



Adsorption of Isonicotinamide on Loughlinitite (Natural Na-Sepiolite): An FT-IR Spectroscopic Study

SEVIM AKYUZ* and TANIL AKYUZ

Istanbul Kultur University, Science and Letters Faculty, Physics Department, Atakoy Campus, 34156 Bakirkoy, Istanbul, Turkey

*Corresponding author: Fax: +90 212 4658318; Tel: +90 212 4984401; E-mail: s.akyuz@iku.edu.tr

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In this study adsorption of isonicotinamide on loughlinitite (Na-sepiolite) has been investigated by FT-IR spectroscopy. The adsorption of isonicotinamide showed a considerable alteration on both Si-OH stretching and deformation peaks of loughlinitite structure. Spectroscopic results indicate that adsorbed isonicotinamide molecules onto loughlinitite are coordinated to surface silanol groups and/or Lewis acidic centers by H-bonding interaction through pyridine ring nitrogen lone pairs. The amino nitrogen is found to be relatively in active to adsorbing sites.

Keywords: Adsorption, Clays, IR spectroscopy, Isonicotinamide, Loughlinitite, Sepiolite.

INTRODUCTION

Compounds containing pyridine rings are distributed over a wide space in nature and have several important applications. Isonicotinamide (pyridine-4-carboxamide, $C_6H_6N_2O$) is a pyridine derivative with amide group in the 4-position and has a pharmaceutical importance due to its antitubercular, antipyretic and antibacterial properties¹⁻³. Furthermore, mixed salts of this molecule find extensive use in drug industry⁴.

Loughlinitite, which is known as natural Na-sepiolite, belongs to palygorskite-sepiolite group of phyllosilicates class of clay minerals^{5,6}. Sepiolite and loughlinitite have a fibrous like morphology with a distinctive layered appearance⁵⁻⁸. Loughlinitite⁵ has the structural formula $Na_2Mg_3Si_6O_{16} \cdot 8H_2O$ and sepiolite⁷ the formula $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$. Both sepiolite and loughlinitite are chain minerals. Sepiolite is structurally formed by an alteration of blocks and channels that grow up in the fibre direction (*c*-axis)⁸. Each structural block is build up of two tetrahedral silica sheets enclosing a central octahedral magnesia sheet in a similar way that occurs in other 2:1 silicates such as talc, but in sepiolite there are discontinuities and inversions of the silica sheet that give rise to those structural channels⁸. Loughlinitite is virtually identical in appearance to sepiolite both in a hand specimen and microscopically. However, field observations and mineralogical determinations indicate that loughlinitite and sepiolite are formed authigenically and independently in different physicochemical environments rather than being the product of transformation of one to the other⁶.

In our previous studies, we were investigated the interaction of isonicotinamide with montmorillonite and saponite⁹. Continuing our studies on the adsorption of drugs on the clay surfaces⁹⁻¹², in this study the sorption of 4-pyridinecarboxamide (isonicotinamide) onto natural Na-sepiolite (loughlinitite) from Anatolia has been investigated using FT-IR spectrometry. Up to our best of knowledge no study has been reported on the adsorption of isonicotinamide onto loughlinitite. The objective of this paper is to examine the generated surface species on the clay and to investigate the interaction between isonicotinamide and loughlinitite framework.

EXPERIMENTAL

In the present work, loughlinitite from Mihaliccik-Eskisehir region of Anatolia (Turkey) was employed. The clay sample was ground to fine powder of > 0.5 mm particle size and was analysed by X-ray diffraction, differential thermal and IR spectroscopic techniques for purity. The results indicate that loughlinitite is associated with analcime (approximately 8 %) and Al_2O_3 (approximately 6 %), and has detectable calcite impurity (IR; 1435 cm^{-1}). The chemical composition of loughlinitite was given in previous study¹⁰. Isonicotinamide used was reagent grade (Fluka) and used as received. Isonicotinamide treated loughlinitite was prepared by immersing clay in either aqueous solution of the organic molecule in sealed bottle at room temperature for 2 d or by solid-solid reactions between clay and the organic molecule, analogous to that described by Ogawa *et al.*¹³ and Khaorapong *et al.*¹⁴. In the former case clay organic suspension was centrifuged at 7000 g for 10 min.

IR spectra of the clay organic complexes were recorded on a Bruker Tensor spectrometer in the 4000-400 cm^{-1} region (0.5 cm^{-1} resolution) by using KBr pellet technique.

RESULTS AND DISCUSSION

The molecular model of isonicotinamide is given in Fig. 1. FT-IR spectra of solid isonicotinamide, starting loughlinitite and isonicotinamide treated loughlinitite are given in Fig. 2. In the 2700-2600 cm^{-1} region of the IR spectra of isonicotinamide treated loughlinitite, we did not observe any band which could be attributed to the N^+H stretching vibration, indicating that cationic surface species were not generated on loughlinitite.

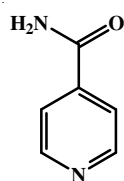


Fig. 1. Molecular model of isonicotinamide

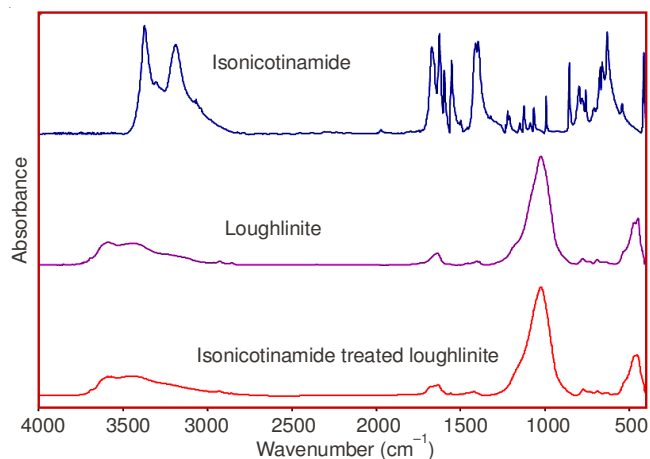


Fig. 2. FT-IR spectra of solid isonicotinamide (top), loughlinitite (middle) and isonicotinamide treated loughlinitite (bottom)

The possible binding sites of isonicotinamide are the ring nitrogen, the amino nitrogen and/or the carbonyl oxygen. It is well known that the adsorption of the organic molecule onto clay surface gives rise to the changes in the IR spectra of the interacting species. In order to determine the interaction

mechanism of adsorbed isonicotinamide molecules by loughlinitite, the vibrational wavenumbers of adsorbed molecules are carefully investigated, by taking into account the coordination effects through the ring, through the NH_2 group and through the $>\text{C}=\text{O}$ group. If the coordination occurs through the amino nitrogen atom, it is expected that a great reduction would take place in the NH_2 and the $\text{C}-\text{NH}_2$ stretching wavenumbers¹⁵ due to the perturbation of the amino group by coordination. For example in the case of aniline, benzidine or *p*-phenylenediamine complexes, the values of the NH_2 and the $\text{C}-\text{NH}_2$ stretching modes were found at lower values than the corresponding ones in the free molecule and the red shifts were 150-220 cm^{-1} for NH_2 stretching and 50-60 cm^{-1} for $\text{C}-\text{NH}_2$ stretching vibrations^{15,16}. On the other hand, it was known that the ring stretching vibrations around 1600-1400 cm^{-1} and the ring-breathing mode increase in wavenumber upon H bond formation or adsorption at Lewis acid sites¹⁷. In order to investigate clay-organic interaction, we compared our results with those of solid isonicotinamide, isonicotinamide isolated in cryogenic inert matrixes¹⁸ and $\text{Ni}(\text{isonicotinamide})_2 \text{Ni}(\text{CN})_4$ complex, in which the coordination of the isonicotinamide with the metal occurs through the pyridine nitrogen¹⁹. The vibrational wavenumbers of adsorbed isonicotinamide are tabulated in Table-1, in comparison to those of solid isonicotinamide, isonicotinamide in Xe matrix and isonicotinamide complex.

Although the NH_2 stretching vibrations are obscured by strong OH stretching vibrations of the clay framework, the $\text{C}-\text{NH}_2$ stretching mode is clearly observed in IR spectra of isonicotinamide treated loughlinitite. The $\text{C}-\text{NH}_2$ stretching vibration is observed at 1391 cm^{-1} in the IR spectra of solid isonicotinamide as a strong band¹⁹. The 1800-1300 cm^{-1} region of the FTIR spectra of starting loughlinitite and isonicotinamide treated loughlinitite are given in Fig. 3 comparatively. The FT-IR spectrum of isonicotinamide treated loughlinitite, after subtraction of loughlinitite bands is given in Fig. 4 in comparison to that of solid isonicotinamide. The strong band observed at 1395 cm^{-1} in the IR spectra of solid isonicotinamide is attributable to $\text{C}-\text{NH}_2$ stretching mode (Fig. 4). The corresponding mode of the adsorbed isonicotinamide is assigned to 1420 cm^{-1} medium band, observed in the IR spectrum of isonicotinamide treated loughlinitite (Fig. 3). This mode is clearly seen in the subtracted IR spectrum of clay-organic complex (isonicotinamide treated loughlinitite-loughlinitite), shown in Fig. 4. Therefore, the investigation of the vibrational spectra of isonicotinamide

TABLE-1
WAVENUMBERS (cm^{-1}) OF ADSORBED ISONICOTINAMIDE (INA)

Assignment	INA solid	INA in Xe matrix (20 K) ^a	INA complex ^b	INA on loughlinitite
$\nu(\text{C}=\text{O})$	1668	1711-1708	1682	1693-1681
$\delta(\text{NH}_2)$	1624	1578-1571	1629	1625
ν_{ring}	1596	1586	1617	1601
ν_{ring}	1552	1559	1551	1556
ν_{ring}	1496	1507 ^c	1504	1505-1498
δCH	1410	1407	1418	1439
$\nu(\text{CN})_{\text{amide}}$	1395	1360	1400	1420
ν_{ring}	994	993	1030	1004
$\gamma(\text{C}-\text{C})$	757	748	761	759
γ_{ring}	412	418	419	420

INA = Isonicotinamide; ^aTaken from ref.¹⁸. ^b $\text{Ni}(\text{INA})_2 \text{Ni}(\text{CN})_4$ complex taken from ref.¹⁹. ^cObserved in an Ar matrix at 10 K

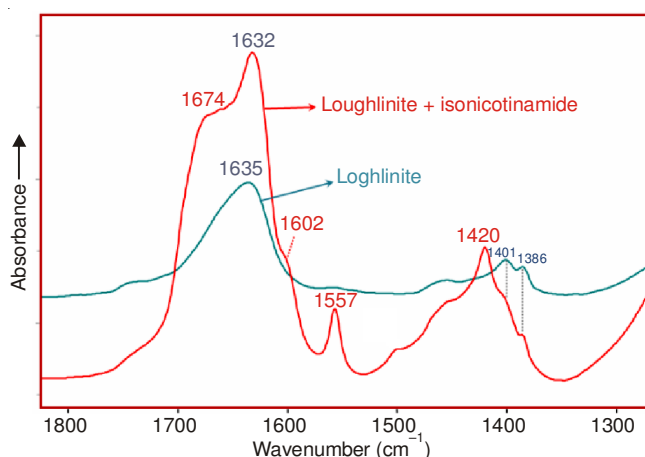


Fig. 3. 1800-1300 cm^{-1} region of the FT-IR spectra of loughlinité before and after treatment with isonicotinamide

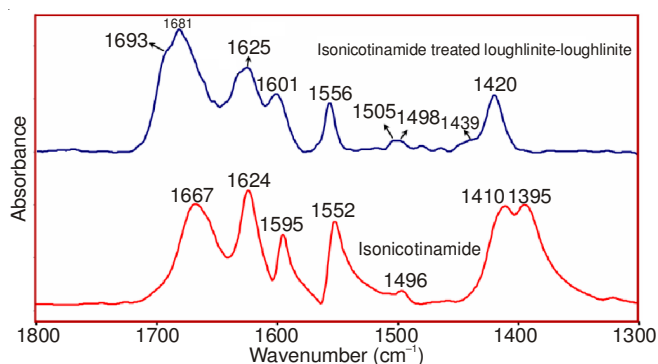


Fig. 4. The 1800-1300 cm^{-1} region of the FT-IR spectra of solid isonicotinamide (bottom) and isonicotinamide treated loughlinité after subtraction of loughlinité bands

treated loughlinité indicates that no reduction in frequency on the CN vibrational mode of adsorbed molecule in comparison to that of solid phase is present. Contrarily this vibrational mode is found to be higher in wavenumber than those solid isonicotinamide. The C-NH₂ stretching mode was observed at 1400 cm^{-1} in the IR spectrum of Ni(isonicotinamide)₂Ni(CN)₄ complex¹⁹, in which the coordination occurs through the ring nitrogen. The increase in frequency of the C-NH₂ stretching mode upon adsorption of isonicotinamide indicates the increase of pi character of the C-N (NH₂) bond. Thus, the spectral results suggest that the amino nitrogen of isonicotinamide is not involved in the coordination.

In a recent study¹⁷, the adsorption of 2-chloropyridine on oxide surfaces were investigated and the vibrational wavenumber shifts that accompany the different types of interaction of the aromatic molecule with surface sites were calculated. It was shown that the ring stretching vibrations around 1600-1400 cm^{-1} , increase in wavenumber upon H bond formation or adsorption at Lewis acid sites¹⁷. In our previous study the coordination through the ring nitrogen effects on isonicotinamide²⁰ and isoniazid²¹ vibrational wavenumbers were calculated using a model compound of INA-Al(OH)₃ complexes (INA = isonicotinamide or isoniazid) and the results were in agreement to the previous findings¹⁷. It was found that in addition to the pyridine ring and CH modes around 1600-1400 cm^{-1} , ring breathing mode is also sensitive to coordination

through pyridine ring to nitrogen. The ring mode around 1000 cm^{-1} is obscured by strong Si-O stretching mode of loughlinité. But The second derivative profiles of the absorption spectra give valuable information about the positions of the overlapping bands (Fig. 5). Comparison of the second derivative profiles of starting loughlinité and isonicotinamide treated loughlinité indicates an additional peak at 1004 cm^{-1} in the latter case, which is not present in the former, that can be attributed to the ring breathing mode of adsorbed isonicotinamide. Table-1 showed that the vibrational wavenumbers of adsorbed isonicotinamide are found to be more close to those of isonicotinamide coordinated through ring nitrogen, than free isonicotinamide. The results indicate that adsorbed isonicotinamide molecules are coordinated through the ring nitrogen lone pairs.

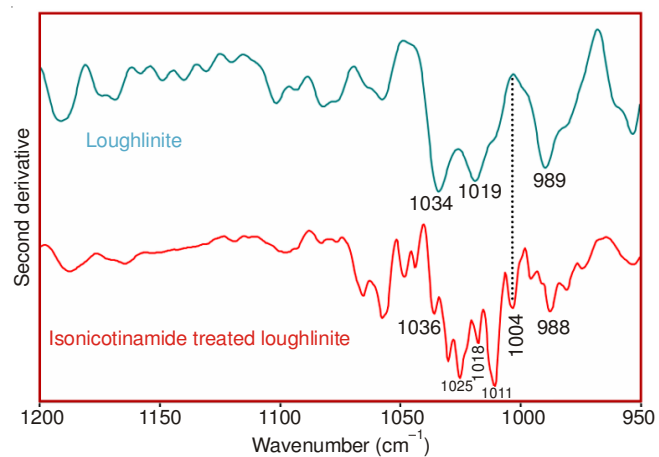


Fig. 5. The second derivative profiles of the absorption IR spectra of starting loughlinité (top) and isonicotinamide treated loughlinité (bottom)

The most probable binding sites of sepiolite group of clays⁸ are expected to be surface hydroxyls and Lewis acidic centers. It is well known that in this group of clays, the broken Si-O-Si bonds of the terminal silica tetrahedra on the external surfaces of compensate their residual charge by accepting a proton or hydroxyl group and form Si-OH groups⁸. The Si-OH stretching and the deformation vibrations are expected around 3700 and 800 cm^{-1} , respectively²². Alterations of these bands indicate interactions of the adsorbate with the silanol groups. The OH stretching region of isonicotinamide treated loughlinité is given in Fig. 6. As seen in Fig. 6, the intensity of Si-OH vibration is found to increase and shift to lower wavenumber upon adsorption of isonicotinamide. This mode is observed at 3693 and 3683 cm^{-1} in the IR spectra of loughlinité and isonicotinamide treated loughlinité, respectively. We also observed the alterations of the Si-OH deformation bands around 800 cm^{-1} . The Si-OH deformation bands of loughlinité before and after treatment with isonicotinamide is shown in Fig. 7, comparatively. The center of the band profile of the Si-OH deformation region is found to shift slightly to lower wavenumber upon adsorption of isonicotinamide. In order to see the alterations of the Si-OH deformation band, we performed band component analysis. The band component analyses of the Si-OH deformation bands of isonicotinamide treated loughlinité are given in Fig. 8. The two main components of the Si-OH deformation bands are observed at 778 and 769 cm^{-1} in

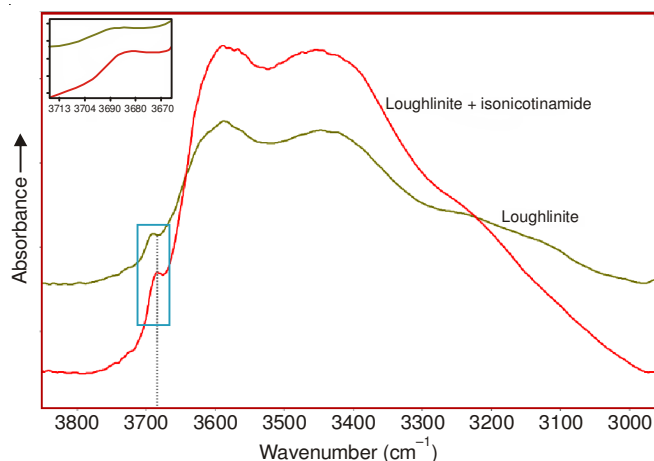


Fig. 6. 3800-3000 cm^{-1} region of the FT-IR spectra of natural loughlinite and isonicotinamide treated loughlinite. The 3745-3675 cm^{-1} regions of both samples is shown comparatively in the small frame given above

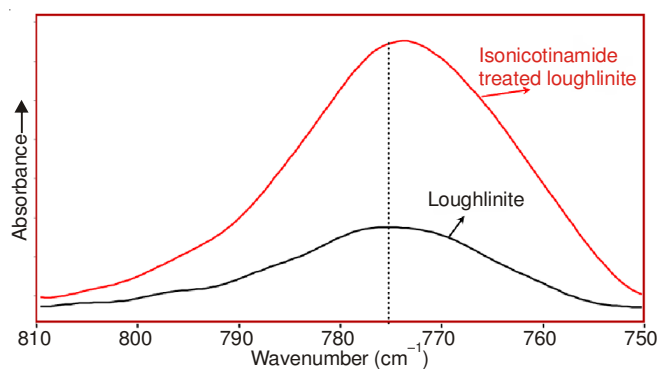


Fig. 7. Si-OH deformation band of loughlinite and isonicotinamide treated loughlinite

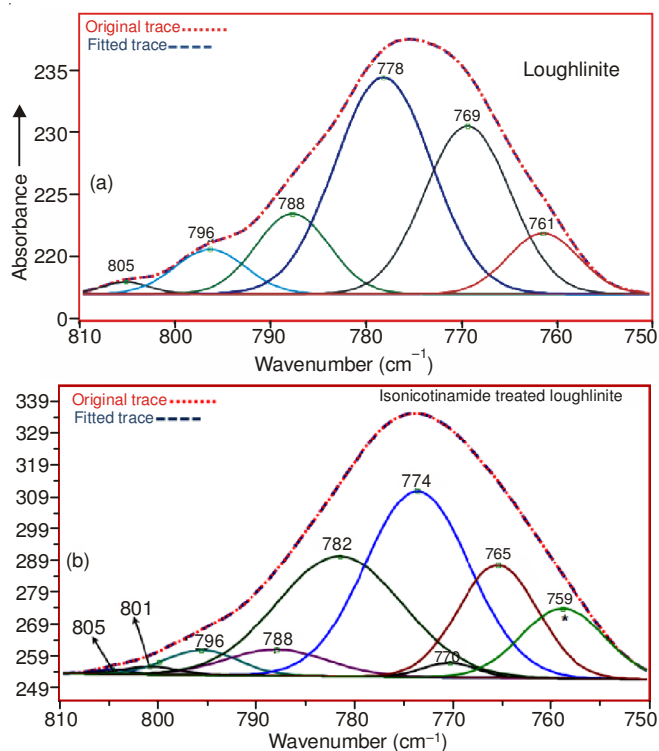


Fig. 8. The band component analysis of the 810-750 cm^{-1} region of the FT-IR spectra of loughlinite (a) and isonicotinamide-treated loughlinite (b). *Isonicotinamide band

the IR spectrum of pure loughlinite, corresponding components are observed at 774 and 765 cm^{-1} , in that of isonicotinamide treated loughlinite. If adsorbed isonicotinamide molecule interacts with surface silanol groups, alterations in the Si-OH stretching and deformation bands are expected. That is what we observed. Thus, the spectroscopic results indicate that isonicotinamide molecules adsorbed on loughlinite are mostly coordinated to surface hydroxyls by H-bonding interaction. Direct or indirect (though the water bridges) coordination to Lewis acidic centers can not be excluded.

Conclusion

The IR spectroscopic investigations are found to be very informative in shedding light on the nature of the surface species formed on clays. Based on the spectroscopic investigations, we propose isonicotinamide molecules adsorbed on loughlinite are coordinated to surface hydroxyls and/or Lewis acidic centers by H-bonding interaction through pyridine ring nitrogen lone pairs.

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