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DEINTERCALATION OF HYDRAZINE-INTERCALATED LOW-DEFECT KAOLINITE

RAY L. FROST,[1] J. THEO KLOPROGGE,[1] JANOS KRISTOF,[2] AND ERZSEBET HORVATH[3]

[1] Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Q 4001, Australia

[2] Department of Analytical Chemistry, University of Veszprem, H 8201 Veszprem, PO Box 158, Hungary

[3] Research Group for Analytical Chemistry, Hungarian Academy of Sciences, H 8201 Veszprem, PO Box 158, Hungary

Abstract—The deintercalation of a low-defect kaolinite intercalated with hydrazine was studied by X-ray diffraction, diffuse reflectance infrared spectroscopy (DRIFT), and Raman microscopy over 30 d. X-ray diffraction showed that the kaolinite was fully intercalated. More than 120 h were required for the hydrazine-intercalate to decompose. The Raman spectra of the hydrazine intercalate showed only a single band at 3620 cm^{-1}, which was 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 proceeded, the bands assigned to the inner-surface hydroxyl groups at 3695, 3682, 3670, and 3650 cm^{-1} occurred 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. 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 antisymmetric stretching bands. Deintercalation was 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 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 a band at 3626 cm^{-1} in the DRIFT spectra.

Key Words—Hydrazine, Hydrogen Bonding, Hydroxyl Groups, Intercalation of Kaolinite, Powder X-ray Diffraction, Raman Microscopy.

INTRODUCTION

Kaolinite is classified as a non-expandable clay. However, when molecules such as hydrazine are intercalated between the 1:1 layers, some expansion occurs (Wada, 1961; Ledoux and White, 1966; Olejnik *et al.*, 1970). Hydrazine intercalation of kaolinite has been studied by various workers, including Ledoux and White (1966), Cruz *et al.* (1969, 1973), and Johnston and Stone (1990). Ledoux and White showed that kaolinite can be expanded with hydrazine to 10.4 Å. Deintercalation occurred through mild heating and the structure partially collapsed to 9.4 Å. Infrared spectra of the hydrazine-intercalated kaolinite showed a substantial reduction in intensity from the the inner-surface hydroxyls. The Raman spectrum (Johnston and Stone, 1990) showed a single band centered at 3620 cm^{-1} with intensity in the bands at 3695, 3688, 3668, and 3652 cm^{-1} owing to incomplete intercalation. Johnston and Stone showed the effect of evacuation on the kaolinite-hydrazine complex with subsequent collapse of the structure from 10.4 to 9.6 Å.

The hydrazine molecule interacts with the 1:1 layer surfaces through the lone pair of electrons of the nitrogen and the hydrogens of the NH_2 group. The interaction of the N is expected to be similar to that of potassium acetate and Raman bands ~3605 cm^{-1} are predicted. The interaction of the H is expected to be similar to urea. Thus, there would be no additional hydroxyl bands and no decrease in the spectrum relating to the inner-surface hydroxyl intensities. Here we report the deintercalation of a hydrazine-intercalated kaolinite as a function of time using powder X-ray diffraction (XRD), diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), and Raman microscopy.

MATERIALS AND METHODOLOGY

Kaolinite intercalate

The kaolinite used is a low-defect kaolinite from Kiralyhegy, Hungary. This mineral was previously characterized by XRD and by Raman spectroscopy (Frost *et al.*, 1997). The kaolinite was purified by sedimentation and the 2–20-μm size fraction was selected for intercalation. The intercalate was prepared by mixing 300 mg of the kaolinite with 5 cm^3 of an 85% hydrazine-hydrate aqueous solution for 80 h at room temperature and magnetically stirring in a closed ampoule. The excess solution was decanted and the intercalated kaolinite was immediately subjected to spectroscopic analysis.

X-ray diffraction

XRD patterns of the intercalated kaolinite at different time intervals after exposure to air were obtained

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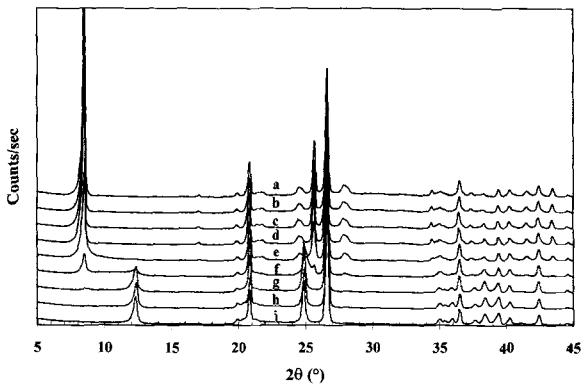


Figure 1. XRD patterns of kaolinite intercalated with hydrazine and exposed to air for (a) 0.0 h, (b) 0.5 h, (c) 3 h, (d) 4.5 h, (e) 22 h, (f) 50 h, (g) 120 h, (h) 168 h, and (i) 30 d.

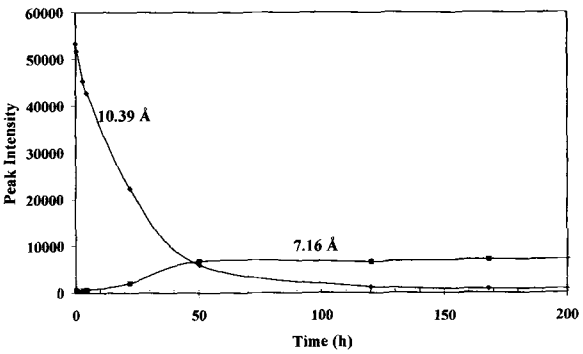


Figure 2. Relationship between the areas of the *d*(001) peaks of the intercalated and deintercalated-hydrazine complex as a function of time.

using a Philips PW 1050 type X-ray diffractometer with CuKα radiation operating at 35 kV and 40 mA. A 1° divergence and scatter slit were combined with a normal focus Cu tube at 6° take-off angle and a 0.2 mm receiving slit. The samples were measured in step-scan mode from 2θ = 2–40° with steps of 0.05° and a counting time of 2 s. XRD slides were prepared from suspensions and studied *in situ* as a function of time.

Combined thermogravimetry-mass spectrometry

The thermogravimetric-mass spectrometric (TG-MS) investigation of the intercalate was performed with a 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 a rate of 10°C per min from ambient to 600°C.

DRIFT spectroscopy

DRIFT analyses were undertaken using a Bio-Rad 60A spectrometer using 512 co-added scans at a resolution of 2 cm^{-1} with a mirror velocity of 0.3 cm/sec. Approximately 3 wt. % 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. Samples were studied *in situ* and spectra obtained as a function of time as the hydrazine-intercalated kaolinite decomposed.

Raman microprobe spectroscopy

Small portions of the hydrazine-intercalated kaolinite were placed on a stainless steel surface on the stage of an Olympus BHSM microscope, equipped with 50× objective lenses (Frost *et al.*, 1997). 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) with an incident power output of 1 mW, recorded at a resolution of 2 cm^{-1} in sections of 1000 cm^{-1}. Spectra were calibrated using the 520.5-cm^{-1} line of a silicon wafer. Raman spectra were obtained by studying the decomposing hydrazine-intercalate *in situ* as a function of time.

RESULTS AND DISCUSSION

Lattice expansion and contraction—XRD results

Figure 1 shows kaolinite intercalated with hydrazine hydrate after exposure to air. The kaolinite has been fully intercalated after 30 d at ambient temperatures, and 100% intercalation is required to make interpretations less complicated. Hydrazine adsorbed on the 1:1 layer surfaces show characteristic 'intercalation' type spectra, although the XRD data may not show a fully expanded phase. Apparently 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 (IR) spectra is not as reliable as XRD to determine if intercalation is complete. The *d*(001)-value for fully intercalated kaolinite is 10.39 Å, which is consistent with 10.4 Å observed by others (Weiss *et al.*, 1963, 1966; Ledoux and White, 1966; Barrios *et al.*, 1977; Johnston and Stone, 1990).

Upon exposure to air, the kaolinite deintercalates as the hydrazine is lost spontaneously. The kaolinite loses stacking order from 50 to 120 h, as indicated by the loss of intensity of the *d*(001) reflections. After the 120-h period (Figure 2), the 10.39-Å peak was no longer observed. The intensity of the 7.16-Å peak increased only after 200 h. The decrease in intensity of the 10.39-Å peak without the consequent formation of the 7.16-Å peak indicates that stacking order is restored only after deintercalation. The intensity loss of the 10.39-Å peak is exponential with time suggesting that the deintercalation reaction follows first-order kinetics. These results are consistent with the reverse reaction reported by Johnston and Stone (1990). Note that the intercalation reaction of Johnston and Stone

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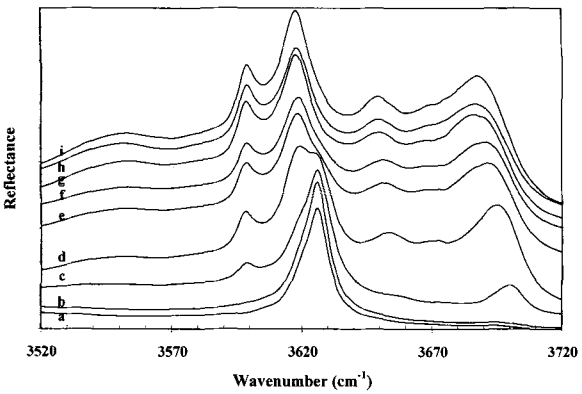


Figure 3. DRIFT spectra of the hydroxyl-stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) 0.0 h, (b) 0.5 h, (c) 3 h, (d) 4.5 h, (e) 22 h, (f) 50 h, (g) 120 h, (h) 168 h, and (i) 30 d.

did not go to completion. In our study, the 7.16-Å peak after deintercalation is different from the untreated kaolinite. The peak is broad and asymmetric on the low-angle side with portions extending to 7.39 Å. This suggests that some interlayers remain slightly expanded. This slight expansion may result from the incorporation of H_2O between the layers.

Kaolinite hydroxyl stretching

DRIFT spectroscopic results. The DRIFT spectra of the deintercalation of the hydrazine-intercalated kaolinite are reported in Figure 3 and Table 1. The OH-stretching region shows the complete absence of the ν_1, ν_2, and ν_3 bands owing to the breaking of the H bonding of the inner-surface hydroxyls, which is consistent with expansion as indicated by XRD. If kaolinite is not fully intercalated then significant intensity remains in the bands caused by the inner-surface hydroxyl groups. An additional band is observed upon intercalation with hydrazine at 3626 cm^{-1}, and this band is assigned to the inner-surface hydroxyls hydrogen bonded to the hydrazine-water complex. The band attributed to the inner hydroxyls at 3620 cm^{-1} is superposed by the 3626-cm^{-1} band and appears as a shoulder. Note that the 3626-cm^{-1} band occurs at 1 bar and 25°C. In previous work (Johnston and Stone, 1990), a band at 3628 cm^{-1} was reported at reduced pressures only. 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.

The XRD data of Johnston and Stone (1990) showed ~95% intercalation of the kaolinite with hydrazine and the IR spectra clearly showed significant intensity in the inner-surface hydroxyl bands. Considering the rapid decomposition of the hydrazine-intercalated kaolinite, the loss of hydrazine would occur more rapidly at low pressure. Cruz *et al.* (1969) described the 3626-cm^{-1} (ν_6) band as red-shifted inner-

Table 1. Band-component analyses of the DRIFT spectra of the hydroxyl-stretching region of the low-defect kaolinite intercalated with hydrazine and exposed to air for various periods.

Deintercalation time (h)	Band characteristics	ν_7	ν_5	ν_6	ν_3	ν_2	ν_4	ν_1
0.0	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	Band position (cm^{-1})		3620	3626				3695
	Bandwidth (cm^{-1})		17.0	8.3				11.8
	% Relative area		56.1	42.6				1.3
3.0	Band position (cm^{-1})	3599	3620	3626	3653	3673	3685	3699
	Bandwidth (cm^{-1})	21.3	15.9	11.7	21.0	17.0	12.3	13.4
	% Relative area	7.4	27.7	33.0	18.5	4.5	3.3	3.5
4.5	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	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	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	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	Band position (cm^{-1})	3599	3618	3533	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
720	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

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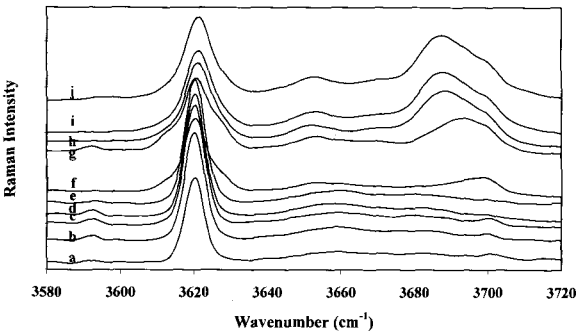


Figure 4. Raman spectra of the hydroxyl-stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) 0.0 min, (b) 30 min, (c) 60 min, (d) 105 min, (e) 150 min, (f) 220 min, (g) 300 min, (h) 480 min, (i) 10 hr, and (j) 24 h.

surface hydroxyl groups for kaolinites intercalated with formamide, dimethyl formamide, and N-methylacetamide. Upon exposure to air, the occurrence of the ν_1, ν_2, and ν_3 bands show a spectral shift towards their original (lower) frequencies upon decomposition. The frequency shift in the partially decomposed complex is due to the formation of an intermediate structure where the inner-surface hydroxyls can temporarily move freely, *i.e.,* without hydrogen bonding to the siloxane layer. This agrees with the XRD 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.

With the intensity decrease of the 3626-cm^{-1} band, however, another band occurs at 3599 cm^{-1}, which is attributed to intercalated H_2O. Thermal analysis (not shown) implies that H_2O is present in the intercalate. The simultaneous loss of water and hydrazine occurs at 140°C. DRIFT spectroscopy of the kaolinite heated to 200°C for 1 h showed that the band at 3599 cm^{-1} does not occur. Upon heating the deintercalated kaolinite, the DRIFT spectrum resembles that of untreated kaolinite. Flat, broad bands centered around 3550 cm^{-1} owing to loosely bonded water in the decomposing intercalate are observed. Thus, hydrazine is replaced by H_2O upon deintercalation. For kaolinite intercalated with potassium acetate, the H-bonded surface OH groups produce a peak at 3605 cm^{-1} (Frost *et al.,* 1997). Because 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, this indicates a weaker hydrogen-bonding interaction. Therefore, we propose that the intercalating hydrazine (in fact, hydrazine hydrate) is hydrogen bonded to the inner-surface hydroxyls via H_2O molecules.

At zero time, peaks are observed at 3626 and 3620 cm^{-1} with 70.0 and 28.3% of the total band intensity. Such intensities are near the theoretical, *i.e.,* 75.0% for the inner-surface hydroxyls and 25.0% for the inner hydroxyl. At 3 h, the intercalate decomposes and the kaolinite interlayer-hydrogen bonding is reforming, as indicated by the appearance of a band at 3695 cm^{-1}, the loss in intensity of the 3626-cm^{-1} band, and the appearance of another band at 3599 cm^{-1}. Bands are observed at 3699 and 3653 cm^{-1} with 3.5 and 18.5% intensity. The 3626-cm^{-1} band intensity decreases to 33.0% and the 3620-cm^{-1} band remains nearly constant at 27.7%. After 4.5 h, the 3626-cm^{-1} band decreases in intensity to 13.5% with significant intensity in bands at 3696, 3685, 3673, and 3654 cm^{-1}. Most changes in the DRIFT spectra have taken place by this time. After 22 h and 30 d, the observed changes are smaller. As the 3626-cm^{-1} band decreases in intensity, the 3599-cm^{-1} band and the bands relating to the inner-surface hydroxyls increase. Thus, the 3599-cm^{-1} band is due to H_2O bonding to the 1:1 layer surface. Deintercalation of kaolinite as a mechanism for hydrating the 1:1 layer surfaces is possible (Costanzo *et al.,* 1984; Costanzo and Giese, 1986, 1990). The incorporation of H_2O between the 1:1 layers as intercalated H_2O is consistent with the IR band observed at 3599 cm^{-1} and the XRD results where a broad, low intensity 001 peak occurs.

Raman spectroscopy. The Raman spectra of the hydroxyl-stretching region of hydrazine-intercalated kaolinite are shown in Figure 4 and the results of the band component analyses in Table 2. The Raman spectrum of the hydrazine-intercalated kaolinite consists of one band at 3620 cm^{-1} with a bandwidth of 5.7 cm^{-1} attributed to the inner-hydroxyl group. No band corresponding to the DRIFT band at 3626 cm^{-1} is observed in the Raman spectrum indicating a Raman inactive and IR active band. Such a band occurs when there is a large change in dipole moment and no change in the polarizability of the OH bond. Such bands often occur where H_2O is involved. These observations help determine the assignment of the 3626 cm^{-1} band, because the band is attributed to the hydrogen bonding of the hydrazine-water unit and the inner-surface hydroxyls.

The band-component analysis of the spectra at 30, 60, and 105 min show similar results, with low-intensity broad bands in the 3630–3690-cm^{-1} region. The spectrum after 150 min shows significant intensity in the 3658 and 3682-cm^{-1} bands with relative intensities of 9.6 and 13.1% (Table 2). At 200 min, bands at 3613 and 3627 cm^{-1} occur. The 3627-cm^{-1} band corresponds to the DRIFT 3626-cm^{-1} band. The band is not observed in early stages of deintercalation. However, as deintercalation progresses, reorientation in the hydrazine-water hydrogen-bonding unit occurs, thereby increasing the symmetry enabling the Raman spectrum. The assignment for the 3613-cm^{-1} band is uncertain, but the deintercalation of the hydrazine-intercalated kaolinite may possibly cause folding of the ka-

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Table 2. Band-component analyses of the Raman spectra of the hydroxyl-stretching region of the low-defect kaolinite intercalated with hydrazine and exposed to air for various periods.

Deintercalation time (min)	Band characteristics	ν_7	ν_5	ν_6	ν_3	ν_2	ν_4	ν_1
0	Band position (cm^{-1})		3620					
	Bandwidth (cm^{-1})		5.7					
	% Relative area		100					
30	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	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	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	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	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	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	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	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	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
480	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	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	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
1440	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

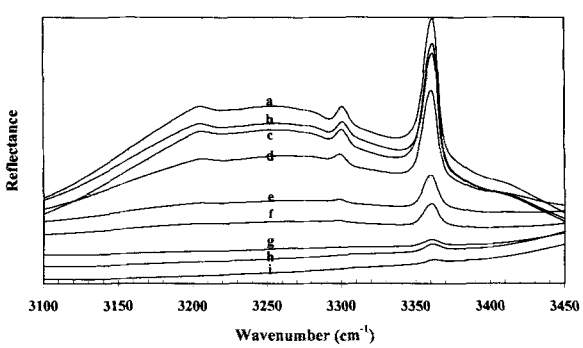


Figure 5. DRIFT spectra of the amine-stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) 0.0 h, (b) 0.5 h, (c) 3 h, (d) 4.5 h, (e) 22 h, (f) 50 h, (g) 120 h, (h) 168 h, and (i) 30 d.

olinite layers. Thus, the 3613-cm^{-1} band may be the inner-hydroxyl groups of the folded units. Costanzo and Giese (1990) described this band relating to interlayer water.

Amine-stretching region

DRIFT spectroscopy. The DRIFT spectra of the NH region of the hydrazine and water OH-stretching regions are shown in Figure 5. The band observed at 3301 cm^{-1} is attributed to symmetric stretching, and the bands at 3356 and 3362 cm^{-1} to the antisymmetric stretching of the NH vibrations. (During *et al.*, 1966). The symmetric-stretching band is weak in intensity with 8% relative intensity and a bandwidth of 8.0 cm^{-1}. The bandwidths of the 3362 and the 3356-cm^{-1} bands are 8.4 and 9.1 cm^{-1}, respectively. The band-

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Table 3. Band-component analyses of the Raman spectra of the amine-stretching region of the low-defect kaolinite intercalated with hydrazine and exposed to air for various periods.

	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	3620	3285			3346	
	Bandwidth (cm^{-1})	56.1	50.6	40.1			32.2	
	% Relative area	27.9	9.5	46.5			16.1	
Deintercalation time (min)								
0	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	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
60	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	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	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	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	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	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	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	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	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	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	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	Band position (cm^{-1})				3302	3312		3363
	Bandwidth (cm^{-1})				13.6	12.0		15.2
	% Relative area				44.0	22.8		33.2

width of the 3301 cm^{-1} band is 8.0 cm^{-1}. Bands are observed in the Raman spectra of the amine-stretching region at 3346 cm^{-1} for pure hydrazine and at 3363 and 3338 cm^{-1} in the hydrazine-intercalated kaolinite (Table 3). The 3362 cm^{-1} band is both IR and Raman active. However, the 3356-cm^{-1} band is IR active only. Thus, this band is attributed to the antisymmetric-stretching frequency of the amine NH vibration of the $[NH_3]^+$ unit. Two bands observed at slightly different frequencies in the antisymmetric-stretching region suggest that there are two types of interaction between the hydrazine and the 1:1 layer surfaces. One interaction may occur between both the lone pairs of electrons of the hydrazine nitrogen coordinated to water. This complex ion then interacts with the inner-surface hydroxyls.

Hydrazine functions as a weak monoacid base forming a monohydrate. We therefore propose a model based on the formation of $[NH_2\text{-}NH_3]^+$ $[OH]^-$ units. The interaction of the hydrazine complex occurs between the negative charge on the OH group and the inner-surface hydroxyls. This suggests that the band occurs at 3626 cm^{-1} because the interaction of the $[NH_2\text{-}NH_3]^+$ $[OH]^-$ unit and the inner-surface hydrox-

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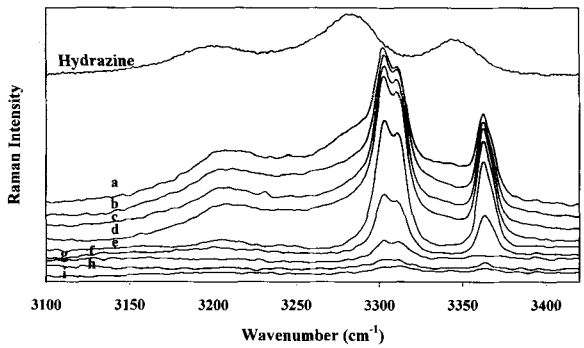


Figure 6. Raman spectra of the amine-stretching region of kaolinite intercalated with hydrazine and exposed to air for (a) 0 min, (b) 30 min, (c) 60 min, (d) 105 min, (e) 150 min, (f) 220 min, (g) 300 min, (h) 480 min, and (i) 600 min.

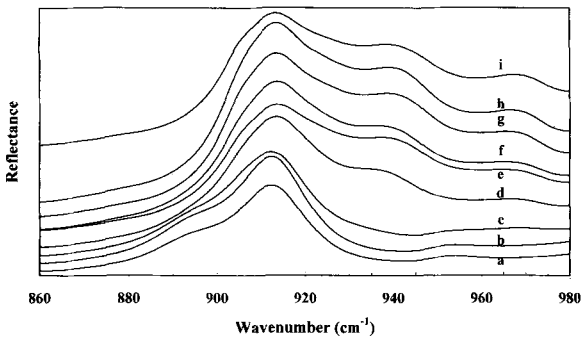


Figure 7. DRIFT spectra of the hydroxyl-deformation region of kaolinite intercalated with hydrazine and exposed to air for (a) 0.0 h, (b) 0.5 h, (c) 3 h, (d) 4.5 h, (e) 22 h, (f) 50 h, (g) 120 h, (h) 168 h, and (i) 30 d.

yls of the kaolinite is weak. A second interaction can occur between the hydrogen atoms of the hydrazine and the siloxane layer. Whereas the hydrated part of the hydrazine molecule bonds to the inner-surface hydroxyls, the opposing end of the molecule bonds to the siloxane surface between the amine hydrogen atoms and the oxygen atoms of the siloxane surface. 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}, relating to strongly bonded or coordinated H_2O. Thus the 3206-cm^{-1} band is attributed to the OH bonds of the H_2O, which are hydrogen bonded to the hydrazine in the intercalated complex.

Raman spectroscopy. The Raman spectra of the amine-stretching region of kaolinite intercalated with hydrazine is shown in Figure 6 and the analyses in Table 3. The band component analysis reveals four broad bands at 3346, 3285, 3260, and 3199 cm^{-1} with 16.1, 46.5, 9.5, and 27.9% relative intensity. Upon intercalation of the kaolinite with hydrazine, bands are observed at 3363, 3342, 3312, 3304, 3283, 3263, and 3206 cm^{-1}. At time zero and at 30 min, NH-stretching bands are observed at ~3363, 3342, and 3304 cm^{-1}. At 60 min, an additional band at 3312 cm^{-1} is only observed after deintercalation. The three bands at 3340, 3286, and 3209 cm^{-1} are assigned to the normal vibrations of adsorbed hydrazine. The band at 3363 cm^{-1} is assigned to the antisymmetric-stretching vibration. Note that only one band is observed in the Raman spectrum whereas two bands were observed in the DRIFT spectra. Thus, the 3356-cm^{-1} band in the DRIFT spectrum is IR active, but Raman inactive. Such a band results from large changes in dipole moment with no or minor changes in polarizability. The band at 3363 cm^{-1} is common to both the DRIFT and Raman spectra. Bands at 3312 and 3302 cm^{-1} are observed in the Raman spectrum of the symmetric-stretching region of the amine, whereas in the DRIFT spectra only one band is observed. The 3302-cm^{-1} band is common to both the DRIFT and Raman spectra, whereas the 3312-cm^{-1} band is only Raman active. The hydrazine bands of the intercalated kaolinite are at higher frequencies than for the hydrazine liquid. A broad band centered on 3200 cm^{-1} is attributed to H_2O associated with the hydrazine, although H_2O is difficult to determine in the Raman spectra. The spectra clearly show a decrease in intensity of both H_2O and hydrazine bands as deintercalation progresses. After 220 min (Figure 6, spectrum f), little intensity remains in the 3200-cm^{-1} H_2O band, although some intensity remains in the symmetric-stretching NH region of the hydrazine. These results are consistent with the DRIFT results of this region.

Spectroscopic evidence supports the concept of the hydrazine having two different NH_2 groups in the intercalated kaolinite. In the IR spectra, two antisymmetric vibrations are observed at 3362 and 3356 cm^{-1} with only one IR 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, whereas 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 [$-NH_2$] hydrogen bonded to the siloxane sheet. 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 sheet, then the other half of the molecule is asymmetric to the gibbsite-like sheet.

Hydroxyl-deformation region

Hydroxyl deformation data are given in Figure 7 and in Table 4. The hydroxyl-deformation region

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Table 4. Band-component analyses of the DRIFT spectra of the hydroxyl-deformation region of the low-defect kaolinite intercalated with hydrazine and exposed to air for various periods.

Deintercalation time (h)	Band characteristics	ν_{lib6}	ν_{lib5}	ν_{lib4}	ν_{lib3}	ν_{lib2}	ν_{lib1}
0.0	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
0.5	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
3.0	Band position (cm^{-1})	895	904	913	930		956
	Bandwidth (cm^{-})	20.1	9.7	17.8	12.6		9.1
	% Relative area	27.2	2.9	65.6	3.9		0.4
4.5	Band position (cm^{-1})	896	905	913	923	937	956
	Bandwidth (cm^{-})	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	Band position (cm^{-1})	896	905	913	923	938	962
	Bandwidth (cm^{-})	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	Band position (cm^{-1})		905	913	923	939	962
	Bandwidth (cm^{-})		13.0	17.5	14.9	19.5	8.4
	% Relative area		13.9	44.5	12.8	27.9	0.9
120	Band position (cm^{-1})		905	913	925	939	962
	Bandwidth (cm^{-})		10.9	16.9	14.2	19.4	8.4
	% Relative area		12.0	45.5	13.1	28.5	0.9
168	Band position (cm^{-1})		905	913	924	940	966
	Bandwidth (cm^{-})		10.9	16.6	15.6	23.5	14.3
	% Relative area		12.9	34.2	12.4	34.5	6.0
720	Band position (cm^{-1})		905	913	924	940	967
	Bandwidth (cm^{-})		10.4	16.6	14.9	25.2	13.5
	% Relative area		12.0	34.6	10.4	37.4	5.5

shows broad bands around 940 and 970 cm^{-1}, which are attributed to the inner-surface hydroxyl deformation modes, in addition to the inner-hydroxyl deformation band at 913 cm^{-1} (Frost, 1998). 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 in the 895-cm^{-1} band is attributed to the hydroxyl deformations of weakly hydrogen bonded inner-surface hydroxyls. Additional minor intensity occurs in the 925 and 953-cm^{-1} bands. Hydroxyl-deformation vibrations show little change at 0.5 h, but at 3 h, however, a significant decrease in intensity of the 895-cm^{-1} band occurs (27.2%). A weak band also occurs at 904 cm^{-1}. At 4.5 h, the intensity of the 895-cm^{-1} band is 11.6% and the 905-cm^{-1} band is 6.7%. Significant intensity is found in other hydroxyl-deformation modes at 923 and 937 cm^{-1} with 12.9 and 22.6% intensity. In the spectra at 22, 50, 168 h, and 30 d, the intensity of the 923-cm^{-1} band remains constant within experimental error, whereas the band at ~937 cm^{-1} increases in intensity. The spectrum of the deintercalated kaolinite after 30 d resembles closely that of the untreated kaolinite.

The hydroxyl-stretching region of the fully intercalated kaolinite at zero time showed bands at 3620 and 3626 cm^{-1}. The hydroxyl-deformation region also shows bands at 913 and 895 cm^{-1}. Upon deintercalation of the hydrazine-intercalated kaolinite to 3 h, the intensity of the bands at 913 and 895 cm^{-1} remains essentially constant. At 4.5 h, the inner-surface hydroxyl bands at 3653 and 3696 cm^{-1} show significant intensity. At this stage, the deformation bands at 923 and 937 cm^{-1} show increased intensity. At 50 h, hardly any to no intensity remains in either the 895 or the 3626 cm^{-1} band. Thus, the 895-cm^{-1} band is the hydroxyl-deformation band corresponding to the 3626-cm^{-1} hydroxyl-stretching band. After 50 h the band at 905 cm^{-1} has 13.9% intensity. Note that there is no intensity in the 962-cm^{-1} band after 50 h. As further deintercalation occurs, the results after 120 h are similar to the 50-h spectrum, but at 168 h significant intensity occurs in the 966-cm^{-1} band. This result corresponds to the XRD patterns where there is no 13.9-Å peak remaining, and the 7.2-Å peak occurs. The 966-cm^{-1} peak is related to the hydroxyl deformation of the inner-surface hydroxyls, which are strongly hydrogen bonded to the hydrazine-water complex. This hydroxyl-deformation band also corresponds with the increased intensity of the 3599-cm^{-1} band. Thus the formation of the hydrated kaolinite through deintercalation seems to indicate that the 966-cm^{-1} band is associated with the interaction of the intercalated water and the Al-OH surface (Tunney and Detellier, 1994).

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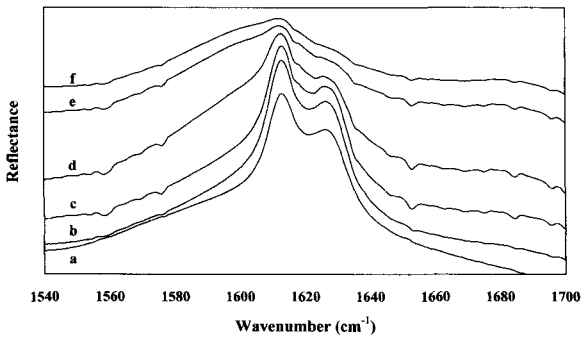


Figure 8. DRIFT spectra of the water-bending region of kaolinite intercalated with hydrazine and exposed to air for (a) 0.0 h, (b) 0.5 h, (c) 3 h, (d) 4.5 h, (e) 22 h, and (f) 50 h.

The observations made in the analysis of the hydroxyl-stretching region are consistent with the results of the hydroxyl-deformation region. With deintercalation, bands associated with weakly hydrogen-bonded inner-surface hydroxyl groups decrease in intensity and bands relating to the inner-surface hydroxyl groups hydrogen bonded to the adjacent siloxane sheet increase in intensity. The spectrum of the hydroxyl deformation region after 7 and 30 d closely resembles that of the untreated kaolinite. The only difference is the band observed at 966 cm^{-1}. The band at 895 cm^{-1} is due to the NH wag and the disappearance of this band at higher temperatures or longer periods shows the loss of hydrazine from the intercalate.

Water-bending region

The frequencies of H_2O-vibrational modes are sensitive to the interaction of H_2O in intercalated kaolinite. Figure 8 shows the DRIFT spectra of H_2O-bending modes and Table 5 provides the analyses. The spectra show three distinct water bands with HOH-bending modes at 1613 and 1627 cm^{-1} and a broad band at 1597 cm^{-1}. This latter band is attributed to 'free' or non-hydrogen bonded H_2O and is similar to water vapor. The 1613-cm^{-1} band is attributed to H_2O-bending modes of the hydrogen of H_2O bonded to the hydrazine. The band at 1627 cm^{-1} corresponds to adsorbed H_2O molecules. After 120 h, the bands at 1613 and 1627 cm^{-1} broaden and the band profile shows no distinct features, which coincides with the loss of hydrazine from the intercalate.

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Table 5. Band-component analyses of the DRIFT spectra of the H_2O-bending region of the low-defect kaolinite intercalated with hydrazine and exposed to air for various periods.

Deintercalation time (h)	Band characteristics	ν_{H_2O} bend-1	ν_{H_2O} bend-3	ν_{H_2O} bend-2	ν_{H_2O} bend-1
0.0	Band position (cm^{-1})	1597	1613	1927	1658
	Bandwidth (cm^{-})	64.0	11.5	16.1	46.0
	% Relative area	47.7	18.3	21.4	11.1
0.5	Band position (cm^{-1})	1601	1613	1627	1660
	Bandwidth (cm^{-})	53.8	16.0	16.0	5.1
	% Relative area	42.0	19.0	27.3	9.7
3.0	Band position (cm^{-1})	1600	1613	1627	1665
	Bandwidth (cm^{-})	46.0	10.6	16.8	53.8
	% Relative area	40.2	18.2	30.9	10.7
4.5	Band position (cm^{-1})	1599	1612	1627	1669
	Bandwidth (cm^{-})	42.9	11.6	20.9	46.5
	% Relative area	45.2	15.1	28.4	11.3
22	Band position (cm^{-1})	1597	1612	1625	1677
	Bandwidth (cm^{-})	40.7	11.5	39.0	39.6
	% Relative area	44.0	6.6	35.4	14.0
50	Band position (cm^{-1})	1594	1612	1618	1677
	Bandwidth (cm^{-})	34.5	16.2	47.0	33.9
	% Relative area	28.8	11.0	49.2	11.0
120	Band position (cm^{-1})	1588	1606	1616	1677
	Bandwidth (cm^{-})	30.4	32.0	27.1	32.4
	% Relative area	19.9	42.0	25.0	13.1

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E-mail of corresponding author: r.frost@qut.edu.au

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