

Author version of:

Frost, Ray and Medelovici, Efrain (2006) Modification of fibrous silicates surfaces with organic derivatives: An infrared spectroscopic study. . *Journal of Colloid and Interface Science* 294(1):47 -52.

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MODIFICATION OF FIBROUS SILICATES SURFACES WITH ORGANIC DERIVATIVES – AN INFRARED SPECTROSCOPIC STUDY

Abstract

This contribution explores the interaction of the fibrous silicates, palygorskite, sepiolite and chrysotile with a wide range of organic agents. Infrared spectroscopy (IR) methods are essential for the characterization of solid surfaces and for the investigation of the kind of bonds formed between the surface of these silicates and the organic moieties. Thus, when sepiolite or palygorskite are treated e.g. with polyurethanes, isocyanates, amines or pyridines, specific Si-NH-C or Si-O-C bonds are derived from the linkage of the differently located OH groups in these fibrous silicates with the organic moieties. On the other hand, more stable, covalent Si-O-Si-C bondings are formed when the fibrous silicates, especially chrysotile, are reacted with heterofunctional silylating agents like chlorosilanes or ethoxysilanes carrying , alkyl, alkenyl or aryl groups. Such reactions may occur in presence or absence of HCl. An absorption band at 960 cm^{-1} -which we assigned to Si-OH groups- is detected only in presence of HCl. The evolution of this band is related to the degree of grafting of the organic radicals with the silanol groups of the silicates. HCl-generated silanol groups are the main bridges for the coupling of organosilyl groups on chrysotile and other silicates by covalent bonding, leading the way to the preparation of interesting new materials, including fibrous sheet polymers.

INTRODUCTION

Organically modified silicates have selective applications in many areas and have thus called the attention of a number of investigators in the last three or four decades. Organic derivatives of fibrous silicates like palygorskite (also known as attapulgite), sepiolite and chrysotile deserve a special chapter because of their interesting applications. As infrared

spectroscopy has been an important tool to study and characterize the structure of such fibrous organomineral products, we undertake here a review of works done in this field.

Two kinds of organic treatments of these fibrous silicates will be considered. Treatments with organic agents based mostly on carbon, nitrogen, arsenic, etc. (e.g. amines, isocyanates, alcohols, polyurethanes, organic acids) and with organosilicon compounds, based mostly on silicon and carbon (e.g. siloxanes, chlorosilanes, alkoxy silanes, etc.). The presence and absence of HCl in the mentioned treatments will also be discussed. Acid treatments *per se* may result in solids with increased surface areas, high porosity and acid centers. Such acid-treated silicates may find applications in catalysis, as bleaching agents, etc.

Modification of palygorskite by HCl and organic compounds

Palygorskite consists of chains of a 2:1 phyllosilicate structure and has an arrangement of inversed silica tetrahedral sheets linked together through apical oxygens. The octahedral sheet containing mostly Mg and Al atoms is continuous in only one direction, while the tetrahedral sheets are linked infinitely in two dimensions. This structural arrangement allows the formation of channels which lodge water molecules randomly distributed (so called zeolitic water) attached to the silica unit. The channels measure $3.7 \times 6.4 \text{ \AA}$ in cross section. At the edges exposed OH groups are neutralized by protons forming more resistant H_2O molecules coordinated to the octahedral elements. The discernment of IR absorption bands due to these different kinds of water molecules and to the presence of OH groups coordinated to the metallic cations have been reported [1-7]. Frost et al. [6] carried out this investigation not only in the mid-infrared region but

also in the near-infrared region. The application of near-IR spectroscopy is very helpful for the understanding of the interaction between the surface hydroxyls of palygorskite and water molecules.

Water molecules play an important role in the interaction of palygorskite with e.g. some ethoxysilanes[8], polyurethane prepolymer [9] or with some organic amines and pyridine [10]. In the mentioned works, IR spectroscopy has been quite helpful in determining the stability and type of bridges between the organic compounds and palygorskite.

Mendelovici [1] studied D₂O as well as HCl treated palygorskite by using IR absorption spectroscopy to detect changes in bands assigned to Si-O, Si-O-Si and non-equivalent OH vibrations. Generally, the assignments of some of the lower frequency modes presented for palygorskite in this study, such as the 1198 cm⁻¹ mode assigned to Si-O vibrations, are in agreement with the lattice dynamics calculations published by McKeown et al [6]. Other valuable IR studies on the structural changes resulting from the HCl treatment of palygorskite followed [4, 11].

When palygorskite was reacted with dimethyldiethoxysilane in presence of HCl, organosilyl radicals –produced by the acid hydrolysis of the alkoxy silane–were coupled through HCl-generated silanol groups on the surface of the silicate[8]. Figure 1, reproduced from the latter work show the IR spectra of the methanol washed solid separated from the reaction mixture. The hydrolysis of dimethyldiethoxysilane in strongly acid media favors the production of cyclic or low molecular weight linear polymers. After an exhaustive benzene extraction of this product, only chemically bonded dimethylsiloxy radicals remained grafted on the mineral by covalent bonding, the non bonded fraction, presumably formed by the more volatile dimethylpolysiloxanes being dissolved in benzene. Therefore, a decrease in intensity of the absorption bands due to the methyl groups attached to silicon

at, 2960, 1382, 1260 and 800 cm^{-1} in the infrared spectrum of the extracted product was observed.(Fig.1, b-c). In addition , a weak shoulder appeared at 955-960 cm^{-1} (Fig. 1,c) not detected in the spectrum of neat palygorskite (Fig. 1,a). The frequency at 960 cm^{-1} has been assigned to a Si-O-H vibration in HCl-treated palygorskite [1]. The reaction of palygorskite with dimethyldiethoxysilane was also carried out in absence of HCl [8]. In absence of HCl however, the incorporation of the organosilyl groups on palygorskite occurred by a different mechanism. In this case the ethoxysilane may be hydrolyzed by a fraction of the water contained in palygorskite.

IR spectroscopy was also used to study the interaction of palygorskite with a prepolymer based on polytetrahydrofurandiol and toluene 2,4-diisocyanate [9]. According to this study, zeolitic water from the channels of palygorskite may interact with the isocyanate groups of the prepolymer. Moreover, Si-OH groups positioned along the edges of the palygorskite ribbon and characterized by a weak absorption at about 3705 cm^{-1} [1] also interacted with the prepolymer molecules forming urethane-like bonds which are readily hydrolyzed. The adsorption of polyvinyl-alcohol (PVA) on palygorskite has also been investigated by IR spectroscopy [12]. This work shows that the polymer macromolecules (PVA) are adsorbed mostly on the external oxygen surface via hydrogen bonds, the groups involved in the hydrogen bond being CH and the surface oxygens of palygorskite. The adsorption of PVA occurs also via coordinated water molecules, depending both types of adsorption on the concentration of PVA in the reactive solution. Short chain primary alcohols, like methanol and ethanol can penetrate inside the channels of palygorskite, suggesting that these channels are accessible to small molecules of high polarity .

References on these sort of interactions are given by Serratos [13] .Sorption of non-polar

organic compounds on palygorskite is strongly influenced by the size and shape of the sorbate molecules [14].

Organic derivatives of sepiolite

The structure of sepiolite is similar to that of palygorskite, differing essentially in the dimensions of the channels and in the replacements within the structure. The channel size in sepiolite (3.7x 10.6 Å) is about 50% wider than in palygorskite. Moreover the metallic cations distribution also differs from that in palygorskite. Palygorskites contain Mg, Al and Fe cations, whereas the sepiolites contain Mg only.

The IR spectroscopy study on the comparative thermal treatment of both, sepiolite and palygorskite with butylamine (and related compounds), revealed that the amines are adsorbed in the channels of the silicates mostly by interaction with zeolitic water [10]. Associations between butylamine and bound water were observed in sepiolite but not in palygorskite. A number of mechanisms were proposed for these associations, mostly via hydrogen bonds with octahedral sites of the silicate. A significant feature about the effect of water which should also be considered is that butylamine and other liquid n-alkylamines give a quite crystalline X-ray diffraction (XRD) pattern when exposed to atmospheric moisture, due to the formation of an amine-water complex [15].

Fourier transform IR spectroscopy (FTIR) was employed to report as well the associations of both, sepiolite and palygorskite with pyridine [10, 16]. Former IR investigations on the interactions of pyridine with montmorillonite [17] and with silica-alumina oxides derived from X-zeolites [18] are quite useful for understanding these interactions and to discuss the possible role of Bronsted or Lewis acid centers in sepiolite and palygorskite.

In another kind of reactions, sepiolite was treated with butyl and phenyl isocyanates in vapor phase as well as in solution [19]. IR spectroscopy results showed that the 3716 cm^{-1} absorption band of sepiolite disappeared upon exposure of sepiolite to butyl isocyanate vapor, but this treatment did not affect the band at 3676 cm^{-1} . A frequency at 3740 cm^{-1} was assigned to structural hydroxyls attached to silicon atoms (silanol groups) in sepiolite, whereas a band at 3674 cm^{-1} was attributed to a hydroxyl on a magnesium ion located in the octahedral sheet [20]. Urethane-like bonds, of the type Si-O-CO-NH-R, (R = organic radical) were identified in the IR spectra [19]. Water adsorbed on the sepiolite surface reacted with the isocyanate producing 1, 3 substituted ureas and regenerated the silanol groups in sepiolite. The reaction with the isocyanates in benzene solution gave similar reaction products, but the excess isocyanate (starting reagents) present in the vapor phase reaction were not detected, because they were dissolved in the benzene solution.

The treatment of epoxides (styrene oxide and allyl-glycidyl ether) in vapor phase with sepiolite has also been reported [21]. The reaction takes place through the large amount of external SiOH groups of sepiolite, and its extent has been monitored by IR spectroscopy, by measuring the decrease of the 3720 cm^{-1} absorption band due to the stretching OH vibration of the silanol groups in sepiolite. The SiOH groups induce the opening of epoxide molecules followed by combination with the resulting organic species on the silicate surface, via Si-O-C bonds.

The use of silanes as modifying agents of silicates has been widely explored. Vinyl derivatives of sepiolite have been synthesized by a controlled reaction of HCl-treated sepiolite with methylvinylchlorosilane [22]. The controlled acid attack increases the number of silanol groups on the surface of sepiolite, which are subsequently coupled with the methylvinyl groups. Infrared absorption spectra allowed to identify the grafting of

these groups on the surface of sepiolite, whose basic silicate structure was only weakly affected by this controlled reaction. In this reaction it was also necessary to take in account the conditions which would allow the polymerization of the silylating agent, methylvinyl-dichlorosilane. In addition, it has been reported the grafting of sepiolite by a mixture of methylvinyl-cyclosiloxanes [23]. In this case, polymeric species containing polysiloxane chains are grafted on the mineral.

Modification of chrysotile by organic compounds in presence or absence of HCl

Chrysotile asbestos is a fibrous magnesium silicate, but in contrast to palygorskite and sepiolite, it has a 1:1 layered structure formed by the condensation of a silica tetrahedra sheet with a magnesium octahedral sheet, not allowing the formation of channels which lodge water molecules. As the octahedral sheet is filled principally by Mg instead of Al, a strain and bending in the structure results, explaining the fibrous nature of this mineral.

As chrysotile is mostly magnesium mineral, the removal of Mg from its octahedral sheet by HCl is a relatively easy process. Morphological and textural changes of such a process have been described [24]. The HCl attack preserves the fibrous morphology of chrysotile, which is otherwise destroyed if chrysotile is decomposed e.g., by reaction with an other mineral acid like fluorosulfonic acid [25]. We shall consider two aspects of the treatment of chrysotile by organic compounds in presence of (6M) HCl (a) and by direct reaction, in absence of HCl (b).

a) The synthesis of trimethylsilyl derivatives of silicate minerals ranging from ortho to tectosilicates by a procedure involving 6M HCl (diluted by isopropanol, which is a proton acceptor and reaction regulator) and hexamethyldisiloxane as modifying agents (known as the cohydrolysis method) was published by Lentz [26]. Upon cohydrolysis of

the mineral and organosilicon compound by 6M HCl, Si-OH sites are generated in both processes. Based on this method the modification of chrysotile by e.g. HCl plus monofunctional silylating agents which generate trimethyl groups as hexamethyldisiloxane or trimethylchlorosilane were described [27, 28]. SiOH groups, resulting from the hydrolysis and extraction by HCl of the Mg octahedral sheet, formed covalent bondings with the organosilyl groups by a protonation and condensation mechanism. Thus, the Si-O-Mg- bonds of the starting material (chrysotile) are completely replaced by Si-O-Si(CH₃)₃ groups. The resulting solid of this reaction gave no X-ray diffraction (XRD) pattern, thus IR spectroscopy accompanied by kinetic and surface measurements were essential tools in interpreting the reaction mechanism [27, 29]. Such an organosilicate compound has hydrophobic properties and a high surface area. In this case the whole Mg trioctahedral layer was extracted (by HCl) and replaced by the methylsilyl groups. The described reaction can be controlled in such a way that only part of the Mg layer is removed (by HCl) and replaced by the silylating groups. Employing this controlled method, dimethylphenylchlorosilane was used as a modifying agent of chrysotile. The organosilyl derivative resulting from this modification of chrysotile (DMPS) was studied by Fourier transform infrared-photoacoustic spectroscopy (FTIR-PAS) [30]. Table 1 reproduced from this study displays the IR band assignments of the DMPS derivative of chrysotile, eliciting the Si-phenyl vibrations at 1466 and 736 cm⁻¹ which were carefully resolved by band analysis in the mentioned study. Moreover appears the vibration at 957 cm⁻¹ due to HCl-induced Si-OH groups. The Table also shows the frequencies of a distinct dimethylsilyl derivative of chrysotile (DMDS) prepared by direct reaction of the silicate with dimethyldichlorosilane [31]. The corresponding spectrum exhibited a sharp peak at 1260 cm⁻¹ (shown here in Table 1) which was

ascribed to a diagnostic C-H bending mode of the dimethylsilyl groups in DMDS. As the structure of chrysotile was only partially affected in the controlled experimental conditions, the spectra of both DMDS and DMPS derivatives showed also absorption bands of the initial chrysotile, like those at 3690 and 3694 cm^{-1} which are collected in Table 1. These two bands, recently reported but not assigned by Majedova [32] were previously attributed to in-phase, inner surface Mg-OH and inner Mg-OH stretching vibrations, respectively [33]. Chrysotile was also reacted with another monofunctional agent, namely dimethylallylchlorosilane [34]. The corresponding IR analysis showed that presumably, sym-diallyltetramethyldisiloxane, was produced by the condensation of dimethylallylchlorosilane in acid medium and grafted on chrysotile.

The cohydrolysis reaction of chrysotile with difunctional chlorosilanes like methylvinylchlorosilane was also described [27]. IR spectra of the resulting products exhibited absorption bands assigned to the $\text{Si-O-SiR}_1\text{R}_2$, where R_1 and R_2 are methyl and vinyl groups, respectively. These groups were grafted upon gradual replacements of Si-O-Mg- units from chrysotile by a diffusion mechanism as was also shown by chemical and surface analysis and electron microscopy methods (27, 29). The presence of difunctional silylating agents may give rise in the employed experimental conditions polymerization of linear, short siloxanic chains. Moreover, when silylating agents carrying non saturated groups like vinyl are employed, copolymerization thru the C=C bond might take place.

b) Chrysotile was also modified by direct reaction with organic acids like phenylarsonic acid or 2-nitrophenol-4-arsonic acid [35]. FTIR spectra of corresponding products showed strong bands attributed to the organic moieties. The organic groups were grafted via silanol groups formed on a disordered silica surface, like that obtained by HCl

leaching of chrysotile.. During the grafting process the disordered silica structure had to rearrange in order to allow the bonding of the arsonate groups to the disordered silica surface.

The controlled reactions of some alkoxysilanes like gamma-methacryloxypropyltrimethoxysilane and delta-aminibutyldiethoxysilane with partially HCl-leached chrysotile [36] and 3-aminopropyltrimethoxysilane with silica thoroughly leached out from chrysotile [37] were reported. IR spectra of the products resulting from the mentioned reactions showed the appearance of absorption bands due to the organosilyl groups, which were grafted on leached chrysotile by a similar mechanism as that described above.

The interactions between asbestos and polynuclear aromatic hydrocarbons (PAH) has been investigated (see e.g. Fournier and Pezerat [38] and refs. therein). The adsorptions of PAH on the surface of chrysotile are conditioned on the properties of the PAH and asbestos fibers. Chrysotile and other solids having a dominant basic character (magnesia, crocidolite, amosite) revealed the formation of condensed multilayers of PAH. These works are relevant to the health and environmental areas, as a synergetic effect between asbestos and cigarette smoke has been confirmed by animal experimentations, using asbestos and some carcinogen PAH.

Conclusive Remarks

In the treatment procedures of the fibrous silicates here reported, the excess starting reagents were always washed out from the resulting products before their characterization by IR spectroscopy and other methods.

There are some differences in the adsorption mechanisms of some organic molecules by palygorskite and sepiolite. Thus e.g. linear amines and pyridine are adsorbed via hydrogen bonds with the zeolitic water contained in the channels of these two silicates. However, this association is much stronger with sepiolite, via hydrogen bonds with bound water. We must also consider that the channels in sepiolite are 50% wider-hence more accessible- than those in palygorskite, although small molecules of high polarity as well as some non-polar organic compounds may penetrate the channels of palygorskite. On the other hand, Si-OH groups are more abundant -providing more reactive sites- in the structure of natural sepiolite than in that of palygorskite. Thus, the reaction (in vapor phase) of isocyanates or epoxides with sepiolite takes place via such structural silanol groups of sepiolite. The latter should not be confounded with silanol groups generated in sepiolite and in the other fibrous silicates attacked by HCl. This mechanism has been studied by IR spectroscopy by monitoring the 3740 cm^{-1} absorption band due to the Si-O-H vibration in sepiolite.

The described organic derivatives of sepiolite and palygorskite exhibit Si-O-C or Si-NH-C bonds which are not stable, since these kinds of bridges are labile and readily hydrolyzed by water. It is possible, however, the grafting of organic species on silicates through resistant, covalent Si-O-Si-C bondings, employing organochlorosilanes or ethoxysilanes as modifying agents.

In the modification of the fibrous silicates here considered by organochlorosilanes two aspects should be considered, if HCl is included in the reaction and the functionality and nature of the silylating agents. When, for instance, 6M HCl is present in a controlled cohydrolysis reaction of chrysotile, there is a partial or total dissolution of the octahedral metallic unit (the brucite sheet) with generation of Si-O-H bonds, identified by a IR absorption at 960 cm^{-1} . The induced silanol groups formed a covalent bonding with the

organosilyl groups by a protonation and condensation mechanism. Several monofunctional silanes, containing methyl, phenyl or vinyl and allyl silyl groups were grafted by the cohydrolysis method on chrysotile and identified by IR spectroscopic methods. If in this reaction the monofunctional silanes are substituted by difunctional silanes, linear polymerization can take place. Depending of the type of starting materials and silylating agents only a part of the polymeric units may be covalently grafted on the silicates, the non-bonded fraction being extracted in hot benzene. An adequate geometrical positioning of the HCl-induced Si-OH groups in the leached silicate should favor this polymerization. In absence of 6M HCl a different mechanism prevails in the direct reaction of these fibrous silicates with some ethoxysilanes or other organic compounds.

Organosilicate derivatives of chrysotile, sepiolite and palygorskite are interesting materials, because generally, they have the surface and reactivity properties corresponding to the grafted organic molecules while they preserve the mechanical properties of the mineral framework. Moreover, when the attached molecules contain unsaturated groups it becomes possible to copolymerize the organomineral compound with several monomers. IR spectroscopy remains as a useful tool for the study of organosilicates, especially when they can not be examined by other methods like X-ray diffraction.

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ACKNOWLEDGMENTS

To many persons from the IVIC Library and to Mr. Jorge Rivas from the Photographic Service.

Legend to Figure

Fig. 1. IR spectra (KBr disks) of: (a) natural palygorskite (attapulgite); (b) methanol-washed solid product after 5 h refluxing with dimethyldiethoxysilane and HCl ; (c) the same as (b) but after (soxhlet) benzene extraction. (Reproduced with permission of the Clay Minerals Society).

