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Raman spectroscopy of hydrazine-intercalated kaolinite at 77, 298, 323, 343 and 358 K

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The Raman spectrum at 298 K of hydrazine-intercalated kaolinite shows a single band at 3620 cm⁻¹. No other hydroxyl stretching bands are observed. Upon obtaining the spectrum at liquid nitrogen temperature the band is observed at 3616 cm⁻¹, the same position as for the inner hydroxyl of the non-intercalated kaolinite. Hence this band is assigned to the inner hydroxyl of kaolinite. After exposure to the atmosphere for 10 min and upon obtaining spectra at 77 K, two additional bands are observed at 3607 and 3625 cm⁻¹. These additional bands are only observed after the onset of deintercalation. The band observed at 3625 cm⁻¹ is assigned to the inner surface hydroxyls, hydrogen bonded to the hydrazine. The fact that the band is only observed after the onset of deintercalation suggests that the band is Raman inactive and infrared active. Raman spectroscopic analysis indicates that there are two types of hydrazine molecules as evidenced by two NH bands, (a) weakly hydrogen bonded as evidenced by two bands observed around 3300 and 3312 cm⁻¹ and (b) a strongly hydrogen-bonded hydrazine as evidenced by bands at 2890 and 2948 cm⁻¹. The two NH symmetric stretching bands at around 3300 and 3312 cm⁻¹ combined with the two NH antisymmetric stretching bands at 3361 and 3367 cm⁻¹ suggest that there are two slightly different NH₂ units in the hydrazine-intercalated complex. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

The industrial application of kaolinite, an important industrial raw material, is closely related to its reactivity and surface properties. The reactivity of kaolinite internal surfaces can be tested by intercalation, i.e. via the insertion of low molecular weight organic compounds (e.g. potassium acetate, hydrazine, formamide, dimethyl sulphoxide) between the kaolinite layers consisting of the two-dimensional arrangements of tetrahedral (siloxane) and octahedral (gibbsitic) sheets.^{1–4} The mechanism of intercalation is not known with certainty, but it involves the disruption of the hydrogen bonding between the kaolinite layers and the formation of new hydrogen bonds between the kaolinite inner surfaces and the inserted molecule.

Molecules such as formamide and acetamide may connect to kaolinite inner surfaces either through the C=O group, the lone pair of nitrogen, or the amide group.^{4–9} The possibility of intercalating hydrazine into kaolinite has been known for a considerable length of time. Ledoux and White reported the expansion of kaolinite from 7.2 to 10.4 Å

upon introducing hydrazine in the kaolinite structure.³ Mild heating resulted in deintercalation accompanied by the partial collapse of the structure to 9.4 Å. Johnston and Stone showed the effect of evacuation on the kaolinite–hydrazine complex with the subsequent collapse of the structure from 10.4 to 9.6 Å.⁹ A new model was proposed for hydrazine intercalation based on the insertion of a hydrazine–water unit by Frost *et al.*¹⁰ The thermal behaviour of hydrazine-intercalated kaolinite shows a close similarity to that of the formamide-intercalated mineral.⁸ In addition to the involvement of water in the intercalation process (and also in the structure of the complex), hydrazine is also liberated from the intercalated clay in two overlapping stages.⁵ In this study, Raman microscopy using a thermal stage was used to follow the structural changes in hydrazine-intercalated kaolinite upon heating and cooling to 77 K. The objectives were to distinguish between differently bonded hydrazine molecules in the complex and to reveal the role of water in the intercalation process.

EXPERIMENTAL

Intercalation of kaolinite

The kaolinite used in this study is a low-defect kaolinite from Királyhegy in Hungary. This mineral has been

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previously characterized both by x-ray diffraction and by Raman spectroscopy. The kaolinite was purified through sedimentation and the 2–20 μm sized fraction was selected for intercalation. The intercalate was prepared by mixing 300 mg of the kaolinite with 5 cm^3 of 85% hydrazine hydrate aqueous solution for 80 h at room temperature, magnetically stirred in a closed ampoule. The excess solution was decanted and the intercalated kaolinite was immediately subjected to spectroscopic analysis.

Raman spectroscopy

The hydrazine-intercalated kaolinites were prepared in sealed vials. The vials containing the hydrazine-intercalated kaolinites were placed in a Linkham thermal stage of an Olympus BHSM microscope, equipped with $\times 10$, $\times 20$, $\times 50$ and LWD $\times 50$ objectives. The purpose of placing the samples in the stage was to prevent absorption of moisture from the air. Samples were flushed with dry nitrogen or air depending on the type of experiment. The samples were enclosed to prevent evaporation and contamination by the laboratory atmosphere. The samples were measured by focusing through the vial, hence no water entered the hydrazine-intercalated complex or air, as the samples were kept under nitrogen. 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) detector. Raman spectra were excited with a Spectra-Physics Model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range $100\text{--}4000\text{ cm}^{-1}$. 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.

Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments, Waterfield, Surrey, UK). For spectra at 77 K, nitrogen gas from liquid nitrogen was passed through a small hole in this plate immediately below the centre of the glass disc. It was found that the best method of obtaining 77 K was to cool rapidly at 50 K min^{-1} . Because of the increased optics used in collecting data at 77 K, the spectra are noisier and require longer accumulation times. Spectra were obtained using 12 s scans for 20 min using a special short $\times 50$ (ULWD) objective. The intensity of the spectra was found to be decreased in intensity by 0.3 using the ULWD objective compared with the normal $\times 50$ objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long working distance objective. This, combined with the spherical aberration of the stage window, results in decreased signal. It should be noted that the use of the $\times 50$ objective collects scattered light over a much wider angle than the $\times 20$ or $\times 10$ objective. There is less 'polarisation leakage' if $\times 20$ objectives are used. Then, however, the intensity of the scattered light diminishes, making the collection of spectra more difficult.

RESULTS AND DISCUSSION

Raman spectroscopy of kaolinite

The Raman spectrum of untreated kaolinite shows five features with bands observed at 3692 cm^{-1} (ν_1), 3683 cm^{-1} (ν_4), 3668 cm^{-1} (ν_2), 3651 cm^{-1} (ν_3) and 3620 cm^{-1} (ν_5) (Table 1). The bands at 3692 and 3683 cm^{-1} are the longitudinal and transverse optical modes (in-phase hydroxyl stretching vibrations). The bands at 3668 and 3651 cm^{-1} are described as the out-of phase vibrations of the three inner surface hydroxyls. The band at 3620 cm^{-1} is ascribed to the inner hydroxyl stretching vibration. Upon cooling to liquid nitrogen temperature, the bands assigned to the inner surface and inner hydroxyls shift in opposite directions. The band at 3620 cm^{-1} shifts to 3616 cm^{-1} and the band at 3692 cm^{-1} shifts to 3704 cm^{-1} . These shifts may be attributed to increased or decreased interactions between the hydroxyl unit and the adjacent oxygen of the siloxane layer. The inner hydroxyl shifts to lower wavenumbers, indicating a stronger electrostatic interaction between the inner hydroxyl and the adjacent apical oxygen within the kaolinite lattice. The bands assigned to the inner surface hydroxyls shift to higher wavenumbers, suggesting a weakening of the interactions between the hydroxyls and the oxygens of the next adjacent siloxane layer. Upon cooling to liquid nitrogen temperature, contraction of the lattice will occur. Thus the kaolinite layers will be brought closer together. It could be expected that a stronger hydrogen bond would be formed between the inner surface hydroxyls of one layer and the oxygens of the adjacent siloxane layer. However, this is not observed. The conclusion is drawn that the OH—O hydrogen bonds are not linear and that the angle of this bond increases upon contraction of the kaolinite lattice.

Raman spectroscopy of hydrazine hydrate-intercalated kaolinite in the presence of moisture

The Raman spectrum of hydrazine intercalated kaolinite before de-intercalation and after de-intercalation is illustrated in Fig. 1. The results of the band component analyses are presented in Table 1. The Raman spectrum at 298 K for hydrazine-intercalated kaolinite obtained with the sample in the vial shows a single band at 3620 cm^{-1} . No other hydroxyl stretching bands are observed for the hydrazine-intercalated kaolinite. Upon obtaining the spectra at liquid nitrogen temperature, the band is observed at 3616 cm^{-1} , the same position as for the inner hydroxyl of the non-intercalated kaolinite. Hence we attribute this band observed in the Raman spectra at 3620 cm^{-1} at 298 K and 3616 cm^{-1} at 77 K to the inner hydroxyl of kaolinite. Thus the shift in this band upon cooling to liquid nitrogen temperature is identical in behaviour to the inner hydroxyl band for untreated kaolinite. The absence of intensity in the bands assigned to the inner surface hydroxyls is an indication that the kaolinite is fully intercalated and that all of the inner surface hydroxyls are completely reacted with the hydrazine. The band

Table 1. Results of the band component analysis of the Raman spectra of the OH stretching region of thermally treated hydrazine-intercalated kaolinite

	Band characteristics	ν_7	ν_5	ν_6	ν_3	ν_2	ν_4	ν_1
Kaolinite at 298 K	Band position cm^{-1}		3620		3651	3668	3683	3692
	Bandwidth cm^{-1}		3.3		11.1	9.8	11.0	16.3
	% Relative area		24.8		17.0	5.3	30.3	22.1
Kaolinite at 77 K	Band position cm^{-1}		3616		3658	3677	3692	3704
	Bandwidth cm^{-1}		3.3		5.9	4.6	7.7	15.0
	% Relative area		45.0		6.9	8.3	17.6	22.3
Hydrazine-intercalated kaolinite at 298 K, exposed to air	Band position cm^{-1}		3620					
	Bandwidth cm^{-1}		3.8					
	% Relative area		100					
Hydrazine-intercalated kaolinite at 77 K, zero time exposed to air	Band position cm^{-1}		3616					
	Bandwidth cm^{-1}		3.2					
	% Relative area		100					
Hydrazine-intercalated kaolinite at 77 K, after 10 min exposed to air	Band position cm^{-1}	3607	3616	3625				
	Bandwidth cm^{-1}	18.2	7.2	17.9				
	% Relative area	24.8	48.5	26.7				
Partially de-intercalated hydrazine-intercalated kaolinite at 298 K, exposed to air	Band position cm^{-1}	3613	3619	3622	3653	3671	3685	3693
	Bandwidth cm^{-1}	6.6	4.7	9.3	17.9	15.0	11.7	15.4
	% Relative area	4.5	10.9	23.9	21.0	10.0	12.0	20.7
Partially de-intercalated hydrazine-intercalated kaolinite at 77 K, exposed to air	Band position cm^{-1}	3609	3616	3624	3656	3675	3694	3703
	Bandwidth cm^{-1}	28.5	5.0	4.4	8.2	4.4	10.3	13.0
	% Relative area	8.0	23.0	9.8	13.5	3.5	18.4	19.8
Hydrazine-intercalated kaolinite 298 K, exposed to atmosphere of dry nitrogen	Band position cm^{-1}		3620					
	Bandwidth cm^{-1}		3.7					
	% Relative area		100					
Hydrazine-intercalated kaolinite heated to 323 K, exposed to atmosphere of dry nitrogen	Band position cm^{-1}		3620	3627				
	Bandwidth cm^{-1}		11.1	5.7				
	% Relative area		34.0	66.0				
Hydrazine-intercalated kaolinite heated to 343 K, exposed to atmosphere of dry nitrogen	Band position cm^{-1}		3620	3627		3667		3697
	Bandwidth cm^{-1}		5.2	8.5		30.0		13.2
	% Relative area		10.0	66.0		7.6		16.6
Hydrazine-intercalated kaolinite heated to 358 K, exposed to atmosphere of dry nitrogen	Band position cm^{-1}		3620	3627	3654			3696
	Bandwidth cm^{-1}		8.5	10.4	50.8			13.6
	% Relative area		18.0	30.0	20.0			32.0

attributed to the inner hydroxyl at 3620 cm^{-1} is sharp with a bandwidth of 3.8 cm^{-1} at 298 K and 3.2 cm^{-1} at 77 K. These values compare favourably with the values of the bandwidth of the inner hydroxyl for the untreated kaolinite.

After exposure to the atmosphere at 298 K for 10 min and upon obtaining spectra at 77 K, two additional bands are observed at 3607 and 3625 cm^{-1} . These additional bands are only observed after the onset of deintercalation. These bands are broad with bandwidths of 18.2 and 17.9 cm^{-1} . Upon obtaining the Raman spectra of the partially de-intercalated hydrazine-intercalated kaolinite at 298 K, in addition to the normal inner surface hydroxyls of kaolinite,

the two additional bands at 3613 and 3622 cm^{-1} are observed. The bands attributed to the inner surface hydroxyls and observed at 3653, 3671, 3685 and 3693 cm^{-1} correspond well with those of the non-intercalated kaolinite. Upon obtaining the spectra at liquid nitrogen temperature, the band observed at 3619 cm^{-1} shifts to 3616 cm^{-1} , identical with that of the non-treated kaolinite. The Raman band observed at 3622 cm^{-1} shifts to 3625 cm^{-1} at 77 K and the band observed at 3613 cm^{-1} broadens and shifts to 3607 cm^{-1} . The bands observed at 3656, 3675, 3694 and 3703 cm^{-1} , attributed to the inner surface hydroxyls, harmonize extremely well with the bands for the non-treated kaolinite. The hydroxyl stretching

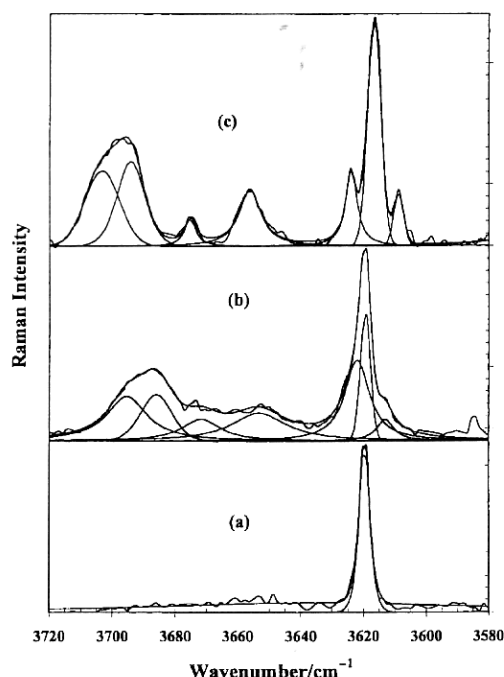


Figure 1. Raman spectra of the hydroxyl stretching region of hydrazine hydrate-intercalated kaolinite exposed to air at (a) 298 K, (b) partially de-intercalated at 298 K and (c) 77 K.

wavenumbers upon cooling to liquid nitrogen temperature all shift to higher values. Hence the band observed at 3625 cm^{-1} is assigned to the inner surface hydroxyls, which are hydrogen bonded to the hydrazine. The band, which is observed at 3613 cm^{-1} in the 298 K spectra, shifts to 3607 cm^{-1} . It is probable that the band is due to water released during the de-intercalation of the hydrazine-intercalated kaolinite. A second possibility, although less likely, is that this band is due to the inner hydroxyl where the differential polarizability of the OH bond has been affected by the presence of the hydrazine inserting into the ditrigonal cavity of the siloxane layer. A third possibility is that this band is due to a shifted inner surface hydroxyl hydrogen bonded to the hydrazine. This possibility is even less likely.

Raman spectroscopy of hydrazine hydrate-intercalated kaolinite in the absence of moisture

The Raman spectra of the hydrazine-intercalated kaolinite heated to 323, 343 and 358 K under an atmosphere of nitrogen are shown in Fig. 2. The results of the band component analysis are reported in Table 1. At 298 K, the Raman spectrum of hydrazine-intercalated kaolinite shows only a single peak at 3620 cm^{-1} . Upon obtaining the Raman spectrum of the hydrazine-intercalated kaolinite *in situ* at 323 K, an additional band at 3627 cm^{-1} is observed. The band is sharp with a bandwidth of 5.7 cm^{-1} . The ratio of the relative intensities of the 3620 and 3627 cm^{-1} bands is 1:2. It

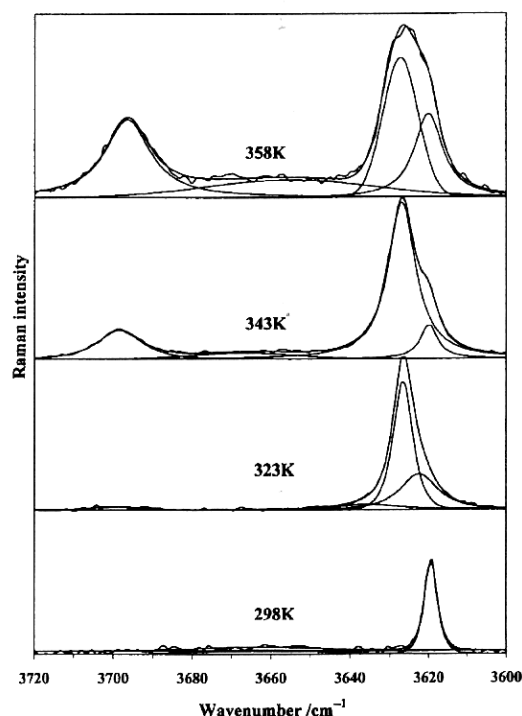


Figure 2. Raman spectra of the hydroxyl stretching region of hydrazine hydrate-intercalated kaolinite at 298, 323, 343 and 358 K.

should be noted that the band observed at 3607 cm^{-1} is no longer observed when the hydrazine-intercalated kaolinite is heated in an inert atmosphere. This observation validates the concept that the 3607 cm^{-1} band is assignable to the hydroxyl stretching vibrations of water released during the de-intercalation of the hydrazine hydrate-intercalated kaolinite. It is possible that the water and/or water hydrazine adsorbed on the kaolinite is lost at this temperature, leaving a 'pure' hydrazine-intercalated kaolinite.

Upon collection of the Raman spectrum *in situ* at 343 K, additional bands are now observed at 3667 and 3697 cm^{-1} . These bands are attributed to the inner surface hydroxyls of the de-intercalated hydrazine-intercalated kaolinite. The relative intensities of the 3667 and 3697 cm^{-1} bands are 7.6 and 16.6%. These values indicate that the kaolinite surfaces are no longer completely covered by hydrazine. This means that the heating of the hydrazine-intercalated kaolinite at 343 K caused some de-intercalation. The band at 3627 cm^{-1} is slightly broader with a bandwidth of 8.5 cm^{-1} . The band still makes up some 66% of the total band intensity in this region. Upon collection of the Raman spectrum at 358 K, further de-intercalation occurs. This may be observed by the increase in intensity of the band at 3696 cm^{-1} to a relative intensity of 32.0% and a decrease in intensity of the band at 3627 cm^{-1} to 30.0%. This loss in intensity is ascribed to the removal of the hydrazine from between the kaolinite layers through evaporation.

Raman spectra of the NH stretching region of hydrazine hydrate-intercalated kaolinite

Hydrazine hydrate is a liquid. Upon intercalation of hydrazine into the kaolinite, hydrazine no longer behaves as a liquid but is molecular-like in behaviour. This is the reason for obtaining the spectrum of solid hydrazine at liquid nitrogen temperature (this work). This then avoids overlap with water bands, which are inherently weak in the Raman spectrum. The Raman spectrum of solid hydrazine at liquid nitrogen temperature shows three overlapping bands at 3348, 3312 and 3273 cm^{-1} . The bandwidths are large with half-widths of 27.2, 45.7 and 34.5 cm^{-1} . The Raman spectrum of hydrazine at 298 K shows a band at 3277 cm^{-1} assigned to the antisymmetric NH stretching vibrations. The Raman spectrum of hydrazine at 298 K also displays a band at 3189 cm^{-1} , which is observed as two overlapping bands at 3221 and 3208 cm^{-1} at 77 K. The bandwidths are also broad with a half-widths of 21.3 and 21.8 cm^{-1} . This band is ascribed to the NH symmetric stretching vibrations. For hydrazine at 77 K two additional bands are observed at 2962 and 2939 cm^{-1} , with bandwidths of 224 and 113 cm^{-1} , which are also assigned to NH vibrations which are involved in strong hydrogen bond interactions.

The Raman spectra of the NH stretching region of hydrazine-intercalated kaolinite are shown in Fig. 3 and the results of the band component analyses are reported

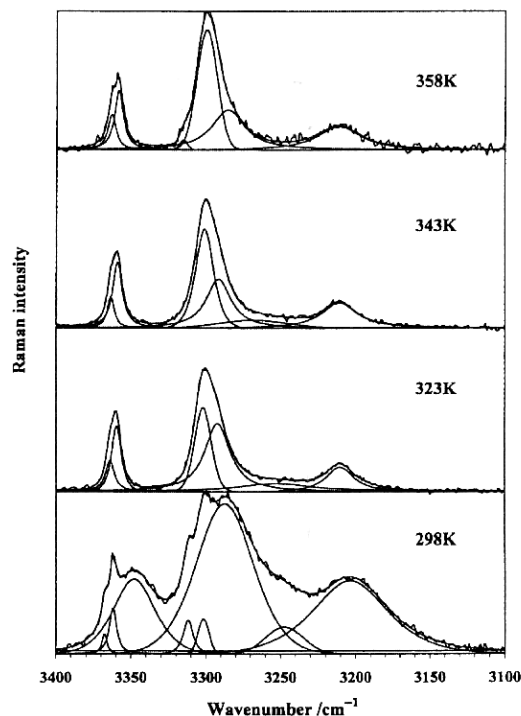


Figure 3. Raman spectra of the NH stretching region of hydrazine hydrate intercalated kaolinite at 298, 323, 343 and 358 K.

in Table 2. The Raman spectrum of hydrazine-intercalated kaolinite shows more complexity than hydrazine liquid. Two bands are observed at 3367 and 3362 cm^{-1} and are attributed to the NH antisymmetric stretching vibrations of the hydrazine in the hydrazine-intercalated kaolinite. These bands are sharp with bandwidths of 4.0 and 5.9 cm^{-1} , respectively. Two bands are also observed at 3287 and 3301 cm^{-1} with bandwidths of 45.6 and 8.9 cm^{-1} . These bands are assigned to the NH symmetric stretching modes. In addition, two broader bands are observed at 3247 and 3203 cm^{-1} with bandwidths of 29.8 and 59.2 cm^{-1} . A broad band is also observed at 3348 cm^{-1} . The reason for the number of NH stretching bands observed in the 298 K spectrum may be attributed to the complexity of the hydrazine-intercalated kaolinite complex. Two types of surfaces exist: (a) hydrazine adsorbed on the external surfaces of the kaolinite and (b) hydrazine reacted with the internal surfaces of the kaolinite (intercalation). A further complexity exists, namely the intercalation of the water-hydrazine mixture. There may be several types of intercalation: (a) intercalation of the hydrazine hydrate, (b) intercalation of hydrazine or (c) intercalation of water.

For the partially de-intercalated kaolinite, bands are observed in similar positions to the non-de-intercalated hydrazine-intercalated kaolinite. It appears that there are two symmetric and two antisymmetric stretching modes. This indicates two different NH units in the hydrazine-intercalated kaolinite, one of which is more strongly hydrogen bonded than the other. Upon obtaining the spectrum of the hydrazine-intercalated kaolinite at liquid nitrogen temperature, the two antisymmetric stretching modes are observed at 3363 and 3372 cm^{-1} . The two symmetric stretching modes are observed at 3303 and 3314 cm^{-1} . In addition, a broad, low-intensity band is observed at 3208 cm^{-1} . Another set of bands is observed at 2890 and 2948 cm^{-1} , which appears to correspond with the bands observed at 2921 and 2962 cm^{-1} for the pure hydrazine. Thus the results of the Raman spectroscopic analysis indicate that there are two types of hydrazine molecules, (a) weakly hydrogen-bonded as evidenced by two bands observed around 3300 and 3312 cm^{-1} and (b) a strongly hydrogen-bonded hydrazine as evidenced by bands at 2890 and 2948 cm^{-1} . The two NH symmetric stretching bands at around 3300 and 3312 cm^{-1} combined with the two NH antisymmetric stretching bands at 3361 and 3367 cm^{-1} suggests that there are two slightly different NH_2 units in the complex.

A very large difference exists between the spectra obtained at 298 and 323 K (Fig. 3). A number of the broad overlapping bands are lost. By obtaining the Raman spectrum at 323 K, the adsorbed hydrazine has been lost, leaving the spectrum of the hydrazine of the intercalated kaolinite. Two bands are observed at 3363 and 3359 cm^{-1} with bandwidths of 7.0 and 7.6 cm^{-1} . These bands are

Table 2. Results of the band component analysis of the Raman spectra of the NH stretching region of thermally treated hydrazine-intercalated kaolinite

	Band characteristics	ν_8	ν_7	ν_6	ν_5	ν_4	ν_3	ν_2	ν_1
Hydrazine-intercalated kaolinite, 298 K	Band position cm^{-1}	3203	3247	3287	3301	3311	3348	3362	3367
	Bandwidth cm^{-1}	59.2	29.8	45.6	8.9	7.9	32.9	5.9	4.0
	% Relative area	22.7	4.0	34.0	1.5	1.6	12.7	2.0	1.2
Hydrazine-intercalated kaolinite, heated to 323 K	Band position cm^{-1}	3210	3253	3292	3301			3359	3363
	Bandwidth cm^{-1}	21.7	60.0	20.3	13.0			7.6	7.0
	% Relative area	9.2	9.7	27.7	16.3			8.4	4.7
Hydrazine-intercalated kaolinite, heated to 343 K	Band position cm^{-1}	3210	3268	3291	3300			3358	3363
	Bandwidth cm^{-1}	28.2	56.2	20.0	14.1			7.7	5.6
	% Relative area	12.0	5.3	16.7	17.8			8.7	3.0
Hydrazine-intercalated kaolinite, heated to 358 K	Band position cm^{-1}	3211	3270	3299	3315			3358	3362
	Bandwidth cm^{-1}	34.8	26.6	16.1	6.0			7.1	6.6
	% Relative area	9.1	14.1	17.6	0.6			5.6	3.1

attributed to the N–H antisymmetric stretching vibrations. The ratio of the relative intensity of these two bands ($3363/3359\text{cm}^{-1}$) is 0.56. Two bands are found at 3301 and 3292cm^{-1} with bandwidths of 13.0 and 20.3cm^{-1} , respectively, and are assigned to the N–H symmetric stretching vibrations. The ratio of the relative intensity of these two bands ($3301/3292\text{cm}^{-1}$) is 0.58. Hence the ratio of the antisymmetric and symmetric stretching modes is identical. Therefore, two different types of NH_2 units are observed with slight differences in the bonding strengths of these units.

A band is also observed at 3210cm^{-1} with a bandwidth of 21.7cm^{-1} . This band may be due to NH coupling. Upon obtaining the spectra at 343 K, the antisymmetric and symmetric NH stretching bands are found at 3363, 3358 and 3300, 3291cm^{-1} . The ratio of the relative intensity of the two antisymmetric stretching modes is 0.34 and of the two symmetric stretching modes is 1.05. Now the intensity ratio is different. This suggests that the hydrazine intercalation at 343 K is significantly different to that at 323 K. At 358 K the two antisymmetric NH stretching vibrations are observed at 3362 and 3358cm^{-1} . The two symmetric stretching vibrations are observed at 3315 and 3299cm^{-1} . There is a significant shift of the bands to higher wavenumbers at the elevated temperature. The band at 3299cm^{-1} makes up 17.6% of the total band intensity compared with 0.6% for the 3315cm^{-1} band. Significant intensity is now found in the band at 3270cm^{-1} .

CONCLUSIONS

The results of the Raman spectroscopic analyses of the hydrazine-intercalated kaolinites at elevated temperatures suggest that two NH_2 units exist with slightly different hydrogen bonding to the kaolinite surfaces. One possibility

is that one NH_2 unit bonds to the siloxane surface and the second to the hydroxyl surface. Whether the hydrazine bonds to both surfaces at the same time is not known. It is possible that the hydrazine is mobile and that the interaction with the surfaces is weak. The fact that the hydrazine is easily lost upon mild heating supports this concept. Thus the hydrazine molecule could be envisaged to be oscillating between the two surfaces. Alternatively, the hydrazine is bonded to both of the kaolinite surfaces. Further, the bonding of hydrazine to hydrazine in the intercalation complex cannot be ruled out. The Raman spectra show that the molecular structure of the hydrazine in the hydrazine hydrate-intercalated complex is different from that of pure hydrazine hydrate.

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