[12–14] in our case most likely Mg^{2+}.

The blue shift of C≡N stretching vibrations as a result of CD$_3$CN adsorption on these strong Lewis acid sites (LAS) was 50 cm^{-1} [Figure 4(*a*)] relative to the frequency in the gas phase (2253 cm^{-1}).[15] After evaporation of CD$_3$CN *in vacuo* at 350 °C, two bands were observed at 2314 and 2291 cm^{-1} overlapping at lower temperature. Two types of LAS with different acidity are involved in the interaction with CD$_3$CN. The blue shifts of C≡N stretching vibrations were 61 and 38 cm^{-1}.

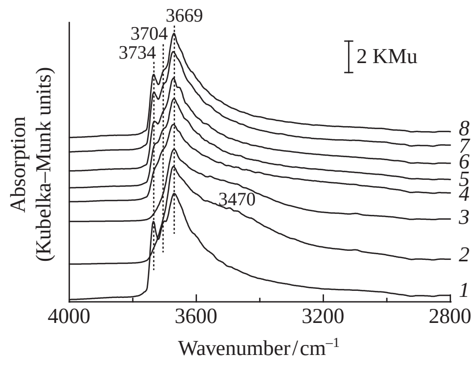


Figure 3 DRIFT spectra (O–H stretching vibration region) of Mg-saponite collected after consecutive treatments: (*1*) *in vacuo*, 350 °C; in CD$_3$CN at room temperature (*2*) 10 min, (*3*) overnight; and *in vacuo*: (*4*) room temperature, 1 h; (*5*) 100 °C, 1 h; (*6*) 200 °C, 1 h; (*7*) 350 °C, 1 h; and (*8*) 350 °C, 2 h.

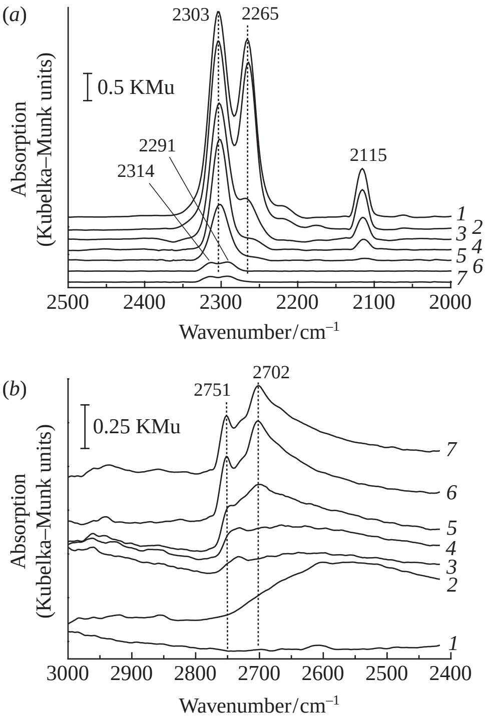


Figure 4 DRIFT spectra of CD$_3$CN adsorption on Mg-saponite: (*a*) C≡N and C–D region; (*b*) OD region; (*1*) CD$_3$CN, room temperature, 10 min; (*2*) CD$_3$CN, room temperature, overnight; *in vacuo*: (*3*) room temperature, 1 h; (*4*) 100 °C, 1 h; (*5*) 200 °C, 1 h; (*6*) 350 °C, 1 h; and (*7*) 350 °C, 2 h.

In addition, the band at 2265 cm^{-1} characteristic of CD$_3$CN adsorbed on weak BAS observed on the surface of Mg-saponite, the blue shift was 12 cm^{-1}. The lower frequency band at 2115 cm^{-1} can be assigned to the C–D bending vibrations in CD$_3$ groups.

The H-D exchange reaction occurred between hydroxyl groups and adsorbed acetonitrile during thermodesorption at 20–350 °C [Figure 4(*b*)]. The bands at 2751 and 2702 cm^{-1} characteristic of OD groups in the spectra of Mg-saponite at increased temperatures (> 100 °C) indicated a low mobility of protons.

The DRIFT spectra in the OH region were collected in CDCl$_3$ adsorption–desorption process at room temperature (Figure 5). After adsorption of CDCl$_3$, the band at 3734 cm^{-1} disappeared, and no new bands appeared in the spectrum. This process was reversible, and the initial spectrum restored after evaporation *in vacuo* at room temperature.

The strength of surface basic oxygen species may be estimated from the shift of frequency of the C–D stretching vibrations

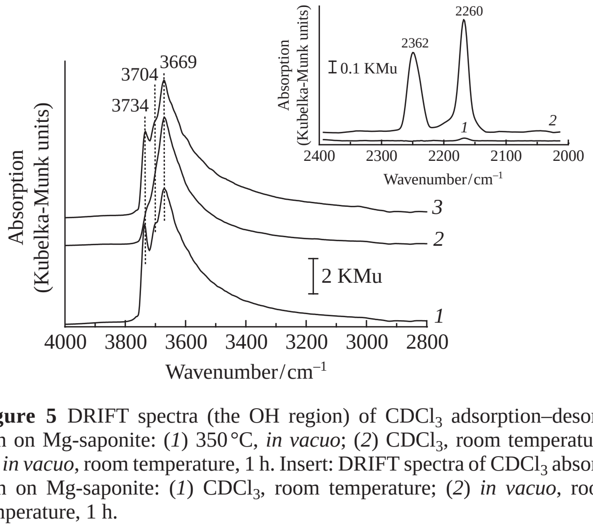


Figure 5 DRIFT spectra (the OH region) of CDCl$_3$ adsorption–desorption on Mg-saponite: (*1*) 350 °C, *in vacuo*; (*2*) CDCl$_3$, room temperature; (*3*) *in vacuo*, room temperature, 1 h. Insert: DRIFT spectra of CDCl$_3$ absorption on Mg-saponite: (*1*) CDCl$_3$, room temperature; (*2*) *in vacuo*, room temperature, 1 h.

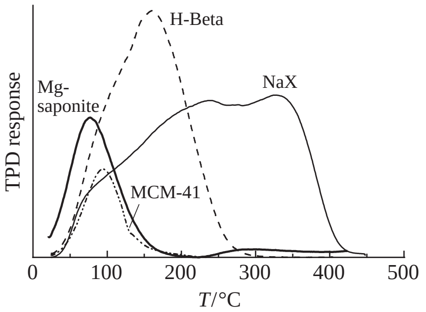


Figure 6 Toluene TPD curves.

Table 1 The pore volume calculated *vs*. that taken from the literature.

Sample	Desorbed toluene volume/$cm^3\ g^{-1}$	Pore volume, reported theoretical data/$cm^3\ g^{-1}$
Mg-saponite	0.047	0.60[21]
NaX (SiO_2/Al_2O_3, 2.5:1)	0.23	0.25[18]
H-Beta (SiO_2/Al_2O_3, 25:1)	0.16	0.18[20]
MCM-41	0.029	0.5–1.0 (*meso*)[19]

relative to the gas phase (2263 cm^{-1}).[16] The larger the shift of the C–D band to lower frequencies (red shift), the higher the strength of surface basic sites (oxygen anions involved in the interaction with chloroform *via* the formation of a σ-complex with an O···D–C bond).

The spectra of $CDCl_3$ adsorbed on Mg-saponite (Figure 5, insert) demonstrated the presence of relatively weak basic species on the surface of the Mg-saponite sample treated *in vacuo* at 350 °C. The spectrum of $CDCl_3$ adsorbed on this sample exhibited an absorption band at 2260 cm^{-1}. The red shift of the C–D stretching vibration band was 3 cm^{-1}. The band position was close to that in the spectrum of the gaseous adsorbate, whereas for alkali forms of zeolites the shift was about 100 cm^{-1}.[17]

The comparison of toluene TPD curves obtained for Mg-saponite, NaX, MCM-41, and H-Beta zeolites (Figure 6)[‡] revealed some differences. The pore volumes (Table 1) were calculated from the amount of desorbed toluene and compared with reported data.[18–21]

MCM-41 has a mesoporous structure (pore size of ~2–3 nm)[21] and the toluene adsorption isotherm for this material corresponds to type IV by the Brunauer’s classification, and toluene is easily removed while purging this sample with He. On the contrary, NaX and H-Beta zeolites have a small pore size (0.7–0.8 nm), and the toluene adsorption isotherms for the zeolites taken for comparison correspond to type I by the Brunauer’s classification.[18]

The pore volume of Mg-saponite was comparable with that of MCM-41 and lower than that observed for both zeolites (NaX and H-Beta). Probably the microspores of Mg-saponite are not accessible for toluene. The presence of mesopores and the sufficiently large pore volume make Mg-saponite a material of choice for CO_2 storage due to the presence of encapsulated amine molecules or Mg cations, which will be the subject of the further research.[22]

The synthetic saponites, due to their controllable acidic and basic properties, as well as mesoporosity, may be chosen as components of hydrotreating and hydrocracking catalysts. Their acidity is lower than that of zeolites, but the synthetic saponites are more resistant towards deactivation making them suitable components of catalysts designed to convert refractory hydrocarbon fractions derived from heavy oil, shale oil, and oil sand bitumen.

Note that layered clays are considered as new hybrid materials that can compete in fine chemicals synthesis with conventional highly porous materials like zeolites, metal organic frameworks, and other nano-engineered systems.[23–25]

The study of Mg-saponite by DRIFT using CD_3CN and $CDCl_3$ probe molecules has shown that the surface of the synthesized material possesses lower Brønsted acidity and low mobility of protons compared to zeolites. On the contrary, strong Lewis acidity is observed in Mg-saponite and this material possesses rather weak basic species on the surface. The pore volume of magnesium aluminosilicate is comparable with that of MCM-41 and lower than that of NaX and H-Beta zeolites.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.031.

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