

FT-IR Spectroscopy Applied for Surface Clays Characterization*

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ABSTRACT

The present paper should be considered as a review of the application of Fourier Transform Infra-Red for surface clay characterization. The application of surface clay materials for water treatment, oil adsorption, excipients or as active in drugs has largely increased these recent years. The surface clay material presents hydroxyl groups, which can link very easily water molecules. These hydroxyl groups can react with organic groups and by their vibration in the infra-red region, FT-IR can be easily used as a technical method for surface clay characterization. In this paper, we focus on the determination of Lewis and Brönsted acid sites on the clay surface, a critical review of the sample preparation, the surface characterization of bulk clay and the modified surface clay samples using FT-IR spectroscopy.

Keywords: Clay Materials; Surface Clays; Hydroxyls; Surface Acidity; IR Spectroscopy

1. Introduction

Clay minerals are a well-known class of natural inorganic materials with well-known structural adsorption, rheological and thermal properties. These materials originally have a hydrophilic character due to the presence of the surface hydroxyl (-OH) groups, which can link very easily water molecules [1].

For many years, the clay materials have been used for adsorption of heavy metals [2,3], dye molecules [4], herbicides [5,6], anions such as nitrates [7], like phosphates and sulphates, or gas adsorption [8], like SO₂.

In industry, these materials are also used as a catalysator in organic syntheses or as excipient in pharmacy. The application of clay materials is greatly governed by their surface properties like adsorption capacities, surface charges, large surface area, charge density, the type of exchangeable cations, hydroxyl groups on the edges, silanol groups of the crystalline defects or broken surfaces and Lewis and Brönsted acidity [9]. Phyllosilicate surfaces contain two basic types, *i.e.*, siloxane surface and hydroxyl surface. The 2:1 clay minerals (e.g., smectite group minerals) only contain siloxane surfaces while the 1:1

clay minerals (e.g., kaolinite group minerals) contain both the two kinds of surfaces (**Figures 1 and 2**).

The hydroxyl surfaces (e.g., Al-octahedral surface in kaolinite) are excellent sites for grafting since the surface hydroxyls can condensate with alkoxy groups and/or the

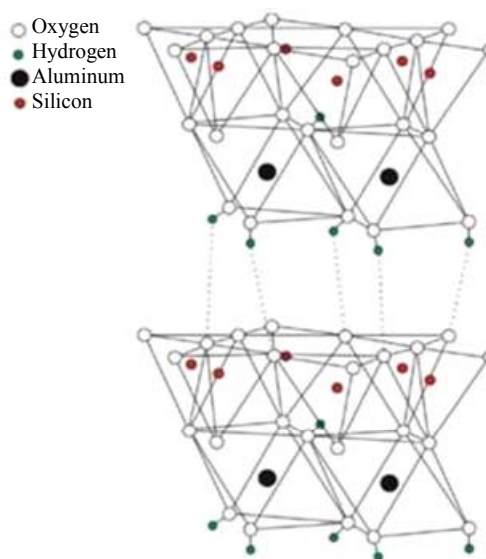


Figure 1. Structure of 1:1 clay mineral [10].

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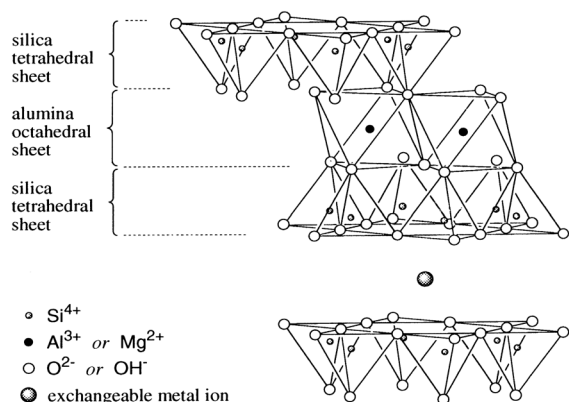


Figure 2. Structure of 2:1 clay mineral [11].

hydroxyls in the hydrolyzed silane. Due to the high ratio of the terminal surface area of the basal surface area, hydroxyl groups located at breaking edges play an important role in the silane grafting reaction. However, due to the variation of the structure and property of phyllosilicates, prominent differences of the grafting mechanism and grafting sites exist among different clay minerals. For swelling clay minerals such as montmorillonite, silane is readily intercalated into the interlayer space [12]. Chemical modifications on the surface of clay with acids, bases, cationic surfactants and certain polyhydroxyl cations were also conducted to improve their sorption capacity. Surface modification of clay minerals has attracted much attention because they obtained products exhibiting properties suitable for many applications in material science [12] and environmental engineering [13].

Several characterization techniques were employed in order to identify the changes in clay: fourier transform-infra-red (FT-IR), X-ray diffraction (XRD), raman spectroscopy, Si/Al NMR, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and nitrogen adsorption-desorption isotherms [14]. FT-IR is a complementary method to X-ray diffraction (XRD) and other methods used to investigate clays and clay minerals. FT-IR is rapid, inexpensive and can be available in many laboratories. For the FT-IR spectroscopy, it is still a discussion about the technique procedure, the nature of bond between the clay surface and the organic molecule after adsorption or grafting. In this paper, we intend to give some recommendations for these questions.

The study presented in this paper is a review aimed at utilization of FT-IR spectroscopic as the surface clay method characterization of bulk materials or modified clay samples, determination of Lewis and Brønsted acid sites on clay surface, and a critical review of the sample preparation.

2. Techniques

Today, infrared studies of the adsorption properties of

clay surfaces may be limited by sample preparation and handling problems. IR absorption spectra of clay minerals are usually obtained from self-supporting films, films sedimented on IR-transparent windows, alkali-halide disks (e.g. KBr), or from oil mulls (the most common mulling agent is Nujol-paraffin oil).

Transmission spectroscopy is the oldest and most commonly used method in the clay mineral studies. Naturally occurring clay minerals are powders or solids that can be ground into powders. The KBr pressed disc technique is frequently used to prepare samples for IR analysis. Convenient means to prepare a clay sample for FTIR spectroscopic analysis is to mix the clay sample with potassium bromide (KBr) and place the KBr/clay mixture into a dye under pressure to form a pellet. In order to minimize the amount of the adsorbed water, the discs should be heated in a furnace overnight at 130°C [15]. In our laboratory, after heated at 130°C, the sample should be immediately submitted for FTIR measurement to avoid atmospheric water adsorption. The pressing of KBr with clay to prepare the KBr pellet may alter the spectrum through the exchange of K into the structure. The danger occurs in the stage of mixing the kaolinite with KBr before the mixture is pressed into a disk [15]. If that mixing is gentle it causes no effect, but if grinding is used in the mixing, severe changes in the intensities of some of the absorption bands occur due to an interaction between the KBr and the kaolinite. Bell *et al.* [16] show that the magnitude of change depends on the absolute pressure, the pressing time and whether a salt matrix is used. Pressing with KBr causes larger differences than pressing neat. This simple experiment shows that IR hydroxyl peaks change irreversibly when kaolinite powder is pressed into pellets. This may be due to optical or chemical effects. According to these authors, due to the hydroxyl intensity changes, the valuable structural information is lost when kaolinite IR spectra are acquired using pressed KBr pellets [16].

The self-supporting film (SSF) is another technique for preparation of samples for FTIR measurement. In this technique, a drop of that aqueous clay suspension is pipetted onto a thin polyethylene sheet and allowed to evaporate to dryness overnight at room temperature. But, the problem with this technique is for smectite clay materials. The important property of smectites is their swelling ability, when exposed to humidity, these minerals swell in a series of steps as water enters the interlayer region to form so-called one-, two- and three-layer hydrates. In studies of smectite dehydration SSF technique is more suitable because it allows examination of a sample without a KBr matrix, known to be hygroscopic [17]. In other points, absorption bands of water molecules adsorbed on KBr and those present in the smectite overlap are not possible to distinguish. Therefore it is good to heat the

sample before measuring, Madejova *et al.* [17] threat for 15 min at 150°C a Montmorillonite for film Self-supporting film. **Figure 3** presents the result of heated and unheated samples. We can see a completely eliminated band near 3400 cm⁻¹ related to H₂O adsorbed on the sample, and a well-resolved band at 3629 cm⁻¹ assigned to OH⁻ stretching vibrations of structural hydroxyls remained. This technique was also useful for the 950 - 800 cm⁻¹ region, where well-resolved absorption bands are present.

Another method to obtain IR spectra of solids are Nujol (mineral oil) mulls between KBr plates. Good results are obtained by this method only if the average particle size of the solid is somewhat less than the wavelength of light the particles are to transmit. The sample should be grounded in a mortar to reduce the average particle size to 1 - 2 μm. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate, a small drop of mineral oil is added and the second window is placed on top. With a gentle circular and back-and-forth rubbing motion of the two windows, evenly distribute the mixture between the plates [18].

The mixture should appear slightly translucent, with no bubbles, when properly prepared. The FT-IR using from oil mulls or Nujol technique modified of the spectra of some organo-clays may occur in alkali halide disks because they may react either with the clay (e.g. cation exchange with the alkali halides, intercalation of the alkali halides, grinding or pressure effects) or with the organic matter (e.g. extracting the organic matter from the clay by Nujol, replacing of adsorbed organic matter by alkali halide) [19].

Attenuated Total Reflection FTIR (ATR-FTIR) is also an alternative method for FT-IR sample preparation where raw material is placed directly onto the diamond crystal for data acquisition [20]. One advantage of ATR-IR over transmission-IR, is the limited path length into

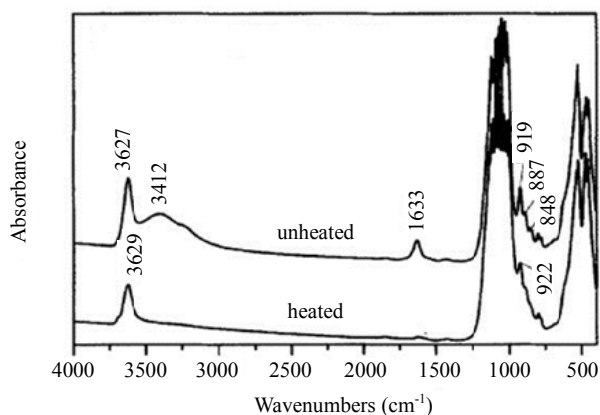


Figure 3. Transmission IR spectra of SWy-2 (montmorillonite) self-supporting film-sampling techniques; slight heating [17].

the sample. This avoids the problem of strong attenuation of the IR signal in highly absorbing media, such as aqueous solutions. During preparation, powdered core samples were settled (<2 μm grain size fraction), dried and heated up at 80°C to minimize the adsorbed water content and then kept in closed vessels covered by parafilm before ATR-FTIR measurements [21].

3. Clay Surface Characterizations

3.1. Characterization of the Hydroxyls at the Surface Clays

The triclinic layer structure of pure kaolinite reveals four well resolved (-OH) bands in IR spectrum. Three of these bands are assigned to the stretching vibrations of surface hydroxyl groups (3652, 3671, and 3694 cm⁻¹) while the fourth (3620 cm⁻¹) is attributed to the vibrations of inner hydroxyl groups. The OH-bending region of kaolinite shows vibrations of the inner surface OH groups at 913 cm⁻¹ and that of surface OH groups near 936 cm⁻¹; additional bands near 701 and 755 cm⁻¹ are associated with the surface hydroxyls. Bands due to ν(AlFeOH) at 865 - 875 cm⁻¹ and stretching at 3607 cm⁻¹ are typical of Fe bearing kaolinites [22]. The four OH-stretching bands in the infrared spectrum of kaolinite are widely used in the study of adsorption and interface reactions of this mineral. Raman spectra of kaolinites exhibit five OH-stretching bands, the additional Raman feature at ~3685 cm⁻¹ being located between bands at about 3696 and 3670 cm⁻¹.

For the halloysite compared with kaolinite, two infrared bands are observed at 1648 and 1629 cm⁻¹ in the halloysite spectrum. The assignment of these latter two bands is to the water HOH bending mode. The fact that two bands are observed suggests that there is water present in the halloysite (10 Å) structure. This corresponds with the hydroxyl stretching wavenumbers above. The band at 1648 cm⁻¹ corresponds to strongly hydrogen bonded water, whereas the band at 1629 cm⁻¹ is attributed to less strongly hydrogen bonded water and corresponds to the position of the water bending mode of liquid water [23].

The structural OH⁻ bending mode in montmorillonite absorbs between 700 and 950 cm⁻¹ and shows a series of discrete peaks that indicates the cation composition in the octahedral sheet. The OH⁻ bending mode of the Al₂OH group absorbs near 920 cm⁻¹; The OH⁻ of Fe(III)AlOH absorbs near 890 cm⁻¹; the OH⁻ MgAlOH absorbs near 840 cm⁻¹; and The OH⁻ Fe(II)Fe(III)OH absorbs near 800 cm⁻¹ [24]. The region above 3000 cm⁻¹ wavenumber of FT-IR contains information about the silanols of montmorillonite. The characteristic vibration peaks of smectite are at 3628 cm⁻¹ (O-H stretching) [25].

3.2. Characterization of Modified Clay Surface Samples

Murakami *et al.* [26] modified a kaolinite with butanediols. The IR spectrum of Kao-1,2BD (kaolinite modified with 1,2-Butanediols) showed the bands at 2970, 2941 cm^{-1} (rasCH₂) and 2885 cm^{-1} (rsCH₂), indicating the presence of the organic component (**Figure 4(d)**). The spectrum of Kao-1,3BD (kaolinite modified with 1,3-Butanediols) also showed a pattern similar to that of Kao-1,2BD (kaolinite modified with 1,2-Butanediols); the bands at 2971, 2931 cm^{-1} (rsCH₂) and 2856 cm^{-1} (rsCH₂) were observed (**Figure 4(d)**). The spectrum of methoxy-modified kaolinite (**Figure 4(b)**) shows the disappearance of the bands at 3668 and 3653 cm^{-1} and the appearance of the bands at 3645 and 3631 cm^{-1} . The shifts are ascribable to the variation in the interlayer environments of the hydroxyl groups. The broad band centered at 3550 cm^{-1} can be due to OH of the interlayer water. The bands at 3645 and 3631 cm^{-1} found for methoxy-modified kaolinite disappeared in the spectrum of Kao-1,2BD (kaolinite modified with 1,2-Butanediols), and a new band at 3599 cm^{-1} was observed (**Figure 4(c)**). The band is ascribable to OH of hydroxyl groups on the interlayer surface hydrogen bonded with grafted 1,2-Butanediols. A broad band at 3550 cm^{-1} due to rOH of interlayer water was also observed. In the spectrum of Kao-1,3BD, the bands at 3645 and 3631 cm^{-1} observed in the spectrum of methoxy-modified client disappeared and a new broadband at 3650 cm^{-1} and a sharp band at 3599 cm^{-1} were observed (**Figure 4(d)**) [26].

Priyanthi *et al.* [27] show that infrared spectroscopy is a powerful method for monitoring and analyzing clay-fluid interactions. They studied the characteristic of IR bands, such as Si–O stretching, O–H stretching of structural O–H group, O–H stretching and H–O–H bending

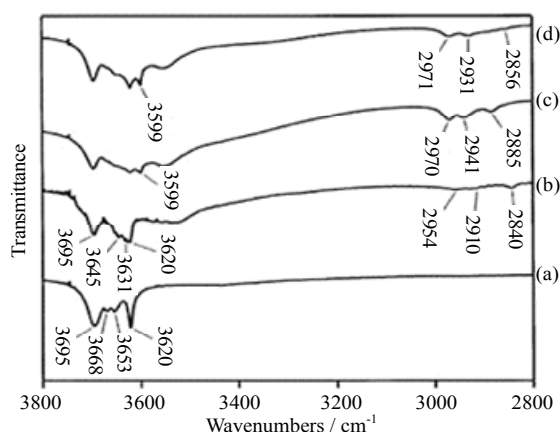


Figure 4. Infrared spectra of (a) kaolinite, (b) dry methoxy-modified kaolinite, (c) Kao-1,2BD, and (d) Kao-13,BD [26].

of interlayer water, in clay, and characteristic IR vibration bands such as C=O and C–C–O stretching bands in solvents, they use these results to understand the clay-fluid interactions at the molecular level. Important is to dry the clay sample in order to remove water before FTIR measurements, however, slight changes in structure during manipulation cannot be ruled out and the results could be wrongly interpreted. We suggest many other techniques in order to compare the results like powder X-ray diffraction.

3.3. Determination of Brönsted and Lewis Acid Sites

There are several methods to determine the surface acidity of clay minerals such as Hammett indicator technique, *n*-butylamine back titration, microcalorimetry and FT-IR spectroscopy of adsorbed basic probe molecules [28]. Brönsted and Lewis acid sites can be distinguished from the IR spectrum of pyridine adsorbed on the clay surface. Brönsted and Lewis acid site concentrations are calculated using the IR bands centered at 1545 cm^{-1} (characteristic of the pyridium ions pyH⁺) and 1455 cm^{-1} (characteristic of the pyL species), respectively, using the following formula:

$$C_{\text{Lewis}} = A_l S * 1000 / \epsilon_l \omega \quad (1)$$

$$C_{\text{Brönsted}} = A_b S * 1000 / \epsilon_b \omega \quad (2)$$

where A_l is the area of the IR band centered at 1450 cm^{-1} , A_b is the area of the IR band centered at 1545 cm^{-1} , S is the area of the pellet (cm^2), ω is the weight of the pellet (mg), and ϵ are the extinction coefficients (in $\text{cm} \mu\text{mol}^{-1}$) $\epsilon_l = 1.28 \text{ cm} \mu\text{mol}^{-1}$, $\epsilon_b = 1.13 \text{ cm} \mu\text{mol}^{-1}$ [28].

The infrared absorption bands in the 1400–1700 cm^{-1} region for pyridine adsorbed on silica-alumina and aluminosilicates have been used to study their acidity since the 1960s [2]. But it is still a problem. It is known that spectra of MMT before pyridine adsorption contain in this region only one band near 1630 cm^{-1} due to the bending OH vibrations of water molecules; therefore it is important to dry the sample before the pyridine adsorption [28].

The Brönsted sites (B) show bands near 1490, 1540, and 1635 cm^{-1} . The 1540 cm^{-1} band is typical of this site; the corresponding species is the pyridinium ion (PyH⁺). It is assumed that tricoordinated aluminum atoms with an electron-free orbit constitute Lewis acid centers (L). Pyridine coordinated to the Lewis sites absorbs near 1455, 1490, and 1610–1625 cm^{-1} ; the 1455 cm^{-1} band is typical of these sites. The third type of site, corresponding to hydrogen-bonded pyridine (H) on the clay solid, has vibrations near 1440 and 1590 cm^{-1} (**Figure 5**) [28]. These bands are probably due to a strong interaction between the cation and the pyridine molecule, by attraction of the cation into the electrostatic field [17].

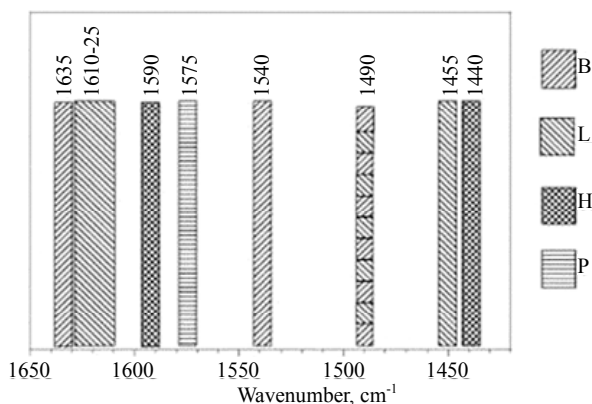


Figure 5. Bands in the IR spectra of acid solids with adsorbed pyridine in the $1420 - 1650 \text{ cm}^{-1}$ region. Pyridine adsorbed on B, Brønsted sites; L, Lewis sites; H, hydrogen-bonded, and P, physisorbed pyridine [28].

The band at 3620 cm^{-1} corresponds to the “inner hydroxyls” located on the plane, common to octahedral and tetrahedral sheets, as described previously. Bands recorded at 3668 and 3652 cm^{-1} are suggested could be attributed to the vibration of the “outer hydroxyls” located at the surface and along broken edges of kaolinite monocrystals [17].

3.4. Clay Surface Complexation

Adsorption of metal ions from aqueous solution on oxides, clay minerals and clays has been a subject of interest in chemistry as well as in other research areas. It is considered that the adsorption of heavy metal ions and complexes on clay minerals occurs as a result of ion exchange, surface complexation, hydrophobic interaction, and electrostatic interaction [9]. The adsorption modes of ions on mineral surfaces are mainly divided into outer-sphere and inner-sphere surface complexes. In general, the chemical interactions in inner-sphere complexes are stronger than those of outer-sphere complexes (**Figure 6**) [9]. These differences in binding strengths influence the mobility of ionic species in the environment. Hence, a distinction between outer-sphere and inner-sphere complexes is significant and FT-IR is helpful for the evaluation of the outer-sphere and inner-sphere surface complexes. The evaluation of outer-sphere and inner-sphere surface complexes needs techniques such as attenuated total internal reflection spectroscopy (ATR-FTIR). Zhang *et al.* [29] studied the Cd(II)-sulfate interactions on the goethite-water interface, ATR-FTIR studies indicated that sulfate adsorption on goethite occurred via both outer- and inner-sphere complexation; the authors assign peaks at 1170 , 1132 , and 1050 cm^{-1} to inner-sphere species. More recently Brechbühl *et al.* [30] studied the competitive sorption of carbonate and arsenic to hematite: combined ATR-FTIR and batch experiments, the ATR-FTIR

spectra indicated the predominant formation of bidentate binuclear inner-sphere surface complexes for both sorbed arsenate and sorbed carbonate.

Moreover, the FT-IR could be used to show the bond between the clay and the metal ion after adsorption, for example, Eren *et al.* [13] modified a bentonite clay using MnCl_2 for copper adsorption, the FT-IR of the sample after copper adsorption presented in **Figure 7** shows that the stretching OH band was shifted up to 3668 cm^{-1} and, moreover, new bands appeared near 3591 and 3460 cm^{-1} in the spectrum of MMB-Cu(II) sample. The IR spectrum of the MMB-Cu(II) sample showed a strong band of water near 3400 cm^{-1} , due to the overlapping asymmetric ν_3 and symmetric $\nu_1(\text{H-O-H})$ stretching vibrations. We are also modified the magnetite clay with Black Eriochrome T, NET and the FTIR spectroscopy help us to show the modification of our sample using KBr technique [4].

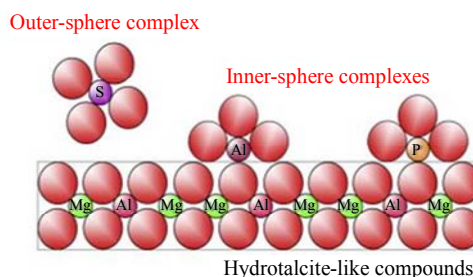


Figure 6. Outer-sphere and inner-sphere surface complexes at the hydrotalcite-like compounds [31].

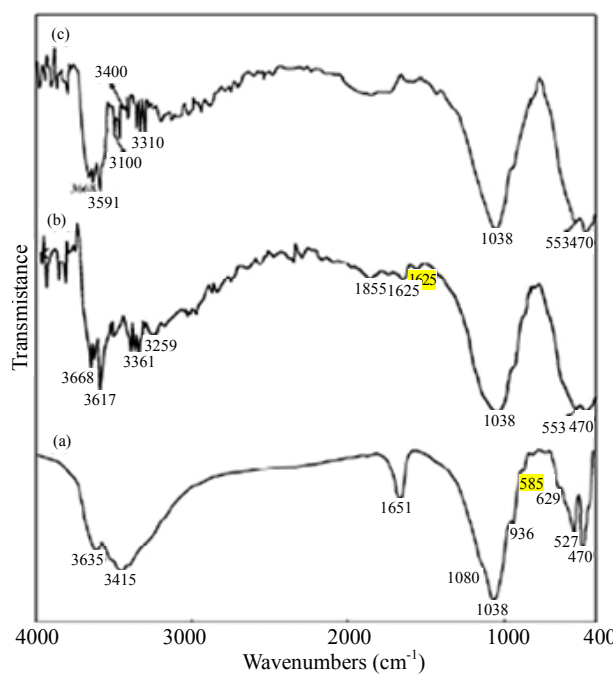


Figure 7. IR spectra of the RB (a) bulk samples, MMB (b) modified with MnCl_2 , and MMB-Cu(II) (c) [13].

Nicolini *et al.* [32] studied the dehydrated halloysite intercalated mechanochemically with urea: Thermal behavior and structural aspects; the absorption bands at 3696 and 3622 cm^{-1} in the FTIR spectrum were assigned to the stretching vibration due to external and internal O–H groups of halloysite, respectively. The intensity of the band at 3696 cm^{-1} is lower than the band at 3622 cm^{-1} , because it is mainly the external hydroxyl groups that are responsible for the interactions with urea through N–H groups and new bands were observed at 3503 and 3390 cm^{-1} indicated the adsorption of urea.

Table 1 gives the wave number values of the hydroxyls group of the most used clay minerals like kaolinite, halloysite and montmorillonite. It appears in this table that these values are between 3000 - 3800 cm^{-1} and these values are really close, most are around 3600 cm^{-1} . It's not sufficient to use only FTIR to characterize clay minerals, other methods like powder X-ray, thermal gravimetric etc. should be combined to have a complete characterization.

4. Conclusion

The present review was aimed to the technical procedural methods used by FT-IR for clay surface characterization because, FT-IR remain is an economical, rapid and common technique. A spectrum can be obtained in a few minutes and the instruments are sufficiently inexpensive as to be available in many laboratories.

An IR spectrum can serve as a fingerprint for mineral identification, but it can also give unique information

Table 1. Wavenumber peaks of the hydroxyl, OH group of most used clays.

Clay minerals	Wavenumber (OH) cm^{-1}	Refs
Kaolinite	3696, 3671, 3650	[33]
Halloysite	3696 (OH-internal), 3622 (OH-external)	[32]
Montmorillonite	3624 (Al-OH), 3422 (Water)	[34]
Verniculite	3675 (Mg-vermiculite), 3594 (Na-vermiculite)	[35]
Bentonite	3625	[15]
Illite	3600	[36]
Chlorite	3670, 3580 (Interlayer) 3440 (water)	[37]
Smectite	3622	[38]
saponite	3740 (Si-OH), 3670 (Mg(OH) ₂), 3570	[39]
Sepiolite	3719 (Si-OH) 3689 (Mg ₃ OH)	[40]
Nacrite	3701 and 3647 (out-of-plane), 3647 (in-plane)	[23]
Dickite	3708, 3654, 36228 (Inner surface OH)	[41]
Lizardite	3686 (Mg-OH)	[42]

about the mineral structure, including the family of minerals to which the specimen belongs, the degree of regularity within the structure, the nature of isomorphic substituents, the distinction of molecular water from constitutional hydroxyl, and the presence of both crystalline and non-crystalline impurities [17].

Among different techniques samples preparing for IR measurement are self-supporting films, films sediment on IR-transparent windows, alkali-halide disks like: KBr, NaCl etc., or from oil mulls. Many parameters influence the results in each case as the pressing, grinding effect and atmospheric water adsorption, therefore the choose of preparing samples should be greatly depending on the type of clay and the results we need to show. As a recommendation for using FT-IR for the surface clay characterization, the Attenuated Total Reflection, the ART-FTIR method, could be a best technique for the sample preparation. It is important to dry the sample up to 100°C to eliminate the adsorbed water on clay sample and this gives a good result and interpretation in the range 3000 - 4000 cm^{-1} where appear the surface hydroxyl bands of clays.

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