Deintercalation of hydrazine intercalated low defect kaolinite

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ABSTRACT

The deintercalation of a low defect kaolinite intercalated with hydrazine has been followed by X-ray diffraction, diffuse reflectance infrared spectroscopy (DRIFT) and Raman microscopy over an extended period of time. X-ray diffraction showed the kaolinite was totally intercalated and that more than 120 hours were required for the hydrazine intercalate to be decomposed. The Raman spectra of the hydrazine intercalate showed only a single band at 3620 cm^{-1} attributed to the inner hydroxyl group. Upon deintercalation additional Raman bands were observed at 3626 and 3613 cm^{-1}. These bands decreased in intensity with further deintercalation. As deintercalation occurs the bands assigned to the inner surface hydroxyl groups at 3695, 3682, 3670 and 3650 cm^{-1} appeared and increased in intensity. DRIFT spectra showed two bands at 3620 and 3626 cm^{-1} for the fully intercalated kaolinite only. Upon deintercalation an additional band assigned to intercalated water was observed at 3599 cm^{-1} and increased in intensity at the expense of the 3626 cm^{-1} band. Further, the bands attributed to the inner surface hydroxyl groups increased in intensity with deintercalation. Both the Raman and DRIFT spectra showed complexity in the NH stretching region with two sets of NH symmetric and asymmetric stretching bands observed. Deintercalation was easily followed by the loss of intensity of these bands. Significant changes were also observed in the hydroxyl deformation and water bending modes as a result of deintercalation. A new model of hydrazine intercalation of kaolinite based on the insertion of a hydrazine-water unit is proposed. The hydrated end of the hydrazine molecule hydrogen bonds with the inner surface hydroxyl groups resulting in the formation of the new band at 3626 cm^{-1} in the DRIFT spectra.

Key Words: Intercalation, hydrazine, kaolinite, hydroxyls, hydrogen bonding, Raman microscopy, X-ray powder diffraction

INTRODUCTION

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The kaolinite minerals have often been classified as non-expandable clays. Wada (1961) introduced a new field of kaolinite research when kaolinites were expanded using potassium acetate and other organic salts. Many organic molecules of the appropriate size for insertion between the kaolinite layers have since been found and molecules such as hydrazine (NH_2-NH_2), urea (NH_2-C=O-NH_2) and formamide (HC=O-NH_2) have been shown to insert between the kaolinite layers (Ledoux and White 1966, Olejnik et al. 1970). The interlayer bonding between kaolinite molecules arises from the hydrogen bonding between the inner surface hydroxyl groups of the octahedral gibbsite-like sheet and the oxygens of the adjacent tetrahedral siloxane sheet. In order for molecules such as hydrazine to penetrate between the kaolinite layers, sufficient energy must be provided for these bonding forces to be overcome. So in research to date, no model to explain this intercalation process has been forthcoming. Kaolinites are often intercalated with hydrazine for X-ray diffraction analysis to reveal the presence of expandable clays such as smectite or halloysite.

The study of hydrazine intercalation of kaolinite has been undertaken over a considerable length of time (Ledoux and White 1966, Cruz et al. 1969, Cruz et al. 1970, Johnston and Stone 1990). The first authors showed that a Georgian kaolinite could be expanded with hydrazine to 10.4 Å. Upon mild heating this structure partially collapsed to 9.4 Å. Prolonged heating caused the kaolinite structure to collapse to 7.2 Å. Further these workers provided the first infrared spectra of the hydrazine intercalated kaolinite. The spectra revealed a substantial reduction in intensity of the bands attributed to the inner surface hydroxyls. Additional bands attributed to hydrazine and water were observed at 2970, 3200, 3310, 3365, 3470 and 3570 cm^{-1}. The Raman spectrum of hydrazine intercalated kaolinite was first reported by Johnston and Stone (1990). The Raman spectrum showed a single band centred at 3620 cm^{-1} with some intensity in the bands at 3695, 3688, 3668, and 3652 cm^{-1} remaining due to incomplete intercalation. These researchers showed the effect of evacuation on the kaolinite-hydrazine complex with the subsequent collapse of the structure from 10.4Å to 9.6Å.

New insights into the spectroscopy of kaolinite and the other polytypes using dispersive Raman microscopy have been forthcoming (Frost et al. 1996, Frost 1996, Frost and Shurvell 1997, Frost and van der Gaast 1997). The application of Raman microscopy to the study of intercalated kaolinites has also proven most useful (Frost et al. 1997a, Frost et al. 1997b, Frost and Kristof 1997). Upon intercalation of kaolinite with urea (NH_2-C=O-NH_2), remarkable intensity changes in the hydroxyl stretching bands occur. Urea is a molecule which contains both the NH_2 unit and the C=O unit and so chemical bonding may take place through either or both of these points of interaction. The decrease in relative intensity of the OuOH groups was attributed to the loss of hydrogen bonding of the inner surface hydroxyls between the adjacent kaolinite layers. The urea disrupted the interlayer hydrogen bonding between the kaolinite layers by the formation of hydrogen bonds between the silica Si-O and the N-H of the urea. This is observed by the formation of new N-H bands of increased intensity at 3392 and 3408 cm^{-1}. Hydrazine (NH_2-NH_2) is not unlike urea in molecular structure in that it also possesses NH_2 groups. The difference is that the C=O group is missing. The hydrazine molecule may interact with the kaolinite surfaces through both the lone pair of electrons of the nitrogen and the

hydrogens of the NH$_2$ group. The hydrazine molecule may react with the kaolinite surface through the nitrogen lone pair of electrons in which case the interaction would be expected to be similar to that of potassium acetate and additional Raman bands at ~3605 cm^{-1} would be expected. In the second case the interaction would be expected to be similar to that of urea. Thus there would be no additional hydroxyl bands found with a concomitant decrease in the inner surface hydroxyl intensities. In this paper we report the alterations to the structure of a kaolinite intercalated with hydrazine followed by the deintercalation process as a function of time using X-ray diffraction, FTIR (DRIFT) spectroscopy and Raman microscopy. The aim of this research is to ascertain the bonding between the hydrazine and kaolinite layers.

EXPERIMENTAL

The kaolinite intercalate

The kaolinite used in this study is a low defect kaolinite from Kiralyhegy in Hungary. This mineral has been previously characterised both by X-ray diffraction and by Raman spectroscopy (Frost et al. 1997b). The kaolinite was purified through sedimentation and the 2-20 micron sized fraction selected for intercalation. The intercalate was prepared by mixing 300 mg of the kaolinite with 5 cm^3 of a 85% hydrazine hydrate aqueous solution for 80 hours at room temperature in a magnetic stirrer. The excess solution was decanted and the intercalated kaolinite was immediately subjected to spectroscopic analysis.

X-ray diffraction

X-ray diffraction patterns of the intercalated kaolinite at different time intervals after exposure to air were obtained using a Philips PW 1050 type X-ray diffractometer using CuK$_\alpha$ radiation operating at 35 kV and 40 mA. A 1° divergence and scatter slit was combined with a normal focus Cu tube at 6° take off angle and a 0.2 mm receiving slit. The samples were measured in stepscan mode from 2.0° 2θ with steps of 0.05° up to 40° 2θ and a counting time of 2 seconds.

Thermogravimetry-Mass Spectrometry

TG-MS investigation of the intercalate was carried out by means of Netzsch TG 209 thermobalance coupled with a Balzers MSC 200 Thermo-cube type mass spectrometer connected via a fused silica capillary for sample introduction. Samples of a few milligrams were heated in a helium atmosphere at the rate of 10 °C per minute.

DRIFT Spectroscopy

Diffuse Reflectance Fourier Transform Infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad 60A spectrometer. 512 scans were co-added at a resolution of 2 cm^{-1} with a mirror velocity of 0.3 cm/sec. Approximately 3 weight % kaolinite or intercalated kaolinite was dispersed in oven dried spectroscopic grade KBr with a refractive index of 1.559 and a particle size of 5-20 μm. Background KBr spectra were obtained and the sample single beam spectra were ratioed to the background.

Raman microprobe spectroscopy

For recording the Raman spectra, small portions of the intercalated mineral were placed on a polished stainless steel surface on the stage of an Olympus BHSM microscope, equipped with 10x, 20x and 50x objective lenses. No additional sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were excited by a Spectra-Physics model 127 HeNe laser (633 nm), recorded at a resolution of 2 cm^{-1} in sections of 1000 cm^{-1}. Repeated acquisitions using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995. Graphics are presented using Microsoft excel.

RESULTS and DISCUSSION

LATTICE EXPANSION AND CONTRACTION - X-ray diffraction results

The results of the X-ray diffraction analyses of the low defect kaolinite intercalated with hydrazine hydrate and exposed to air for periods of time ranging from zero time to one month are illustrated in Figures 1 and 2. Figure 1 shows the complete XRD pattern and Figure 2 the 001 spacings of the intercalated and deintercalated kaolinite. The X-ray diffraction pattern of the hydrazine intercalated kaolinite clearly shows that the clay has been fully intercalated at ambient temperatures. It is imperative to have 100% intercalation of the kaolinite in an attempt to fully interpret spectroscopic data of a complicated system like the hydrazine kaolinite intercalate. Indeed the use of X-ray diffraction patterns proved the only reliable method of determining whether the kaolinite was intercalated or not. It is not possible to rely simply on the loss of intensity of the inner surface hydroxyl bands as a determinant of intercalation or the appearance of additional bands in either the Raman or infrared spectra. Hydrazine has been found to very readily adsorb on kaolinite surfaces showing characteristic 'intercalation' type spectra and yet the kaolinite was not expanded (this work). The (001) d-spacing for fully intercalated kaolinite was determined to be 10.39 Å, which is comparable to the value of 10.4 Å observed by a number of workers (Weiss et al. 1963, Weiss et al. 1966, Ledoux and White 1966, Barrios et al. 1970, Johnston and Stone 1990).

Upon exposure to air, the kaolinite starts to deintercalate as the hydrazine is lost to the atmosphere. This process takes more than 50 hours to finish. The kaolinite

goes through a disordered stacking stage between 50 and 120 hours shown by complete loss of the 001 reflections. After the 120 hour period, no intensity of the 10.39 Å d-spacing remained and the intensity of the 7.16 Å peak start to increase only after an extended period of time (200 hrs). These changes are represented graphically in Figure 3. The decrease in intensity of the 10.39 Å peak without the consequent formation of the 7.16 Å peak indicate loss of the long range ordering in the c-axis direction during the decomposition which is only restored in the final stage of deintercalation. The decrease in intensity is exponential with time suggesting that the rate of deintercalation follows first order kinetics. The changes represented here are in harmony with the changes in the intensities of the XRD (001) peaks for the reverse experiment of intercalation as a function of time as reported by Johnston and Stone (1990). The difference between this work and that of the previous workers is that in the latter case the kaolinite was not fully intercalated. Their results indicate that the intercalation started with the breaking of all Al-OH…O-Si bonds between the kaolinite layers as shown by the disappearance of the 7.16 Å peak causing loss of long range ordening in the c-axis direction or stacking order followed by subsequent restoration of the stacking order in later stages of the intercalation as indicated by the increasing intensity of the 10.39 Å peak. The (001) XRD peak after deintercalation does not resemble that of the original (untreated) kaolinite. The peak is very broad and asymmetric on the low angle side. The significance of this is that not all of the layers returned to the original 7.16 Å d-spacing. In fact the tail goes out to a two theta value of 11° which belongs to a d-spacing of 7.3 Å. This may mean that after the deintercalation the surface of the kaolinite has a wavy pattern with some parts of the layers returning to the original d-spacing and some parts of the layers remaining slightly expanded. It is proposed that these expanded parts result from the incorporation of water between the layers as the deintercalation results in the formation of an hydrated kaolinite.

KAOLINITE HYDROXYL STRETCHING

DRIFT spectroscopic results

DRIFT spectra of the hydroxyl stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) zero time, (b) 0.5 hr, (c) 3 hrs, (d) 4.5 hrs, (e) 22 hrs, (f) 50 hrs, (g) 120 hrs, (h) 1 week and (i) 1 month are shown in Figure 4. The band component analyses of these DRIFT spectra are reported in Table 1. Figure 4 clearly demonstrates the effects of deintercalation of the hydrazine intercalated kaolinite upon exposure to air. The OH stretching region of the intercalate shows the complete disappearance of the ν_1, ν_2 and ν_3 bands as a result of the rupture of the H-bonding of all the inner surface hydroxyls (Figure 4 (a and b)). This is in harmony with the complete expansion of the clay as evidenced by X-ray diffraction. If the kaolinite was not fully intercalated then significant intensity would remain in the bands attributed to the inner surface hydroxyl groups. An additional band is observed upon intercalation with hydrazine at 3626 cm^{-1} which is assigned to the inner surface hydroxyls H-bonded to the hydrazine-water complex. This assignation is based on the rapid decrease in intensity of this band as deintercalation takes place. The band belonging to the inner hydroxyls at 3620 cm^{-1} is buried by this new band showing a shoulder peak, only. It should be noted that the 3626 cm^{-1} band is already formed at 1 bar and 25 °C. In previously published work, a new band at 3628 cm^{-1} was reported to appear at reduced pressures only (Johnston and Stone 1990). Such a band was

described as a blue shifted inner hydroxyl group. However this band was not observed in the Raman spectra at atmospheric pressure in contrast to what should be expected for an inner hydroxyl group. This blue shift of the inner hydroxyl group was interpreted as a result of the NH_2 moiety of hydrazine keyed into the ditrigonal hole. Further whilst the XRD data of Johnston and Stone (1990) showed approximately 95 % intercalation of the kaolinite with hydrazine, the infrared spectra clearly show the presence of significant intensity in the bands attributed to the inner surface hydroxyl groups. Considering the rapid decomposition of the hydrazine intercalated kaolinite even at atmospheric pressure, it is logical to suppose that the removal of hydrazine from the intercalate is even faster under low pressure. It is therefore unlikely that hydrazine can key into the ditrigonal hole whilst the complex is decomposing.

It is very interesting to observe that upon exposure to air, the emergence of the ν_1, ν_2 and ν_3 bands show a spectral shift towards their original, lower frequencies as the complex is decomposing. The frequency shift in the partially decomposed complex is due to the formation of an intermediate structure in which the inner surface hydroxyls can temporarily move freely, i.e. without forming H-bonding to the siloxane layer. This agrees with the X-ray diffraction data where a loss of stacking order is observed. The intensity decrease of the 3626 cm^{-1} band as a function of time indicates the gradual decomposition of the complex. The attribution of the 3626 cm^{-1} band (ν_6) to the inner surface hydroxyls hydrogen bonded to the hydrazine-water complex is at variance with previously published work where this band was assigned to a perturbed inner hydroxyl group (Johnston and Stone 1990). Other work has described the band as red shifted inner surface hydroxyl groups for kaolinites intercalated with formamide, dimethyl formamide and N-methylacetamide. (Cruz et al. 1969).

With the intensity decrease of the 3626 cm^{-1} band, however, a new band is emerging at 3599 cm^{-1} , which is attributed to intercalated water. Thermal analysis showed the presence of water in the intercalate.   DRIFT spectroscopy of the thermally treated kaolinite revealed the loss of the band at 3599 cm^{-1}. Thus this band is assigned to water which is hydrating the kaolinite. Upon heating the deintercalated kaolinite, the DRIFT spectrum closely resembles that of the untreated kaolinite. In addition, the appearance of loosely bonded water in the decomposing intercalate can be seen giving flat, broad bands centered around 3550 cm^{-1}. Therefore, it can be concluded that hydrazine is replaced by water in the course of the deintercalation transformation process. When the clay is intercalated with potassium acetate, the H-bonded surface OH groups give a new peak at 3605 cm^{-1} (Frost et al 1997b). The fact that this H-bonded inner surface OH band appears at 3626 cm^{-1} for hydrazine intercalated kaolinite, rather than at 3605 cm^{-1} as is observed for example in acetate intercalated kaolinites, indicates a weaker hydrogen bonding interaction when the hydrazine is intercalated. Therefore, it is reasonable to propose that the intercalating hydrazine (in fact hydrazine hydrate) is hydrogen bonded to the inner surface hydroxyls via water molecules. Thermoanalytical investigations involving a mass spectrometer showed that water and hydrazine are released simultaneously from the complex upon heating up to 140 °C. Thus no hydrazine is present in the intercalated structure in dehydrated form. Such an observation eliminates the incorporation of hydrazine into the ditrigonal hole.

The band component analyses of the DRIFT spectra of the hydroxyl stretching region of the hydrazine intercalated kaolinites as a function of time are reported in Table 1. At zero time, only two peaks are observed at 3626 and 3620 cm^{-1} and these bands make up 70.0 and 28.3 % of the total band intensity. Such intensities are close to what would be predicted theoretically ie 25.0 % of the intensity for the inner hydroxyl and 75.0 % for all of the inner surface hydroxyls. At 0.5 hour, the intercalate has started to decompose. This is evidenced by the appearance of a band at 3695 cm^{-1}, the decrease in intensity of the 3626 cm^{-1} band and the appearance of a new band at 3599 cm^{-1}. After 3 hours, the intercalate has decomposed considerably. Now two bands are observed at 3699 and 3653 cm^{-1} which make up 3.5 and 18.5 % of the total band intensity. The 3626 cm^{-1} band intensity has decreased to 33.0 % and the 3620 cm^{-1} band remains essentially constant at 27.7%.   After 4.5 hrs, the 3626 cm^{-1} band has decreased in intensity to 13.5 %. At this point, significant intensity exists in the bands assigned to the inner surface hydroxyls at 3696, 3685, 3673 and 3654 cm^{-1}. Most of the changes in the DRIFT spectra have taken place at this point. After 22 hours and up to 1 month in time, the changes observed are smaller. Importantly as the 3626 cm^{-1} band decreases in intensity, the 3599 cm^{-1} band increases as well as the bands ascribed to the inner surface hydroxyls. It is proposed that the 3599 cm^{-1} band is due to water hydrating the kaolinite surface. The concept of the deintercalation of the kaolinite as a mechanism for hydrating the kaolinite surfaces is feasible (Costanzo et al. 1984, Costanzo and Giese 1986, Costanzo and Giese 1990) The incorporation of water between the kaolinite layers as intercalated water is supported by the infrared band observed at 3599 cm^{-1} and the XRD showing a broad low intensity 001 peak.

Raman spectroscopic results

The Raman spectra of the hydroxyl stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) zero time (b) 30 mins (c) 60 mins (d) 105 mins (e) 150 mins (f) 220 mins (g) 300 mins (h) 480 mins (i) and 10 hrs are shown in Figure 5. The results of the band component analyses of these spectra and others not shown are given in Table 2. The Raman spectrum of the hydrazine-intercalated kaolinite consists of only one band at 3620 cm^{-1} with a bandwidth of 5.7 cm^{-1}. Such a band corresponds to the inner hydroxyl group. No band corresponding to the DRIFT band at 3626 cm^{-1} is observed. This means that this band is entirely Raman inactive and infrared active. Such a band occurs when there is a large change in dipole moment and no change in the polarisability of the bond. Such bands often occur when water is involved, and the observations assist in the assignment of the 3626 cm^{-1} band as the band attributed to the hydrogen bonding of the hydrazine-water unit and the inner surface hydroxyls. The question may be asked why the 3626 cm^{-1} band which had been previously assigned to a blue shifted inner hydroxyl band, was not observed at all in the Raman spectra (Johnston and Stone 1990). The attribution of the 3626 cm^{-1} band to an inner hydroxyl group can therefore be not correct. Neither can the blue shift be attributed to the keying in of the NH$_2$ moiety into the ditrigonal hole because of the repulsion of the inner hydroxyl group and the NH$_2$ of the hydrazine. Another model for the assignment of the 3626 cm^{-1} band is therefore required.

The band component analysis of the spectra at 30, 60, 75 and 105 minutes show similar results with low intensity broad bands in the 3630 to 3690 cm^{-1} region.

The 150 minutes spectrum now shows significant intensity in the 3658 and 3682 cm^{-1} bands with relative intensities of 12.3 and 13.1%. It is most interesting that at this stage of deintercalation, two additional bands at 3613 and 3627 cm^{-1} appear. The 3627 cm^{-1} band corresponds to the DRIFT 3626 cm^{-1} band. The band is not observed in the early stages of deintercalation. However as deintercalation takes place some reorientation in the hydrazine-water hydrogen bonding unit occurs increasing the symmetry which enables the Raman spectrum to be obtained. It is not known what the 3613 cm^{-1} band is due to but it is suggested that the deintercalation of the hydrazine intercalated kaolinite may cause folding of the kaolinite layers and that the 3613 cm^{-1} band may be the inner hydroxyl groups of the folded units of the kaolinite. Similar observations have been made for halloysite (Frost and Shurvell 1997, Frost and Kristof 1997).

AMINE STRETCHING REGION

DRIFT Spectroscopy

The DRIFT spectra of the NH region of the hydrazine and water OH stretching regions are shown in Figure 6. Three bands are observed at 3301, 3356 and 3362 cm^{-1}. The first band is attributed to the symmetric stretching and the second two bands to the antisymmetric stretching of the NH vibrations (Durig et al.). The symmetric stretching band is weak in intensity compared to the intensity of the antisymmetric stretching band. The ratio of the intensities of the band is 2/1. The relative area of the 3301 cm^{-1} band is 8% of the total band intensity. The fact that this band is weak in intensity in the infrared and more intense in the Raman suggests that this band is due to the symmetric stretch of the NH vibration. The bandwidths of the 3362 to the 3356 cm^{-1} bands are 8.4 and 9.1 cm^{-1} respectively. The bandwidth of the 3301 cm^{-1} band is 8.0 cm^{-1}. The 3356 cm^{-1} band is both infrared and Raman active. However the 3356 cm^{-1} band is infrared active only. Thus this band is attributed to the antisymmetric stretching frequency of the amine NH vibration of the $[-NH_3]^+$ unit. The fact that two bands are observed at slightly different frequencies in the antisymmetric stretching region suggests that there are two types of interaction between the hydrazine and the kaolinite surfaces. It is proposed that one interaction occurs between both the lone pairs of electrons of the hydrazine nitrogen coordinated to water. This complex ion then interacts with the inner surface hydroxyls. In the intercalation of kaolinite with potassium acetate, the CH_3COO^- ion coordinates through the negative charges distributed equally across the two oxygens of the acetate. Hydrazine is a weak monoacid base that forms a monohydrate. Therefore, for the intercalation of hydrazine in kaolinite, a model based on the formation of a $[NH_2-NH_3]^+[OH]^-$ unit is proposed. The interaction of the hydrazine complex then occurs between the negative charge on the OH group of water and the inner surface hydroxyls. The reason why the band occurs at 3626 cm^{-1} is because the interaction of the $[NH_2-NH_3]^+[OH]^-$ unit and the inner surface hydroxyls of the kaolinite is weaker than that of the acetate. A second interaction can occur between the hydrogens of the hydrazine and the siloxane layer. This second type of interaction fits nicely with the first interaction. As the hydrated part of the hydrazine molecule bonds to the inner surface hydroxyls, the other end of the molecule orients close to the siloxane surface and can easily form a second type of bonding between the amine hydrogens and the oxygens of the siloxane surface. It is proposed that water is essential to the

intercalation of the kaolinite and is intimately involved in the intercalation process. Based on this model there are two types of NH groups and hence two sets of bands are observed in the DRIFT spectra.   An additional band is observed at 3206 cm^{-1}. A band in this position may be attributed to strongly bonded or coordinated water. Thus the 3206 cm^{-1} band is attributed to the water hydroxyls, which are hydrogen bonded to the hydrazine in the intercalated complex.

Raman Spectroscopy

Figure 7 shows the Raman spectra of the amine stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) zero time (b) 30 mins (c) 60 mins (d) 105 mins (e) 150 mins (f) 220 mins (g) 300 mins (h) 480 mins and (i) 600 mins. This figure also shows the Raman spectrum of hydrazine. The band component analysis of the Raman spectrum of the amine NH stretching region of hydrazine reveals four bands at 3346, 3285, 3260 and 3199 cm^{-1} with 16.1, 46.5, 9.5 and 27.9% of the total band intensity. Each of these bands is broad with the 3346 cm^{-1} band being the narrower with a bandwidth of 32.2 cm^{-1}. Upon intercalation of the kaolinite with hydrazine, bands are observed 3363, 3342, 3312, 3304, 3283, 3263 and 3206   cm^{-1}. The band component analysis of the Raman spectrum of the amine NH stretching region for the 30 minutes stage is illustrated by Figure 7(b). Table 3 reports the results of the Band component analysis of the Raman spectra of the amine-stretching region of the low defect kaolinite intercalated with hydrazine and exposed to air for increasing intervals of time. The three bands at 3340, 3286 and 3209 cm^{-1} are assigned to the normal vibrations of hydrazine. The hydrazine is adsorbed on the kaolinite surfaces. The band at 3363 cm^{-1} is assigned to the antisymmetric stretching vibration. It is interesting that only one band is observed in the Raman spectrum whereas two bands were observed in the DRIFT spectra. It is therefore proposed that the 3356 cm^{-1} band in the DRIFT spectrum is infrared active but Raman inactive. Such a band results from large changes in dipole moment but no or minor changes in polarisability. The band at 3362 cm^{-1} is common in both the DRIFT and Raman spectra. Two bands are observed in the Raman spectrum of the symmetric stretching region of the amine at 3312 and 3302 cm^{-1}, whereas in the DRIFT spectra is only one band observed. The 3302 cm^{-1} band is common in both the DRIFT and Raman spectra, while the 3312 cm^{-1} band is only Raman active. The 3312 cm^{-1} band represents a highly symmetric vibration. The hydrazine bands of the intercalated kaolinite are at higher frequencies than in the hydrazine liquid.

As deintercalation takes place an additional band at 3312 cm^{-1} is observed. In the spectra (Figure 7 a to d) a broad band centred on 3200 cm^{-1} is observed and even though water is difficult to determine in the Raman spectra, this broad band is attributed to the water associated with the hydrazine. The spectra clearly show the decrease in intensity of both this water and the hydrazine bands as deintercalation takes place. After 150 minutes (Figure 7 spectrum f), little intensity remains in the 3200 cm^{-1} water band, although some intensity remains in the symmetric stretching NH region of the hydrazine. Such results fit well with the DRIFT results of this region.

Hydroxyl Deformation Region

As well as studying the stretching vibrations of hydroxyl groups, it is also worthwhile to study the hydroxyl deformation of these groups. Such bands occur between 890 and 950 cm^{-1}. The variation in the hydroxyl deformation region as a function of the deintercalation of the hydrazine intercalated kaolinite is shown in Figure 8 (a). The band component analysis of the DRIFT spectrum of the hydrazine intercalated kaolinite exposed to air for 30 minutes and exposed to air for 1 month are shown in Figures 8 (b) and (c). Table 4 reports the results of the band component analysis of the DRIFT spectra of the hydroxyl deformation region of the low defect kaolinite intercalated with hydrazine and exposed to air for increasing intervals of time. The hydroxyl deformation region of the intercalate shows the intensity of the OH libration as broad bands at 940 and 970 cm^{-1}, in addition to that of the inner OH group at 915 cm^{-1}. In the DRIFT spectrum of the hydroxyl deformation region of the hydrazine intercalated kaolinite at zero time, the 913 cm^{-1} band attributed to the inner hydroxyl group contains 59.6% of the total band intensity. The remaining intensity is ascribed to the 895 cm^{-1} band. This band may be attributed to the hydroxyl deformations of weakly hydrogen bonded inner surface hydroxyl groups. Some minor intensity remains in the 923 and 953 cm^{-1} bands. The data for the hydroxyl deformation vibrations show little change at 0.5 hour. At 3 hours, however, a significant decrease in intensity of the 895 cm^{-1} band occurs. The value at 3 hours is 27.2%. A weak band also appears at 905 cm^{-1}. At the 4.5 hr mark, the intensity of the 895 cm^{-1} band has been reduced to 11.6% and the 905 cm^{-1} band has increased to 6.7%. Significant intensity is now found in the other hydroxyl deformation modes at 923 and 937 cm^{-1} with 12.9 and 22.6% intensity. In the spectra at 22, 50, 168 hours and 1 month, the intensity of the 923 cm^{-1} band remains constant within experimental error. The band at ~937 cm^{-1} increases in intensity.

The hydroxyl stretching region of the fully intercalted kaolinite at zero time showed only two bands at 3620 and 3626 cm^{-1}. The hydroxyl deformation region also shows two bands at 913 and 895 cm^{-1}. It is therefore concluded that the 895 cm^{-1} band is the hydroxyl deformation band of the 3626 cm^{-1} hydroxyl stretching band. Upon deintercalation of the hydrazine intercalated kaolinite for periods of time up to 3 hrs, the intensity of the two bands at 913 and 895 cm^{-1} remains essentially constant. At the 4.5 hour stage, the inner surface hydroxyl bands at 3653 and 3696 cm^{-1} show significant intensity. At this stage the two deformation bands at 923 and 937 cm^{-1} show increased intensity. At the 50 hour stage, no intensity remains in the 895 cm^{-1} band, and the 3626 cm^{-1} band has also little intensity. The band at 905 cm^{-1} now has 13.7 % intensity. It is noteworthy that there is no intensity in the 962 cm^{-1} band at this time interval. As further deintercalation occurs the results for the 120 hour stage are similar to the 50 hour stage but at 168 hours significant intensity is now found in the 966 cm^{-1} band. This stage corresponds to the point in the X-ray diffraction patterns where there is no 13.9 Å peak remaining and the 7.2 Å peak appears. Thus the 966 cm^{-1} peak is related to the hydroxyl deformation of strongly hydrogen bonded inner surface hydroxyls which are hydrogen bonded to the adjacent siloxane layer. This point also corresponds with the increased intensity of the 3682 cm^{-1} band. *********

Thus the observations made in the analysis of the hydroxyl stretching region are supported by the analyses of the hydroxyl deformation region. As deintercalation occurs, bands associated with weakly hydrogen bonded inner surface hydroxyl groups decrease in intensity and bands associated with the inner surface hydroxyl groups hydrogen bonded to the adjacent siloxane layer increase in intensity. Thus the

spectrum of the hydroxyl deformation region after 1 week and one month closely resembles that of the untreated kaolinite. The only difference is the band which is observed at 966 cm^{-1}. The band at 895 cm^{-1} may also be due to the NH wag and the disappearance of this band shows the loss of hydrazine from the intercalate.

Water Bending Region

Often valuable information can be obtained about the intercalation of kaolinites by studying the role of water. The frequencies of water vibrational modes are very sensitive measures of the interaction of water in the intercalated kaolinite. Figure 9 reports the DRIFT spectra of the water bending modes. Table 5 shows the results of the band component analyses of the DRIFT spectra of the water bending region of the low defect kaolinite intercalated with hydrazine and exposed to air for intervals of time. The spectra clearly show two distinct water bands with HOH bending modes at 1613 and 1627 cm^{-1} and with a broad band at 1597 cm^{-1}. This last band may be attributed to water which is 'free' or non hydrogen bonded. Such water molecules may be described as zeolitic water which is simply filling the interlamellar spaces. The 1613 cm^{-1} band is attributed to water bending modes of a coordinated water. Such water molecules are hydrogen bonded to the hydrazine. The band at 1627 cm^{-1} corresponds to adsorbed water molecules. After 120 hours, the first two bands broaden and the band profile becomes very broad with no features present. The disappearance of the two well resolved bands coincides with the loss of hydrazine from the intercalate. Thermal analysis has proven that the hydrazine and water are lost from the intercalate simultaneously.

CONCLUSIONS

Deintercalation of a low defect kaolinite intercalated with hydrazine has been followed by using X-ray diffraction, DRIFT and Raman spectroscopy. X-ray diffraction showed that the kaolinite was expanded to 10.39 Å and was totally intercalated. Deintercalation was followed by the decrease in intensity of the (001) spacing of the intercalated kaolinite and the increase in intensity of the (001) spacing of the deintercalated kaolinite. Deintercalation took more than 120 hours to occur. The (001) peak was very broad upon deintercalation and a spread of spacings between 7.18 and 7.3 Å was found. The proposal was made that water was incorporated into the kaolinite interlayer spaces resulting in the incomplete collapse of the kaolinite structure to the original d-spacing.

The advantages of studying the deintercalation of hydrazine intercalated kaolinite with DRIFT spectroscopy rests with measurement of the water, kaolinite hydroxyl stretching and deformation modes. DRIFT spectroscopy showed the two bands for the fully intercalated kaolinite at 3620 and 3626 cm^{-1}. Upon deintercalation, the 3626 cm^{-1} band decreased in intensity and simultaneously the bands attributed to the inner surface hydroxyl groups at 3695, 3682, 3668, and 3652 cm^{-1} increased in intensity. At the same time an additional band at 3599 cm^{-1} increased in intensity. The band at 3626 cm^{-1} was attributed to the formation of a hydrogen-bonded complex between the kaolinite inner surface hydroxyl groups and the hydrated hydrazine. The frequency of this band was attributed to the weak interaction of this hydrazine complex and the inner surface hydroxyls of the kaolinite. This band was found to be infrared active and Raman inactive. Such a band shows a

high degree of change in dipole moment with no change in polarisability. Such a spectroscopic feature is typical of water and assists in the confirmation of the 3626 cm^{-1} band as due to a water-hydrazine complex. The significance of the 3599 cm^{-1} band rests with its assignment to the incorporation of water molecules into the intercalate resulting in the formation of a hydrated kaolinite. As deintercalation occurs, the increase in intensity of the adsorbed water band at 3550 cm^{-1} also occurs. This suggests that as the hydrazine water molecule is lost, two types of water are observed, namely intercalated water and adsorbed water.

Raman spectra also proved useful for the determination of deintercalation of the hydrazine intercalated kaolinite. The Raman spectrum of the fully intercalated kaolinite shows only a single band at 3620 cm^{-1}. The fact that the 3626 cm^{-1} band was not observed in the Raman spectrum suggests that the band is not attributable to a blue shift of the inner hydroxyl group. As deintercalation occurs, the intensity of two bands at 3613 and 3626 cm^{-1} increases and then decreases. These bands are attributed to firstly the inner surface hydroxyl group coordinated to the water-hydrazine complex and secondly to the inner hydroxyl group of the folded kaolinite. The amine NH symmetric and antisymmetric stretching bands are more readily observed in the Raman spectra. As deintercalation occurs, the intensity of the bands assigned to the inner surface hydroxyl groups increases. Interestingly the bands start at high frequencies and move to lower frequencies as the deintercalation takes place. Finally after 1 month the Raman spectrum corresponds to that of the untreated kaolinite except for the additional 3599 cm^{-1} band. Two sets of NH stretching frequencies are observed, showing two types of NH groups present in the intercalate complex. Such an observation fits well with the intercalation of the hydrazine monohydrate.

A model based on the intercalation of a hydrated hydrazine molecule with the formation of the $[NH_2\text{-}NH_3]^+[OH]^-$ unit was suggested. It is proposed that hydrogen bonding occurs between this unit through the negative charge on the water hydroxyl and the inner surface hydroxyl groups. This interaction is weaker than the interaction between for example the acetate ion and the inner surface hydroxyl groups and consequently occurs at a higher frequency. At the same time the NH_2 part of the complex can interact with the siloxane layer. Spectroscopic evidence supports the concept of the hydrazine having two different NH_2 groups in the intercalated kaolinite. In the infrared spectra, two antisymmetric vibrations are observed at 3362 and 3356 cm^{-1} with only one infrared symmetric vibration at 3302 cm^{-1}. In the Raman spectra only one antisymmetric vibration is observed at 3363 cm^{-1}. However two symmetric vibrations are observed at 3312 and 3302 cm^{-1}. The 3302 cm^{-1} band is common in both the DRIFT and Raman spectra, while the 3312 cm^{-1} band is only Raman active. The 3312 cm^{-1} band therefore represents a highly symmetric vibration. It is proposed that the 3312 cm^{-1} band arises from amine NH stretching of the hydrazine $[-NH_2]$ from the hydrogen bonding of the hydrazine to the siloxane layer. The hydrazine molecule is rigid in structure and the hydrogens are not freely rotating. Therefore if the NH_2 forms a symmetric linkage with the siloxane layer, then the other half of the molecule is asymmetric to the gibbsite-like layer.

ACKNOWLEDGMENTS

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Deintercalation Time	Band Characteristics	ν_7	ν_5	ν_6	ν_3	ν_2	ν_4	ν_1
Zero time	Band position (cm^{-1})		3620	3626				3693
	Bandwidth (cm^{-1})		12.4	9.4				13.3
	% Relative area		28.3	70.0				1.7
0.5 hours	Band position (cm^{-1})		3620	3626				3695
	Bandwidth (cm^{-1})		17.0	8.3				11.8
	% Relative area		27.1	72.9				1.3
3.0 hours	Band position (cm^{-1})	3599	3620	3626	3653			3699
	Bandwidth (cm^{-1})	21.3	15.9	11.7	21			13.4
	% Relative area	7.4	27.7	33.0	18.5			3.5
4.5 hours	Band position (cm^{-1})	3599	3620	3626	3654	3673	3685	3696
	Bandwidth (cm^{-1})	9.2	15.4	11.0	22.1	16.7	12.3	16.9
	% Relative area	5.5	27.8	13.5	17.1	8.0	4.6	23.5
22 hours	Band position (cm^{-1})	3599	3620	3627	3653	3669	3682	3694
	Bandwidth (cm^{-1})	9.4	15.7	11.5	25.7	14.1	14.5	18.0
	% Relative area	6.4	29.4	4.6	22.1	6.2	8.4	22.8
50 hours	Band position (cm^{-1})	3600	3620	3629	3652	3668	3682	3694
	Bandwidth (cm^{-1})	9.6	15.8	11.6	25.0	13.8	15.4	18.3
	% Relative area	6.5	29.6	2.9	22.7	6.2	9.9	22.2
120 hours	Band position (cm^{-1})	3599	3620	3633	3651	3667	3681	3693
	Bandwidth (cm^{-1})	9.4	15.4	14.1	21.7	14.1	16.3	18.6
	% Relative area	7.8	30.6	3.5	17.3	7.5	13.0	20.3
168 hours	Band position (cm^{-1})	3599	3618	3633	3649	3667	3682	3692
	Bandwidth (cm^{-1})	9.4	15.9	12.5	18.7	17.5	21.5	21.9
	% Relative area	7.6	30.9	2.4	15.3	9.8	13.2	20.8
1 month	Band position (cm^{-1})	3598	3618	3634	3650	3666	3680	3692
	Bandwidth (cm^{-1})	9.2	16.3	11.7	19.0	15.7	20.2	20.4
	% Relative area	8.4	31.6	2.0	14.6	8.3	14.5	20.5

Table 1. Band component analysis of the DRIFT spectrum of the hydroxyl-stretching region of the low defect kaolinite intercalated with hydrazine

Deintercalation Time	Band Characteristics	ν_7	ν_5	ν_6	ν_3	ν_2	ν_4	ν_1
0 mins	Band position (cm^{-1})		3620					
	Bandwidth (cm^{-1})		5.7					
	% Relative area		100					
30 mins	Band position (cm^{-1})		3620		3657	3683	3684	3700
	Bandwidth (cm^{-1})		5.9		23.4	51.0	8.6	7.5
	% Relative area		47.3		17.9	30.6	0.9	3.3
60 mins	Band position (cm^{-1})		3620		3656.6	3675	3685	3699
	Bandwidth (cm^{-1})		6.3		20.9	33.5	14.7	4.2
	% Relative area		57.9		21.2	15.9	3.3	1.6
75 mins	Band position (cm^{-1})		3620		3658	3675	3685	3700
	Bandwidth (cm^{-1})		6.4		18.7	28.7	16.4	6.1
	% Relative area		62.9		14.2	13.8	4.4	4.7
105 mins	Band position (cm^{-1})		3620		3658	3674	3684	3699
	Bandwidth (cm^{-1})		6.3		24.9	49.6	15.0	8.9
	% Relative area		54.6		17.3	19.2	6.0	2.9
150 mins	Band position (cm^{-1})		3620		3658	3678	3682	3700
	Bandwidth (cm^{-1})		6.3		39.0	18.2	22.8	5.2
	% Relative area		64.2		9.6	12.3	13.1	0.8
220 mins	Band position (cm^{-1})	3613	3620	3627	3654	3674	3694	3700
	Bandwidth (cm^{-1})	6.7	6.2	7.2	18.2	34.4	14.5	6.9
	% Relative area	6.3	33.9	11.2	13.9	16.6	13.2	4.9
260 mins	Band position (cm^{-1})	3613	3620	3627	3652	3665	3692	3700
	Bandwidth (cm^{-1})	7.3	6.5	7.8	12.9	31.6	14.2	8.8
	% Relative area	8.0	25.7	14.3	5.9	18.4	21.8	5.9
280 mins	Band position (cm^{-1})	3613	3620	3627	3653	3669	3690	3698
	Bandwidth (cm^{-1})	7.2	6.5	7.4	16.8	16.5	15.4	12.0
	% Relative area	6.7	23.4	11.4	18.0	7.3	22.3	10.9
300 mins	Band position (cm^{-1})	3613	3620	3627	3653	3670	3691	3698
	Bandwidth (cm^{-1})	6.9	6.7	7.4	18.6	13.7	17.0	12.0
	% Relative area	6.7	21.3	10.8	16.4	5.9	33.9	10.9
450 mins	Band position (cm^{-1})	3613	3620	3627	3652	3672	3687	3700

	Bandwidth (cm^{-1})	7.8	7.3	8.0	14.2	18.5	12.1	12.8
	% Relative area	5.7	21.0	7.9	12.6	11.3	23.8	5.0
480 mins	Band position (cm^{-1})	3614	3620	3627	3652	3670	3687	3699
	Bandwidth (cm^{-1})	8.5	6.9	8.0	16.2	15.6	14.7	12.0
	% Relative area	6.4	18.6	7.5	15.6	8.7	29.8	13.4
540 mins	Band position (cm^{-1})	3615	3620	3626	3652	3669	3687	3699
	Bandwidth (cm^{-1})	13.0	6.2	10.2	16.9	13.9	15.1	12.5
	% Relative area	8.9	11.3	11.6	15.5	7.1	31.4	14.2
600 mins	Band position (cm^{-1})	3616	3620	3624	3652	3670	3687	3699
	Bandwidth (cm^{-1})	9.9	5.9	9.4	18.0	11.9	15.0	12.1
	% Relative area	9.5	10.8	11.6	18.6	6.1	30.4	13.0
24 hours	Band position (cm^{-1})	3614	3620	3624	3652	3670	3685	3695
	Bandwidth (cm^{-1})	9.8	6.6	11.5	16.2	13.2	13.2	17.3
	% Relative area	3.9	14.5	12.5	16.5	6.6	23.6	22.4

Table 2. Band component analysis of the Raman spectrum of the hydroxyl-stretching region of the low defect kaolinite intercalated with hydrazine

Deintercalation Time	Band Characteristics	ν_{NH-7}	ν_{NH-6}	ν_{NH-5}	ν_{NH-4}	ν_{NH-3}	ν_{NH-2}	ν_{NH-1}
Hydrazine	Band position (cm^{-1})	3199	3260	3285			3346	
	Bandwidth (cm^{-1})	56.1	50.6	40.1			32.211	
	% Relative area	27.9	9.5	46.5			6.1	
0 mins	Band position (cm^{-1})	3206	3263	3283	3304		3342	3363
	Bandwidth (cm^{-1})	48.0	66.3	29.2	25.5		29.8	14.2
	% Relative area	20.3	20.4	16.6	21.6		11.8	9.3
30 mins	Band position (cm^{-1})	3207	3258	3281	3306		3338	3363
	Bandwidth (cm^{-1})	52.3	30.0	52.8	11.2		26.0	12.8
	% Relative area	21.2	6.1	29.0	12.5		6.7	11.5
60 minutes	Band position (cm^{-1})	3207	3263	3302	3302	3312	3338	3363
	Bandwidth (cm^{-1})	9.7	60.0	44.8	10.1	11.4	21.6	12.3
	% Relative area	26.3	16.8	20.9	7.9	10.9	4.2	13.0
75 minutes	Band position (cm^{-1})	3206	3259	3293	3302	3312	3335	3363
	Bandwidth (cm^{-1})	56.2	61.0	39.9	10.8	13.3	25.0	12.0
	% Relative area	21.1	16.8	14.5	10.4	16.8	5.9	14.5
90 minutes	Band position (cm^{-1})	3207	3257	3298	3302	3312	3338	3363
	Bandwidth (cm^{-1})	60.6	49.1	42.7	9.6	11.8	19.0	11.9
	% Relative area	27.2	9.1	22.9	8.4	13.9	3.7	14.6
105 minutes	Band position (cm^{-1})	3207	3255	3300	3302	3312	3339	3363
	Bandwidth (cm^{-1})	51.7	54.1	45.8	9.9	11.4	18.0	12.1
	% Relative area	20.1	12.6	24.4	10.6	14.0	3.0	15.0
150 minutes	Band position (cm^{-1})	3206			3301	3311		3364
	Bandwidth (cm^{-1})	22.9			11.8	13.6		11.6
	% Relative area	4.2			36.4	32.9		26.5
220 minutes	Band position (cm^{-1})	3205			3302	3312		3364
	Bandwidth (cm^{-1})	33.9			12.6	11.0		11.5
	% Relative area	6.7			42.4	25.7		25.1
260 minutes	Band position (cm^{-1})	3200			3302	3312		3364
	Bandwidth (cm^{-1})	61.9			12.7	11.4		12.0
	% Relative area	13.1			38.9	23.3		24.7
300 minutes	Band position (cm^{-1})	3203			3302	3312		3364
	Bandwidth (cm^{-1})	66.9			12.7	11.4		11.6
	% Relative area	18.6			37.8	21.2		22.4

420 minutes	Band position (cm^{-1})	3189			3302	3312		3364
	Bandwidth (cm^{-1})	68.0			12.8	11.5		41.4
	% Relative area	17.0			33.8	17.9		31.3
480 minutes	Band position (cm^{-1})				3302	3312		3364
	Bandwidth (cm^{-1})				12.8	11.5		16.2
	% Relative area				46.1	24.2		29.7
540 minutes	Band position (cm^{-1})				3302	3312		3363
	Bandwidth (cm^{-1})				13.1	11.6		15.9
	% Relative area				44.5	25.1		30.4
600 minutes	Band position (cm^{-1})				3302	3312		3363
	Bandwidth (cm^{-1})				13.6	12.0		15.2
	% Relative area				44.0	22.8		33.2

Table 3. Band component analysis of the Raman spectrum of the NH stretching region of the low defect kaolinite intercalated with hydrazine

Deintercalation Time	Band Characteristics	ν_{l6}	ν_{l5}	ν_{l4}	ν_{l3}	ν_{l2}	ν_{l1}
0 mins	Band position (cm^{-1})	895		913		925	953
	Bandwidth (cm^{-1})	21.7		16.0		15.1	10.0
	% Relative area	35.2		59.6		3.6	1.7
30 mins	Band position (cm^{-1})	896		913		926	955
	Bandwidth (cm^{-1})	21.7		16.1		13.3	15.0
	% Relative area	34.3		60.3		3.0	2.2
3 hours	Band position (cm^{-1})	895	904	913		930	956
	Bandwidth (cm^{-1})	20.1	9.7	17.8		12.6	9.1
	% Relative area	27.2	2.9	65.6		3.9	0.4
4.5 hours	Band position (cm^{-1})	896	905	913	923	937	956
	Bandwidth (cm^{-1})	18.3	10.7	16.5	17.0	19.0	12.5
	% Relative area	11.6	6.7	45.4	12.9	22.6	0.8
22 hours	Band position (cm^{-1})	896	905	913	923	938	962
	Bandwidth (cm^{-1})	16.1	10.6	17.4	15.7	19.6	9.7
	% Relative area	3.6	7.3	49.7	12.3	25.9	1.2
50 hours	Band position (cm^{-1})		905	913	923	939	962
	Bandwidth (cm^{-1})		13.0	17.5	14.9	19.5	8.4
	% Relative area		13.9	44.5	12.8	27.9	0.9
120 hours	Band position (cm^{-1})		905	913	925	939	962
	Bandwidth (cm^{-1})		10.9	16.9	14.2	19.4	8.4
	% Relative area		12.0	45.5	13.1	28.5	0.9
168 hours	Band position (cm^{-1})		905	913	924	940	966
	Bandwidth (cm^{-1})		10.9	16.6	15.6	23.5	14.3
	% Relative area		12.9	34.2	12.4	34.5	6.0
1 month	Band position (cm^{-1})		905	913	924	940	967
	Bandwidth (cm^{-1})		10.411	16.6	14.9	25.2	13.5
	% Relative area		2.0	34.6	10.4	37.4	5.5

Table 4. Band component analysis of the DRIFT spectrum of the hydroxyl deformation region of the low defect kaolinite intercalated with hydrazine

Deintercalation Time	Band Characteristics	ν_{H2O} bend-4	ν_{H2O} bend-3	ν_{H2O} bend-2	ν_{H2O} bend-1
Zero time	Band position (cm^{-1})	1597	1613	1627	1658
	Bandwidth (cm^{-1})	64.0	11.5	16.1	46.0
	% Relative area	47.7	18.3	21.4	11.1
0.5 hours	Band position (cm^{-1})	1601	1613	1627	1660
	Bandwidth (cm^{-1})	53.8	16.0	16.0	51
	% Relative area	42.0	19.0	27.3	9.7
3 hours	Band position (cm^{-1})	1600	1613	1627	1665
	Bandwidth (cm^{-1})	46.0	10.6	16.8	53.8
	% Relative area	40.2	18.2	30.9	10.7
4.5 hours	Band position (cm^{-1})	1599	1612	1627	1669
	Bandwidth (cm^{-1})	42.9	11.6	20.9	46.5
	% Relative area	45.2	15.1	28.4	11.3
22 hours	Band position (cm^{-1})	1597	1612	1625	1677
	Bandwidth (cm^{-1})	40.7	11.5	39	39.6
	% Relative area	44.0	6.6	35.4	14.0
50 hours	Band position (cm^{-1})	1594	1612	1618	1677
	Bandwidth (cm^{-1})	34.5	16.2	47.0	33.9
	% Relative area	28.8	11.0	49.2	11.0
120 hours	Band position (cm^{-1})	1588	1606	1616	1677
	Bandwidth (cm^{-1})	30.4	32.0	27.1	32.4
	% Relative area	19.9	42.0	25.0	13.1

Table 5. Band component analysis of the DRIFT spectra of the water-bending region of the low defect kaolinite intercalated with hydrazine

LIST OF FIGURES:

Figure 8 (c)   **Band component analysis of the DRIFT spectrum of the hydroxyl deformation region of hydrazine intercalated kaolinite exposed to air for 1 month.**

Figure 8 (d)   **Band component analysis of the DRIFT spectrum of the hydroxyl deformation region of untreated kaolinite.**

Figure 9   **DRIFT spectra of the water bending region of kaolinite intercalated with hydrazine and exposed to air for (a) zero time (b) 0.5 hr (c) 3 hrs (d) 4.5 hrs (e) 22 hrs (f) 50 hrs (g) 120 hrs (h) 168 hrs (i) 1 month**

LIST OF TABLES:

Figure 1
**C:\Ray-Frost\Xlfiles\Lulea\hydrazine
XRD data**

Figure 2
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XRD data**
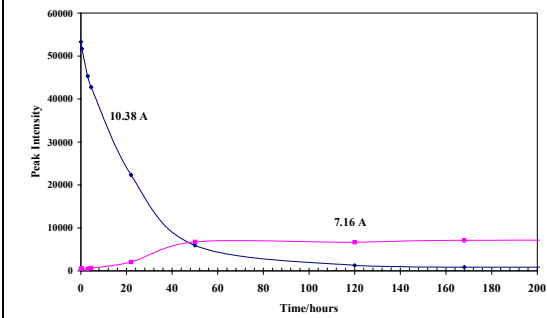
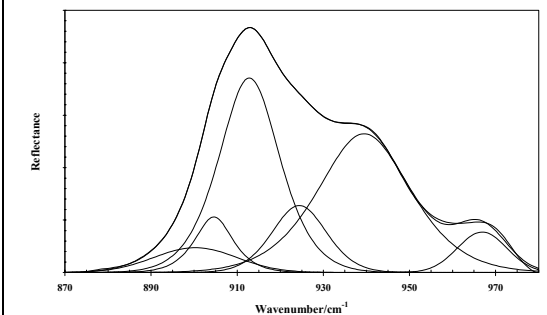**Figure 3**
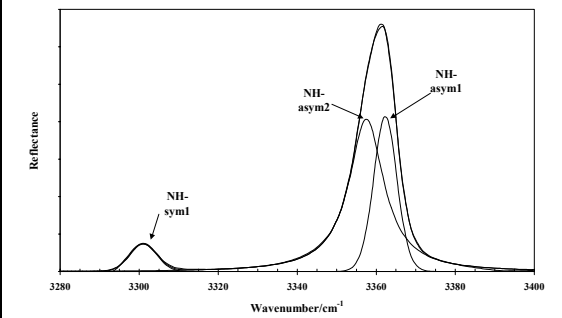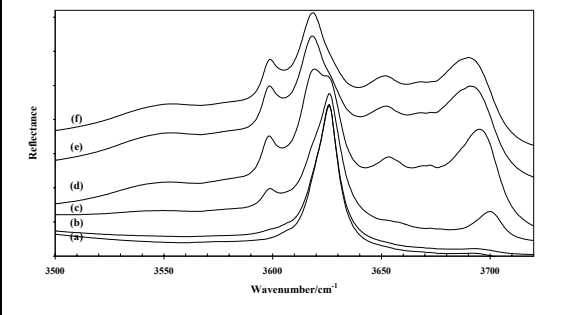

115-1-nh.xls
Figure

Figure 8b
Kj115-8-deform.xls

Figure 4
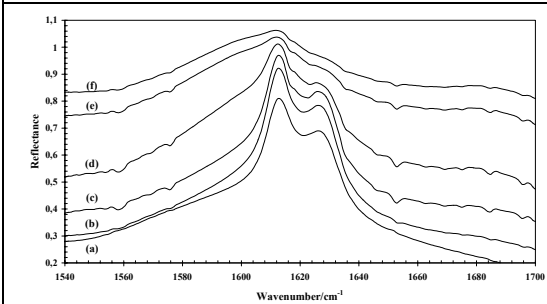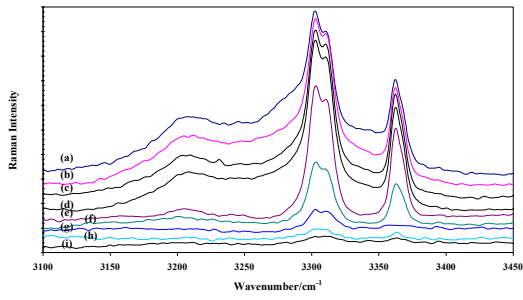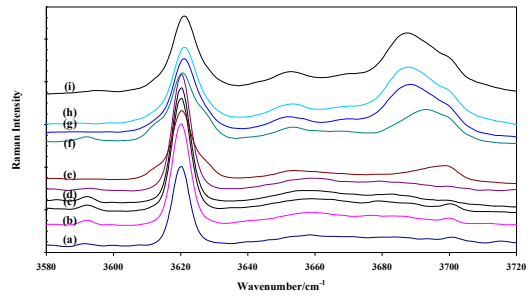**C:\Ray-Frost\Xlfiles\Lulea\hydraz-
2.xls**
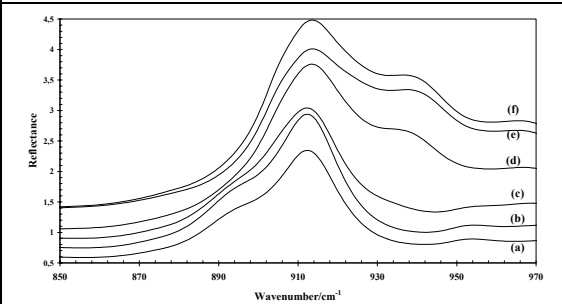
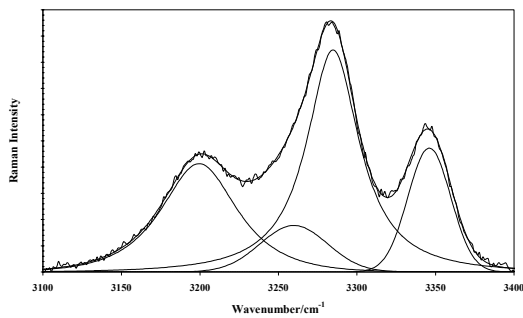| Figure 9	Figure 8
Figure 7 **C:\spectracalc\hydrazines\janos-k** **H30_OHBS**	**Figure 5** **C:\spectracalc\hydrazines\janos-k** **H30_OHBS**
C:\ray-frost\spectyracalc\lulea\bandfit **Kj115-1-deform.xls**	**Figure 7b** **C\Ray-** **frost\spectracalc\Raman\intercalates** **Hydrazine\janos-kristof** **H30bsmod2.xls**
Figure 7 (c) **Raman of hydrazine**	
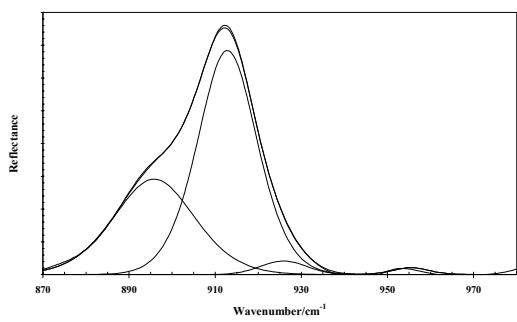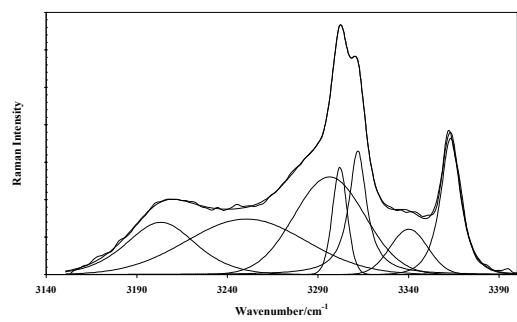
Kaolinite intercalated with hydrazine	Band Characteristics	ν_{N-H} sym	ν_{H2O}	ν_7	ν_5	ν_6	ν_3	ν_2	ν_4	ν_1
Zero time	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115			3619 9.7 4.6	3625 12.4 22.4				3696 52.0 3.5
1 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-1		3591 94.3 16.0	3619 11.1 5.0	3626 9.7 17.5				3690 25.5 0.9
4.5 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-2	3554 75.7 11.8	3599 21.3 7.4	3619 15.9 9.4	3626 11.7 16	3653 37 3.5			3699 13.4 3.5
12 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-3	3552 100.0 29.2	3598 16.9 5.9	3619 15.8 12.8	3626 12.7 6.9	3653 26.2 8.4	3673 30.9 9.3		3695 20.1 9.6
21 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-4	3552 95 29.3	3599 15.3 8.3	3619 13.1 11.4	3626 9.5 4.4	3651 30.0 13.9	3677 27.4 11.8		3695 18.2 7.9
50 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-5	3554 84.8 26.2	3600 19.5 10.0	3619 13.0 11.8	3627 15.0 4.4	3651 31.5 15.3	3675 27.9 11.1	3685 12.3 1.7	3694 18.4 7.7
120 hrs		115-6								
171 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-7		3598 16.3 7.2	3618 15.6 12.1	3629 17.4 1.8	3650 31.8 13.4	3673 26.5 10.2	3684 13.3 1.6	3693 20.4 5.9
120 hours	Band position (cm^{-1}) Bandwidth (cm^{-1}) % Relative area	115-8								

Table X. Band component analysis of the DRIFT spectrum of the hydroxyl-stretching region of the low defect kaolinite intercalated with hydrazine

The Raman spectra of the NH stretching region show significant changes as compared to the spectrum of pure hydrazine hydrate and also, as a function of time of deintercalation. A split can be observed in both the ν_sNH and ν_{as}NH bands at 3310 and 3375cm^{-1}, respectively. The split of the former band is more pronounced, since a symmetric vibration suffers a higher deformation upon hydrogen bonding that an asymmetric one. The broad bands between ca. 3020 and 3280 cm^{-1} can be due to the bonding between hydrazine and water. The fact that this band disappears only when hydrazine is no longer present in the system, supports this observation. Also, this is an indication of the strong connection between hydrazine and water. In addition, this is an indication that the hydrazine is connected to the inner surface hydroxyls via water. The relatively narrow ν_sNH and ν_{as}NH bands indicate a connection to an ordered structure (ie. to the siloxane layer) , in contrast to the less structured, less defined gibbsite-like layer as a result of the insertion of water between the layer of the intercalating hydrazine and that of the inner surface OH groups.

The separation of the ν_sNH and ν_{as}NH bands in the intercalation complex is higher that that in pure hydrazine. The extent of band separation is similar to that of a primary amine. This observation can be due to the weaker connection between hydrazine and water (water is connected to one end of hydrazine, only). As a general observation, all three hydrazine bands move to higher frequencies upon intercalation. This can be due to the fact that the interaction between hydrazine molecules is not so strong than in a liquid phase.

Table 3 Results of the Band component analysis of the DRIFT spectra of the amine-stretching region of the low defect kaolinite intercalated with hydrazine and exposed to air for intervals of time

$[NH_2\text{-}NH_3]^{\delta+}[OH]^{\delta-}$ unit