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# A DRIFT spectroscopic study of potassium acetate intercalated mechanochemically activated kaolinite

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## Abstract

Kaolinite has been mechanochemically activated by dry grinding for periods of time up to ten hours. The kaolinite was then intercalated with potassium acetate and the changes in the structure followed by DRIFT spectroscopy. Intercalation of the kaolinite with potassium acetate is difficult and only the layers, which remain hydrogen bonded, are intercalated. The mechanochemical activation of the kaolinite may be followed by the loss of intensity of the hydroxyl-stretching vibrations. The intensity of the 3695 and 3619  $\text{cm}^{-1}$  bands reach a minimum after 10 hours of grinding. The observation of a band at 3602  $\text{cm}^{-1}$  is indicative of the intercalation of the kaolinite with potassium acetate. The degree of intercalation decreases with mechanochemical treatment. The effect of exposure of the intercalated mechanochemically activated kaolinite to moist air results in de-intercalation. The effect of the mechanochemical treatment is loss of layer stacking which prevents the intercalation of the kaolinite.

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*Keywords:* Kaolinite, intercalation, mechanochemical activation, XRD, Raman microscopy, DRIFT spectroscopy

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## **1. Introduction**

Studies of the grinding of kaolinite have been undertaken over a considerable period of time [1-7]. The milled kaolinite shows an increased surface area and some degree of amorphicity occurs [8-10]. The mechanochemical activation through dry grinding caused destruction in the crystal structure of kaolinite by the rupture of the O-H, Al-OH, Al-O-Si, and Si-O bonds. Studies of the surface properties of kaolinite show that significant changes occur in the hydroxyl-stretching region of the kaolinite [11, 12]. The destruction of the hydroxyl layer results in the formation of water, which hydrates the surface of the kaolinite. Two types of hydration were observed namely simple adsorption and secondly hydration of the surface through chemical reaction [11, 12]. Intercalation of kaolinite with potassium acetate has proven most useful in the study of the kaolinite surfaces [13-17]. Water plays an important role in this intercalation and effects the degree of expansion of the kaolinite [13, 18, 19]. The application of DRIFT spectroscopy to the study of the kaolinite surfaces enables most useful information to be obtained. Here we report a study of the changes in structure of kaolinite, which has been mechanochemically treated, followed by intercalation with potassium acetate.

## **2. Experimental**

### *2.1 Materials*

The kaolin used in the experiments was the high-grade natural kaolin from Sedlec (Zettlitz) in Slovakia. Its chemical composition in wt. % is MgO, 0.26; CaO, 0.54; SiO<sub>2</sub>, 46.97; Fe<sub>2</sub>O<sub>3</sub>, 0.37; K<sub>2</sub>O, 1.21; Al<sub>2</sub>O<sub>3</sub>, 36.32; TiO<sub>2</sub>, 0.05; loss on ignition, 13.38. The major mineral constituent is low-defect kaolinite (92 wt. %) with a Hinckley index of around 0.7. Some minor amounts of quartz (4 wt. %) and illite (4 wt. %) are also present. This kaolin was selected for this experiment because of its low quartz content. The specific surface area is 18.5 m<sup>2</sup>/g. The arithmetic mean

diameter determined by a Fritsch Laser-Particle-Sizer “analysette 22” is 4.4  $\mu\text{m}$ . The kaolin contains 10.1 % of particles less than 1  $\mu\text{m}$  and 9.3 % of particles greater than 10  $\mu\text{m}$  in size.

## 2.2 Milling procedure

A Fritsch pulverisette 5/2-type laboratory planetary mill was used to grind the mixtures of kaolinite and quartz. Samples were ground for 0, 1, 2, 3, 4, 6 and 10 hours. Each milling was carried out with a 10 g air-dried sample in an 80  $\text{cm}^3$  capacity stainless steel (18 % Cr +8 % Ni) pot using 8 (31.6 g) stainless steel balls (10 mm diameter). The applied rotation speed was 374 r.p.m.

## 2.3 X-ray powder diffraction

The normal room temperature and temperature controlled XRD analyses were carried out on a Philips wide angle PW 3020 vertical goniometer equipped with curved graphite-diffracted beam monochromators. The radiation applied was  $\text{CuK}\alpha$  from a long fine focus Cu tube, operating at 40 kV and 40 mA. The samples were measured in static air in stepscan mode with steps of  $0.02^\circ 2\theta$  and a counting time of 1s.

## 2.4 DRIFT spectroscopy

Diffuse Reflectance Fourier Transform Infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad FTS 60A spectrometer. 512 scans were obtained at a resolution of  $2 \text{ cm}^{-1}$  with a mirror velocity of 0.3 cm/sec. Spectra were co-added to improve the signal to noise ratio. Approximately 3 weight % ground kaolinite was dispersed in 100 mg oven dried spectroscopic grade KBr with a refractive index of 1.559 and a particle size of 5-20  $\mu\text{m}$ . Reflected radiation was collected at ~50% efficiency. Background KBr spectra were obtained and spectra ratioed to the background. The diffuse reflectance accessory used was designed exclusively for Bio-Rad FTS spectrometers. It is of the so-called “praying monk” design, and is mounted on a kinematic baseplate. It includes two four-position sample

slides and eight sample cups. The cup (3 mm deep, 6 mm in diameter) accommodates powdery samples mixed with KBr using an agate mortar and pestle in 1-3 % concentration. The reflectance spectra expressed as Kubelka-Munk unit versus wavenumber curves are very similar to absorbance spectra and can be evaluated accordingly.

Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectralcalc software package GRAMS<sup>®</sup> (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.

### *2.5 Intercalation and the types of experiments*

Three hundred milligrams of the mechanochemically treated kaolinite were treated with 30 cm<sup>3</sup> of 7.2 M potassium acetate solution. The sample was shaken for 80 hours in a constant temperature bath at ambient temperature. The excess solution on the clay was removed by centrifugation. The potassium acetate-intercalated kaolinite was allowed to dry in air and stored in a desiccator above anhydrous calcium chloride before spectroscopic analysis.

A number of experiments were undertaken:

- (a) Intercalation of the starting material, dried over silica gel, and exposed to room air for 1 hour
- (b) The kaolinite mechanochemically activated for 1, 2, 6 and 10 hours, intercalated with potassium acetate, dried over silica gel, and the DRIFT spectra measured.

- (c) The kaolinite mechanochemically activated for 1, 2, 6 and 10 hours, intercalated with potassium acetate, dried over silica gel, and exposed to room air for 1 hour
- (d) The kaolinite mechanochemically activated for 1, 2, 6 and 10 hours, intercalated with potassium acetate, dried over silica gel, and exposed to room air for 24 hours

### 3. Results and discussion

#### 3.1 X-ray diffraction

The X-ray diffraction patterns of mechanochemically activated kaolinite are shown in **Figure 1**. The effect of dry grinding causes the loss of the d(001) spacing and after 10 hours of grinding almost no intensity remains in this peak. The significance of the loss of intensity of the d(001) peak means the stacking between the kaolinite layers is disrupted and lost. The mechanochemical treatment has broken the hydrogen bonding between adjacent kaolinite layers. The kaolinite has been completely delaminated through the mechanical grinding process. The implication is that intercalation which depends upon regular layer stacking will not be achievable. This means that the long-range ordering in the layers is disturbed so that there is no regular pattern of atoms, which can cause the diffraction. The XRD pattern only shows a broad peak centred on around 25 degrees two theta. The significance of this pattern rests with the production of a poorly diffracting material through grinding. **Figure 1** also shows the loss of intensity in the second and third order diffractions between 20 to 25 degrees two theta and between 35 to 40 degrees two theta.

The modified kaolinite is not necessarily amorphous, rather it is poorly diffracting. The rapid structural degradation of kaolinite is connected with an increase of the mean lattice distortion and is not the consequence of the reduction of the crystallite size. The first period of mechanochemical treatment (2 hours of grinding) not only changes the morphology of the kaolinite particles but also causes a reduction in particle size. Hence other techniques are sought to study the changes in the structure of the synthesized material. SEM shows only an agglomeration of small spherical particles with no surface morphology. Because the material has little long

range ordering in its crystalline structure, Raman spectroscopy is not suitable and infrared reflectance spectroscopy (DRIFT) is the technique of choice for the study of the changes on the kaolinite surface. This technique enables the changes in surface structure to be followed upon the mechanochemical treatment brought about through dry grinding.

### 3.2 DRIFT Spectroscopy

The DRIFT spectrum of the hydroxyl stretching region of kaolinite shows five important features: Bands are observed at (a) ( $\nu_1$ )  $3695\text{ cm}^{-1}$  which is assigned to the hydroxyl stretching of the inner surface hydroxyl (b) ( $\nu_4$ )  $3684\text{ cm}^{-1}$ , attributed to the transverse optic vibration and is only observed in kaolinite crystals with a high aspect ratio (c) bands ( $\nu_2$ ) at  $3684\text{ cm}^{-1}$  attributed to the out-of-phase vibration of the inner surface hydroxyls (d) bands ( $\nu_3$ ) at  $3653\text{ cm}^{-1}$  attributed to the second out-of-phase vibration of the inner surface hydroxyls and (e) bands ( $\nu_5$ ) at  $3619\text{ cm}^{-1}$  assigned to the inner hydroxyls. The  $\nu_4$  band is not normally observed in infrared spectra but contributes significant intensity in Raman spectra. Upon modification of the kaolinite through mechanochemical treatment such as dry grinding changes to the DRIFT spectra occur [11, 12]. Also if the kaolinite is intercalated with potassium acetate, additional bands ( $\nu_6$ ) are observed at around  $3602\text{ cm}^{-1}$  which are assigned to the hydroxyl-stretching of the inner surface hydroxyls of kaolinite which have been hydrogen bonded to the acetate [14, 20, 21].

In this work we have mechanochemically treated the kaolinite for 1, 2, 6, 10 hours then intercalated the kaolinite with potassium acetate and then dried the modified kaolinite in a desiccator and then exposed the samples to moist air for 0, 1 and 24 hours. The DRIFT spectra of these three experiments are shown in **Figures 2 and 3**. The results of the band component analysis are reported in **Table 1**. The figures clearly show a number of important results:

- (a) The intensity of the hydroxyl stretching bands decreases in intensity with the length of the grinding time
- (b) The phase behaviour of the hydroxyl vibrations disappears with grinding

- (c) The intensity of the vibrations of the hydroxyl stretching of water increases with time of grinding
- (d) An additional band is observed at around  $3602\text{ cm}^{-1}$  and is assigned to the kaolinite hydroxyl hydrogen bonded to the acetate. Bands are also observed in the  $3625$  to  $3630\text{ cm}^{-1}$  region.
- (e) Such bands may arise from the distortion of the kaolinite lattice. Bands are observed in this position in the spectrum of halloysite. The type of lattice, which is found in halloysite, is the more stable structure, since the aluminium octahedron is slightly less in size than the silica tetrahedra.
- (f) It is proposed that the mechanochemical treatment has caused the curvature of the kaolinite layers similar to that which is observed for halloysite.

The decrease in the intensity of the  $\nu_1$  and  $\nu_5$  bands is illustrated in **Figure 4**. There is an apparent exponential decrease in the intensity of the hydroxyl stretching bands with grinding time. The variation in relative intensity of the  $3695$ ,  $3553$  and  $3619\text{ cm}^{-1}$  bands is shown in **Figure 5**. For the inner-surface hydroxyl the percentage relative intensity increases from 1 to 2 hours of grinding and then shows a decrease up to ten hours (**Figure 5a**). The effect of exposure to air for 1 and 24 hours appears to increase the relative intensity of the band. Exposure to air caused an increase in intensity of the band assigned to the stretching vibration of the inner surface hydroxyl. This increase may be attributed to two factors (a) moisture has caused the de-intercalation of the kaolinite resulting in the increase in intensity or (b) moisture enabled some of the hydroxyls removed through the mechanochemical treatment to be restored. It is apparent that after 10 hours of grinding and intercalation with potassium acetate, the relative % area of the three sets of data all end finish at the same point. The effect of moisture exposure on the out-of-phase vibration at  $3553\text{ cm}^{-1}$  is dramatic (**Figure 5b**). The relative intensity of the band with no exposure to air shows a steady decrease from 1 to 6 hours of grinding at which point no intensity remains in the band. Upon exposure to air for 1 hour, the initial intensity drops from 3.6 to 1.1 and then decreases by a further 50% with an additional one hour of grinding. The effect of exposure of the modified kaolinites to moist air for 24 hours is more dramatic. The initial intensity drops from 5.2 to almost zero with the additional one hour of grinding. The uptake of moisture has caused the in-phase out-of-phase



behaviour of the inner surface hydroxyls to be removed. Water molecules must apparently react with the kaolinite surface and cause loss of short range order.

The variation in the relative intensity of the band of the inner hydroxyl at  $3619\text{ cm}^{-1}$  is shown in **Figure 5c**. For the modified kaolinite not exposed to air the relative intensity shows an increase from 1 to 2 hours of grinding and then decreases to a minimum value at 10 hours. Upon exposure to air for 1 hour, the intensity is in a similar position as for the zero exposure, and then decreases exponentially with grinding time. Exposure to air for 24 hours results in a decrease in intensity with grinding time, which is below that of the other two curves. Just as for the intensity of the inner surface hydroxyl, the intensity of the inner hydroxyl stretching vibration ends up at the same point after 10 hours of grinding. The implication is that the kaolinite surface structure has been so changed that the exposure to moist air has no effect on the molecular structure.

Normally when kaolinite is intercalated with potassium acetate significant and large changes occur in the vibrational spectra [13, 19, 22, 23]. An additional band at  $3605\text{ cm}^{-1}$  is observed and is assigned to the hydroxyl stretching vibration of the inner surface hydroxyl hydrogen bonded to the acetate ion. This bonding in moist conditions takes place through a water molecule. This results in an expansion of the kaolinite layers to  $13.9\text{Å}$ . In the absence of water the expansion occurs to a lesser value. In this case the position of the hydroxyl-stretching vibration of the inner surface hydroxyl is found at higher wavenumbers around  $3611\text{ cm}^{-1}$ . This is due to a weaker hydrogen bond formed between the kaolinite inner surface hydroxyl and the acetate ion. When intercalation approaches completeness no intensity remains in the inner surface hydroxyl stretching vibrations at  $3695$ ,  $3668$  and  $3653\text{ cm}^{-1}$ . In **Figures 2 and 3** a shoulder is found on the low wavenumber side of the  $3620\text{ cm}^{-1}$  band at  $3611\text{ cm}^{-1}$  or  $3602\text{ cm}^{-1}$  and this band is that of the acetate hydrogen bonded inner surface hydroxyl. For the potassium acetate intercalated kaolinite ground for 1 hour and not exposed to air (**Table 1**) two bands are observed at  $3611$  and  $3599\text{ cm}^{-1}$ . These bands are assigned to the inner surface hydroxyls hydrogen bonded to the acetate in the two cases described above.

In this research three experiments were undertaken: namely the measurement of the DRIFT spectra after exposure to moist air for (a) 0 (b) 1 (c) 24 hours. In experiment (a) two bands are observed at 3611 and 3599  $\text{cm}^{-1}$ . With a further mechanochemical treatment of 6 and 10 hours, only the band at 3602  $\text{cm}^{-1}$  is observed. In experiment b, only a band at 3602  $\text{cm}^{-1}$  is observed. Likewise for experiment c only the band at 3602  $\text{cm}^{-1}$  is observed. In experiments b and c the intercalated kaolinite has been exposed to moist air for 1 or 24 hours. Thus the band at 3602  $\text{cm}^{-1}$  is observed which is attributed to the inner surface hydroxyl hydrogen bonded to the acetate through a water molecule [14, 24, 25]. **Figure 5d** shows the variation in intensity of the 3602  $\text{cm}^{-1}$  band with time of grinding and with length of exposure to moist air.

A number of conclusions can be made:

- (a) The amount of intercalation as measured by the % relative intensity of the 3602  $\text{cm}^{-1}$  band is low
- (b) The amount of intercalation is highest for the intercalated kaolinite that has not been exposed to air
- (c) The amount of intercalation decreases significantly with length of grinding time
- (d) The amount of intercalation decreases remarkably with exposure to moist air.

The mechanochemical treatment of kaolinite results in an increase in intensity of bands, which are attributed to water hydroxyl-stretching vibrations. Two bands are observed at around 3550 and 3380  $\text{cm}^{-1}$ . Other bands are also resolved in the fitting process. These bands are attributed to adsorbed water and to water, which is coordinating the kaolinite surface. Because the bands are broad variation in the peak position is observed in the band fitting. **Figure 6** shows the variation in the relative intensity of these bands as a function of grinding time and also the time of exposure to moist air. What is readily observed from the data is that the amount of adsorbed water is constant and independent of the time of grinding and the exposure to moist air. Some small differences are observed. The intensity of the sum of the other water bands increases with both grinding time and with exposure to moist air. The significance of this result rests with the conversion of the kaolinite hydroxyls to water and the uptake of water from the atmosphere as the grinding process generates a high

surface area material. The amount of water coordinating the surface increases with grinding time. This water up take must be between the kaolinite layers.

#### **4. Conclusion**

Mechanochemical activation of kaolinite was achieved through dry grinding. This resulted in the delamination of the kaolinite. The changes in the molecular structure of the kaolinite hydroxyls were followed by DRIFT spectroscopy. The intensity of the kaolinite hydroxyl vibrations decreased with grinding time. Intercalation of the mechanochemically activated kaolinite with potassium acetate resulted in the formation of an additional band at 3611 and 3602  $\text{cm}^{-1}$ . These bands are attributed to the inner surface hydroxyls hydrogen bonded to the acetate either without or with a water molecule. The intensity of the 3602  $\text{cm}^{-1}$  band decreased significantly with grinding time and with exposure of the kaolinite material to moist air.

The fact that the intercalation of the mechanochemically treated kaolinite was only to a small amount implies that the layer stacking order no longer exists and the only stacking that remains is that which was not destroyed by the mechanochemical treatment. The role that water plays in further removing any ordering of the kaolinite layers is most interesting 9. The exposure of the mechanochemically treated potassium acetate intercalated complex to moist air apparently removes whatever intercalated material, was present. This lack of intercalation is important as it shows that the mechanochemical activation of the kaolinite has resulted in a single layer mineral.

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**Table 1 Band component analysis of the hydroxyl stretching region of mechanochemically activated kaolinite intercalated with potassium acetate and exposed to air for 0, 1 and 24 hours.**

<b>Kaolinite</b>	<b>Band Parameters</b>	<b>v<sub>1</sub></b>	<b>v<sub>2</sub></b>	<b>v<sub>2a</sub></b>	<b>v<sub>3</sub></b>	<b>v<sub>5a</sub></b>	<b>v<sub>5</sub></b>	<b>v<sub>6</sub></b>	<b>v<sub>7</sub></b>	<b>v<sub>8</sub></b>	<b>v<sub>9</sub></b>	<b>v<sub>10</sub></b>
Ground for 1.0 hr	Band centre/cm <sup>-1</sup>	3694	3668		3653		3619	3611	3599	3521	3383	3192
And intercalated with potassium acetate	%Area	3.2	0.3		2.7		3.5	0.6	8.8	9.5	21.7	25.6
	Bandwidth/cm <sup>-1</sup>	14.2	9.4		32.4		11.7	12.1	15.8	152.0	247.9	318.4
Ground for 2.0 hrs	Band centre/cm <sup>-1</sup>	3693	3668		3650		3619		3599	3564	3384	
And intercalated with potassium acetate	%Area	7.0	2.2		3.6		3.8		1.0	10.6	35.8	
	Bandwidth/cm <sup>-1</sup>	20.7	22.9		31.5		14.1		21.8	158.0	316.3	
Ground for 6.0 hrs	Band centre/cm <sup>-1</sup>	3695	3666		3642	3625	3620	3602		3552	3342	3198
And intercalated with potassium acetate	%Area	3.3	2.0		0.1	4.9	0.5	0.6		7.0	47.6	2.2
	Bandwidth/cm <sup>-1</sup>	18.2	36.0		6.1	60.2	8.9	98.5		146.5	302.7	142.0
Ground for 10.0 hrs	Band centre/cm <sup>-1</sup>	3695	3667			3628	3620	3602		3548	3434	3240
And intercalated with potassium acetate	%Area	2.8	1.9			3.3	0.6	.1		8.2	16.5	41.8
	Bandwidth/cm <sup>-1</sup>	20.4	40.85			62.1	11.5	98.5		146.3	228.5	346.3
Ground for 1.0 hr	Band centre/cm <sup>-1</sup>	3694	3667	3664	3651	3625	3619	3602	3595	3559	3457	3240
And intercalated with potassium acetate	%Area	5.7	0.2	4.0	1.1	3.0	3.4	1.6	0.8	17.8	2.7	24.7
	Bandwidth/cm <sup>-1</sup>	21.2	8.6	28.9	17.8	31.4	10.6	20.7	15.5	154.9	95.7	312.8
exposed to air for 1 hour	Band centre/cm <sup>-1</sup>	3693	3666	3653	3652		3619	3602	3595	3524	3524	3355
And intercalated with potassium acetate	%Area	8.3	0.7	8.9	0.7		3.0	0.6	5.9	12.7	12.7	32.1
	Bandwidth/cm <sup>-1</sup>	20.4	12.5	68.2	12.7		11.2	15.8	106.8	176.2	106.8	307.7
Exposed to air for 1 hour	Band centre/cm <sup>-1</sup>	3695	3668		3652	3625	3620			3550	3377	3180
And intercalated with potassium acetate	%Area	4.7	3.3		0.1	7.6	0.9			10.0	22.6	24.3
	Bandwidth/cm <sup>-1</sup>	16.9	38.8		6.0	58.6	9.1			148.0	265.3	307.9
Exposed to air for 1 hour	Band centre/cm <sup>-1</sup>	3695	3668			3628	3620			3558	3430	3216
And intercalated with potassium acetate	%Area	2.6	1.5			3.0	0.4			9.8	20.9	40.9
	Bandwidth/cm <sup>-1</sup>	20.1	36.7			71.1	10.5			146.5	245.1	347.9
Exposed to air for 1 hour	Band centre/cm <sup>-1</sup>	3693	3666	3653	3651		3619	3602		3569	3482	3173
And intercalated with potassium acetate	%Area	4.9	0.4	0.7	8.3		2.9	0.2		10.1\	4.7	17.1
	Bandwidth/cm <sup>-1</sup>	42.1	10.3	14.2	62.8		10.9	28.0		116.5	115.0	304.5
exposed to air for 24 hour	Band centre/cm <sup>-1</sup>	3694	3667	3655	3652	3625	3619	3602		3566	3419	3206
And intercalated with potassium acetate	%Area	7.6	0.2	8.0	0.2	0.6	1.8	0.05		14.7	27.3	18.7
	Bandwidth/cm <sup>-1</sup>	20.3	9.0	52.0	9.4	14.5	9.6	28.0		169.7	263.	300.1
Exposed to air for 24 hour	Band centre/cm <sup>-1</sup>	3695	3668		3651	3626	3620	3600		3552	3402	3240
And intercalated with potassium acetate	%Area	4.2	2.3		0.1	6.8	0.9	0.01		9.7	34.9	19.8
	Bandwidth/cm <sup>-1</sup>	17.6	35.0		8.1	67.3	9.9	10.2		144.6	237.9	233.6
Exposed to air for 24 hour	Band centre/cm <sup>-1</sup>	3695	3668		3652	3625	3620	3600		3573	3486	3355
And intercalated with potassium acetate	%Area	2.9	0.7		0.1	6.2	0.4	0.01		7.4	42.9	24.4
	Bandwidth/cm <sup>-1</sup>	21.3	28.7		5.0	76.7	11.7	10.2		118.2	176.1	253.5
Exposed to air for 24 hour												

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Figure 1 X-ray diffraction patterns of kaolinite ground for (a) 0 (b) 1 (c) 2 (d) 4 (e) 6 (f) 10 hours

Figure 2 DRIFT spectra of the hydroxyl stretching region of mechanochemically activated kaolinite treated for (a) 1 (b) 2 (c) 6 (d) 10 hours and intercalated with potassium acetate. DRIFT spectra measured at the completion of the experiment.

Figure 3 DRIFT spectra of the hydroxyl stretching region of mechanochemically activated kaolinite treated for (a) 1 (b) 2 (c) 6 (d) 10 hours and intercalated with potassium acetate. DRIFT spectra measured after the samples were exposed to air for 24 hours.

Figure 4 variation in the relative intensity of the OH stretching vibrations of kaolinite as a function of grinding time.

Figure 5a Relative intensity of the  $3695\text{ cm}^{-1}$  band as a function of grinding time.

Figure 5b Relative intensity of the  $3653\text{ cm}^{-1}$  band as a function of grinding time.

Figure 5c Relative intensity of the  $3619\text{ cm}^{-1}$  band as a function of grinding time.

Figure 5d Relative intensity of the  $3602\text{ cm}^{-1}$  band as a function of grinding time.

Figure 6. Variation of the relative intensity of the hydroxyl stretching vibrations of water at around  $3550$  and  $3380\text{ cm}^{-1}$  as a function of grinding time and time of exposure to moist air.

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**Table 1** Band component analysis of the hydroxyl stretching region of mechanochemically activated kaolinite intercalated with potassium acetate and exposed to air for 0, 1 and 24 hours.