Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 408 (2003) 103–113

thermochimica acta

www.elsevier.com/locate/tca

Slow transformation of mechanically dehydroxylated kaolinite to kaolinite—an aged mechanochemically activated formamide-intercalated kaolinite study

Ray L. Frost [a,*], Erzsébet Horváth [b], Éva Makó [c], János Kristóf [d], Ákos Rédey [d]

[a] Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Qld. 4001, Australia
[b] Department of Environmental Engineering and Chemical Technology, University of Veszprem, P.O. Box 158, H8201 Veszprem, Hungary
[c] Department of Silicate and Materials Engineering, University of Veszprem, P.O. Box 158, H8201 Veszprem, Hungary
[d] Department of Analytical Chemistry, University of Veszprem, P.O. Box 158, H8201 Veszprem, Hungary

Received 10 March 2003; received in revised form 28 May 2003; accepted 29 May 2003

Abstract

Formamide-intercalated high defect kaolinite which was mechanochemically activated for periods of time up to 6 h has been aged for up to 1 year. These modified materials were studied using a combination of X-ray diffraction, thermal analysis and DRIFT spectroscopy. Ageing of the formamide-intercalated mechanochemically activated kaolinite results in de-intercalation of the formamide and the de-intercalated kaolinite returns to its original *d*-spacing. Thermal analysis shows that the temperature of dehydration and dehydroxylation increase by up to 30 °C. The temperature of the dehydroxylation of the aged samples was identical to that of the untreated kaolinite. The DRIFT spectroscopy showed that the spectrum of the aged samples approached that of the untreated kaolinite. The kaolinite showed partial de-intercalation and the 6 h sample had reformed to a mineral resembling the untreated kaolinite. The process of ageing the mechanochemically activated kaolinite enabled the reformation of the kaolinite.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Kaolinite; Mechanochemical activation; Differential thermogravimetric analysis

---

1. Introduction

The thermal reactions of kaolinite have been studied for a very long time [1–5]. Fig. 1 provides a summary of these thermal transformations. The formula of kaolinite may be written as $Al_2(OH)_4Si_2O_5$ which is the formula per unit cell. However, it must be kept in mind that kaolinite is an inorganic polymer with a sheet system that can extend in two-dimensions.

The thermal treatment of kaolinite may be considered as taking place in a series of steps. The first step up to 100 °C is a water desorption step. Such dehydration depends on the nature of the kaolinite and the degree of disorder of stacking. After dehydration, the kaolinite goes through a pre-dehydroxylation state. In the temperature range between 450 and 550 °C, the kaolinite dehydroxylates and the product phase is known as metakaolinite. The following reaction may be envisaged:

$$Al_2(OH)_4Si_2O_5 \rightarrow Al_2Si_2O_7 + 2H_2O$$

---

[*] Corresponding author. Tel.: +61-7-3864-2407; fax: +61-7-3864-1804.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00316-2

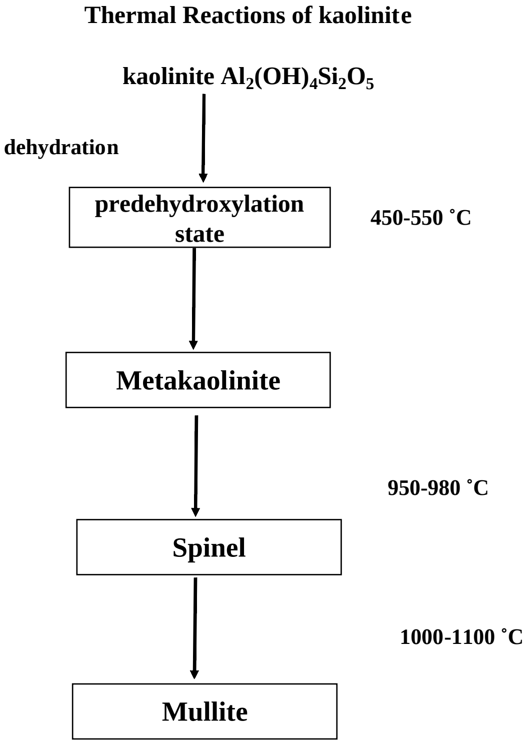

Fig. 1. Summary of the thermal reactions of kaolinite.

The kaolinite still retains its layered structure and will return to the kaolinite structure by the uptake of water as from the atmosphere [6,7]. This bi-dimensional structure is retained up to around 950 °C where a three-dimensional spinel structure is formed. Further heating transforms this phase to mullite and quartz.

There are two mechanisms for synthesising X-ray amorphous kaolinite: (a) firstly, thermal treatment and (b) secondly, through mechanochemical activation [8–10]. In spite of some similarities, a number of substantial differences are justified for thermal and mechanical dehydroxylation of kaolinite [22]. In case of the thermal treatment of kaolinite, the water molecules are lost to the surroundings. In case of the mechanochemical activation of kaolinite, the water is not lost but is retained as coordinated water bonded to the kaolinite ‘backbone’. The product of such activation is a water-containing xerogel with random structure, which develops in several stages via intermediates [11,22]. The two types of kaolinite derivatives namely metakaolinite and mechanochemically dehydroxylated kaolinite are produced by different mechanisms.

Such dehydroxylation must occur though a process of proton hopping. The concept of proton migration through percussive grinding and their combination with hydroxyl units has been known for some time [12]. The generally accepted concept for the dehydroxylation of kaolinite is based upon the interaction of two hydroxyl groups in a two step process to form a water molecule by proton transfer leaving a chemically bonded oxygen, as a superoxide anion, in the lattice. This phenomenon is known as prototropy.

The reaction process may be envisaged chemically as follows:

$$OH^- \leftrightarrow H^+ + O^{2-} \quad \text{and} \quad H^+ + OH^- \leftrightarrow H_2O$$

These reactions take place when mechanochemical activation of the kaolinite occurs. It is highly likely that point contact heating at specific sites as well as deformation and breaking of bonds result in the attainment of high energy sufficient to cause dehydroxylation. This results in the increase in dehydroxylation with grinding time. These steps require proton delocalisation at specific hydroxyl sites. Such delocalisation may occur when the mechanochemical treatment of the kaolinite causes deformation and breaking of Al–OH and O–H bonds and “heat shocks” around cracks. For water to form, these protons must migrate to a second hydroxyl site. Such proton diffusion is enabled if the energy is sufficiently high.

If two adjacent hydroxyls are involved in the two step process then this process will be homogenous; if, however, non-adjacent hydroxyls are involved, such a process would require proton diffusion (sometimes referred to as proton hopping) and probably counteractive cation diffusion with the water molecules being produced at the outer surface. Where hydroxyls of different acidities are to be found, the homogenous process is more likely. It can be argued that kaolinites dehydroxylate by this homogenous process during mechanochemical activation. Some previous studies have shown that prototropy occurs when the kaolinite is diluted with salts [13–16]. It has been suggested that this proton migration leads to lattice defects [14]. In this study, we have started with a highly disordered kaolinite and it appears that proton migration readily occurs without any diluants. There have been many studies on the transformation of kaolinite to mechanochemically dehydroxylated kaolinite [3,5,17]. However, to the best of our knowledge, there have been no studies of the reformation of kaolinite from mechanochemically activated kaolinite.

2. Experimental techniques

2.1. The kaolinite mineral

The kaolinite used in this experiment was a high-grade natural kaolinite from Hungary. The kaolinite used was selected for this experiment because of the low quartz content and high purity. The Szeg chemical composition as determined by classical methods is (wt.%): MgO, 0.71; CaO, 0.53; SiO_2, 46.89; Fe_2O_3, 3.1; K_2O, 0.35; Na_2O, 0.16; Al_2O_3, 33.51; TiO_2, 0.06; loss on ignition, 14.69. The major mineral constituent is high defect kaolinite (95 wt.%) with a Hinckley index of around 0.4. Some minor amounts of quartz (2 wt.%) and feldspar (3 wt.%) are also present.

2.2. Milling procedure

A Fritsch pulverisette 5/2-type laboratory planetary mill was used to grind the kaolin. Samples were ground for 0–4, and 6 h. Each milling was carried out with a 10 g air-dried sample in an 80 cm^3 capacity stainless steel (18% Cr + 8% Ni) pot using eight (31.6 g) stainless steel balls (10 mm diameter). The applied rotation speed was 374 rpm.

2.3. X-ray diffraction

The X-ray diffraction (XRD) analyses were carried out on a Philips PW 3710 based diffractometer equipped with a PW 3020 vertical goniometer and curved graphite-diffracted beam monochromator. The radiation applied for the non-aged and aged samples were Cu Kα from a long fine focus Cu tube (operating at 40 kV and 40 mA) and Cu Kα from a broad focus Cu tube (operating 50 kV and 40 mA), respectively. As references, the XRD patterns of Szegi kaolinite ground for 0 h was measured with both the tubes. The samples were measured in step scan mode with steps of 0.02° 2θ and a counting time of 1 s. Data collection and evaluation were performed with PC-APD 3.6 software.

2.4. Thermal analysis

Thermoanalytical investigations have been carried out under dynamic heating conditions (10 °C/min) in a Netzsch (Germany) TG 209-type thermobalance in flowing argon atmosphere of 99.995% purity (Messer Griesheim, Hungary). The samples of approximately 10 mg were heated in a ceramic crucible up to 1000 °C.

2.5. DRIFT spectroscopy

Diffuse reflectance Fourier transform infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad FTS 60A spectrometer. Five hundred and twelve scans were obtained at a resolution of 2 cm^{-1} with a mirror velocity of 0.3 cm/s. Spectra were co-added to improve the signal to noise ratio. Approximately 3 wt.% 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 μm. 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 4-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 Spectracalc software package GRAMS® (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package, which enabled the type of fitting, function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values >0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2 > 0.995$.

3. Results and discussion

The particular kaolinite used in this study differs from that previously published [11,18,19]. In previous work, low defect kaolinites from Zettlitz and Kiralyhegy were used. These kaolinites had a Hinckley index of 0.78 and 1.35, respectively, thus these kaolinites were highly ordered kaolinites with few stacking faults. In this study, we have chosen a kaolinite with a high defect structure and a low Hinckley index of 0.4. Electron microscopy shows the kaolinite to be highly disordered with many particles with a curved morphology. The kaolinite has *a*–*b*-axis disorder. The kaolinite resembles a broken-up halloysite in morphology. The reason for this work is to study the effects of structural degradation through mechanochemical treatment of a high defect kaolinite.

3.1. X-ray diffraction

The X-ray diffraction patterns of the 1-year aged formamide-intercalated kaolinites are shown in Fig. 2. Formamide-intercalated unactivated kaolinites show 90% expansion upon intercalation and almost no intensity is observed in the *d*(0 0 1) peak of the original kaolinite. The Szeg kaolinite has a *d*-spacing of 7.23 Å which with formamide expands to 10.15 Å. Upon de-intercalation one expansion is observed at 7.23 Å.

The variation in intensity as measured by the relative peak area of the *d*(0 0 1) peaks is shown in Fig. 3a. The ratio of the expanded kaolinite phase decreases with the increasing grinding time, because of the increasing deformation of hydroxyl groups. The kaolinites which have been ground for the longest period of time display the smallest intercalation capability. After ageing, the sample was ground for 6 h, the ratio of expanded kaolinite phase shows an increase. This indicates the rearranging the kaolinite structure that brings an increase in the number of hydroxyl group involved in the intercalation. (The sample contains enough absorbed formamide molecules, which can intercalate with the recovered hydroxyls of kaolinite). The ageing (in the presence of intercalated and adsorbed formamide) and mechanical activation can cause the rearranging of the kaolinite layers together with the recovery of OH groups. The recovered OH groups can intercalate with the formamide molecules. This causes an increase in intensity of the 10.15 Å peak-ratio of the aged sample ground for 6 h. In other words, the mechanochemically activated metakaolinite returns towards its original kaolinite structure.

Such a concept is confirmed by the variation in peak width with grinding time (Fig. 3b). The width of the 7.23 Å peak is the same for both the aged and non-aged samples (within experimental error). Some differences are observed in the width of the 10.15 Å peak especially for the 6 h samples. The width of the peak for the aged sample is much broader compared with the non-aged sample.

3.2. Thermal analysis

The thermal analysis of the formamide-intercalated kaolinites at zero time and after 8 months of ageing are shown in Fig. 4. The dotted line shows the formamide-intercalated kaolinite at zero time and the full line at 8 months of ageing. In each of the thermal analysis patterns, there is a shift of around 30 °C to higher temperatures with ageing. This data is reported in Table 1. The weight loss steps for the kaolinite mechanochemically activated for 0, 3 and 6 h intercalated with formamide before and after ageing are reported. The weight loss Step 1 is attributed to loss of water. In each case, the temperature of dehydration of the non-aged kaolinite is less than that of the aged kaolinite. The weight loss Step 2 is assigned to the loss of formamide. Again significant differences in

Table 1
Results of the thermogravimetric analysis of kaolinite mechanochemically activated for 0, 3 and 6 h and intercalated with formamide aged and non-aged

Step of weight loss	0 h/°C	Aged 0 h	3 h	Aged 3 h	6 h	Aged 6 h
1	95	100	85	90	85	100
2	150	178	185	198	148	148
3	235					
4	258					
5	310	305	295	300	295	305
6	505	510	482	505	470	505

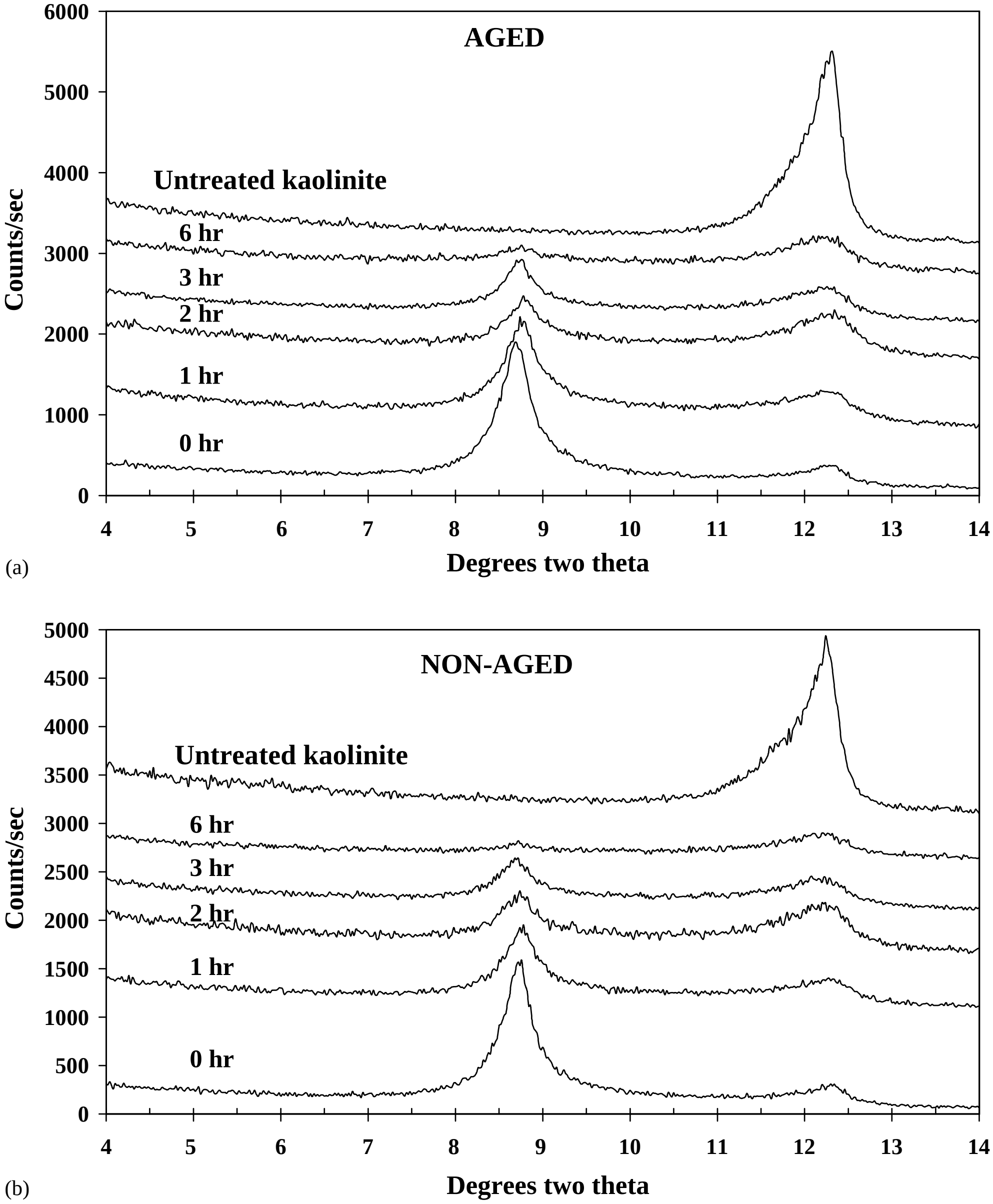

Fig. 2. X-ray diffraction of kaolinite mechanochemically activated and intercalated with formamide.

the weight loss step are observed. For example, the temperatures of the weight loss step for the non-aged and aged formamide-intercalated kaolinite (at 0 h of grinding) are 150 and 178 °C. The values at 3 h are 185 and 198 °C. The values are both 148 °C for 6 h of grinding. The value is almost the same as that for the non-aged, non-mechanochemically activated kaolinite. In other words, the 6 h treated kaolinite has returned to its original structure.

The Szeg kaolinite being a high defect kaolinite dehydroxylates at somewhat lower temperatures than a highly ordered kaolinite [20]. The dehydroxylation temperature of the kaolinite non-mechanochemically activated is 505 °C and after ageing is 510 °C.

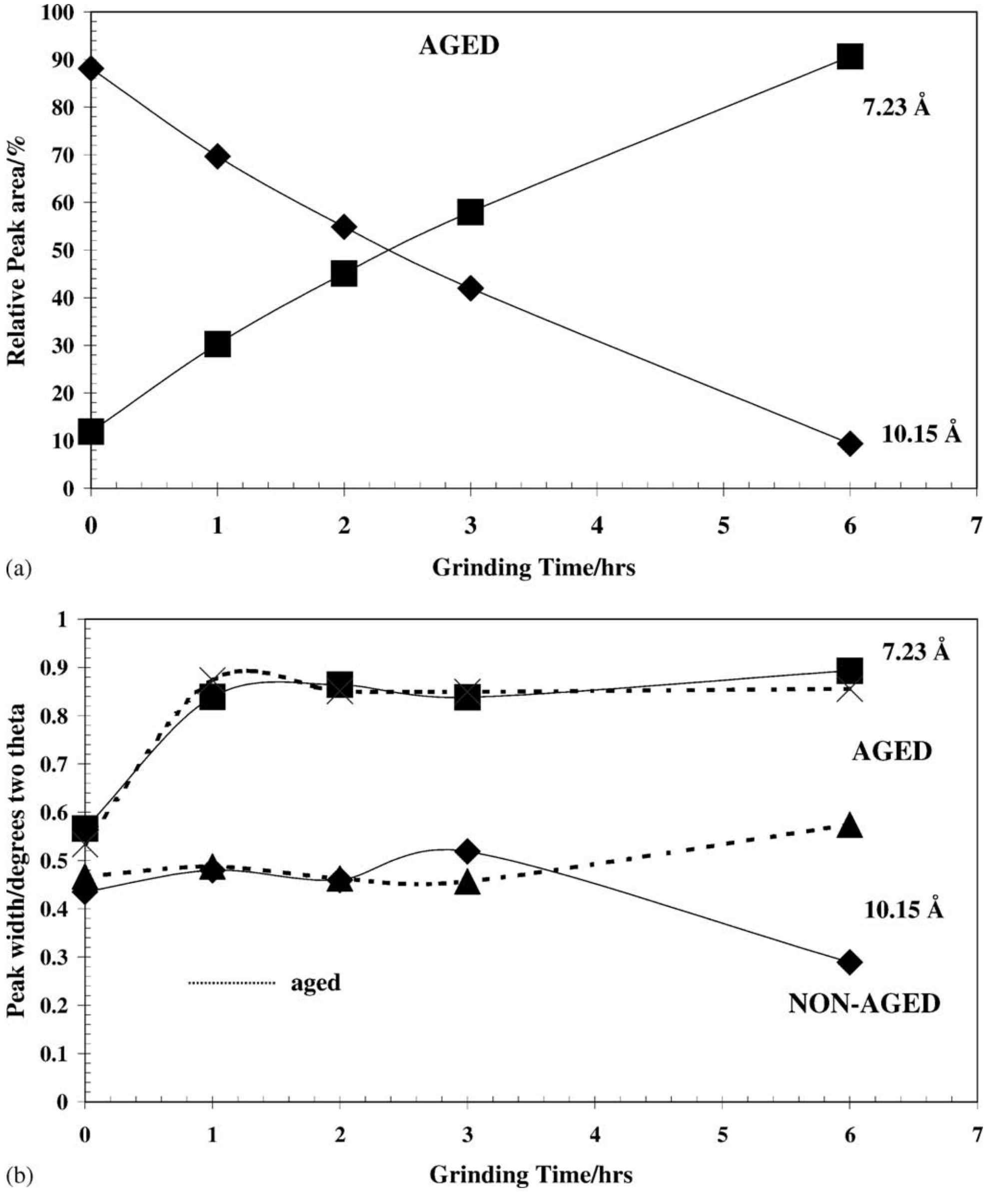

Fig. 3. Variation of the relative intensity of the *d*(0 0 1) peaks with grinding time after 1 year of ageing.

Again the temperature of the dehydroxylation of the non-aged is less than that of the aged kaolinite. The temperature of non-aged mechanochemically activated kaolinite decreases with length of time of grinding. At 0 h the value is 505 °C, after 3 h, 482 °C and after 6 h, 470 °C. Yet the values after ageing are 510, 505 and 505 °C. In other words, the dehydroxylation temperature of the aged kaolinites is the same. There is further evidence that the mechanochemically synthesised metakaolinite has returned to the original kaolinite structure.

Mechanochemical activation of kaolinite disrupts the surface structure of the kaolinite. Yet after the evolution of time the mechanochemically activated

Table 2
Percentage amount of dehydroxylation water in mechanochemically treated formamide-intercalated kaolinite (mg H_2O/100 mg dehydroxylated mineral)

Grinding time (h)	Fresh complex (%)	Aged complex (%)	Δm (%)	ΔT (°C)
0	14.990	14.689	0.305	9
1	13.892	13.654	0.238	10
3	12.069	11.143	0.926	30
6	9.579	9.107	0.472	32

kaolinite returns to its original structure. It is as though the mechanochemically activated kaolinite had some 'memory' structure.

Table 2 shows the percentage amount of dehydroxylation water in mechanochemically treated formamide-intercalated kaolinite (mg H_2O/100 mg dehydroxylated mineral). The residual mass at 900 °C was used as reference (the room-temperature samples cannot be considered as standardised ones, since they contain varying amounts of water, and adsorbed formamide). It means that the reference mass is actually metakaolinite. After half a year, the percentage amount of structural water is (within 1%) the same. (It is interesting that it is slightly higher in the original sample.) Thus, considering ΔT, ageing helps to re-order the layers after the removal of formamide even if no mechanical treatment is made (see 0 h sample). The increase of the dehydroxylation peak temperature (DTG maximum) with ageing and grinding time means that both helps the rearranging of the layers after de-intercalation.

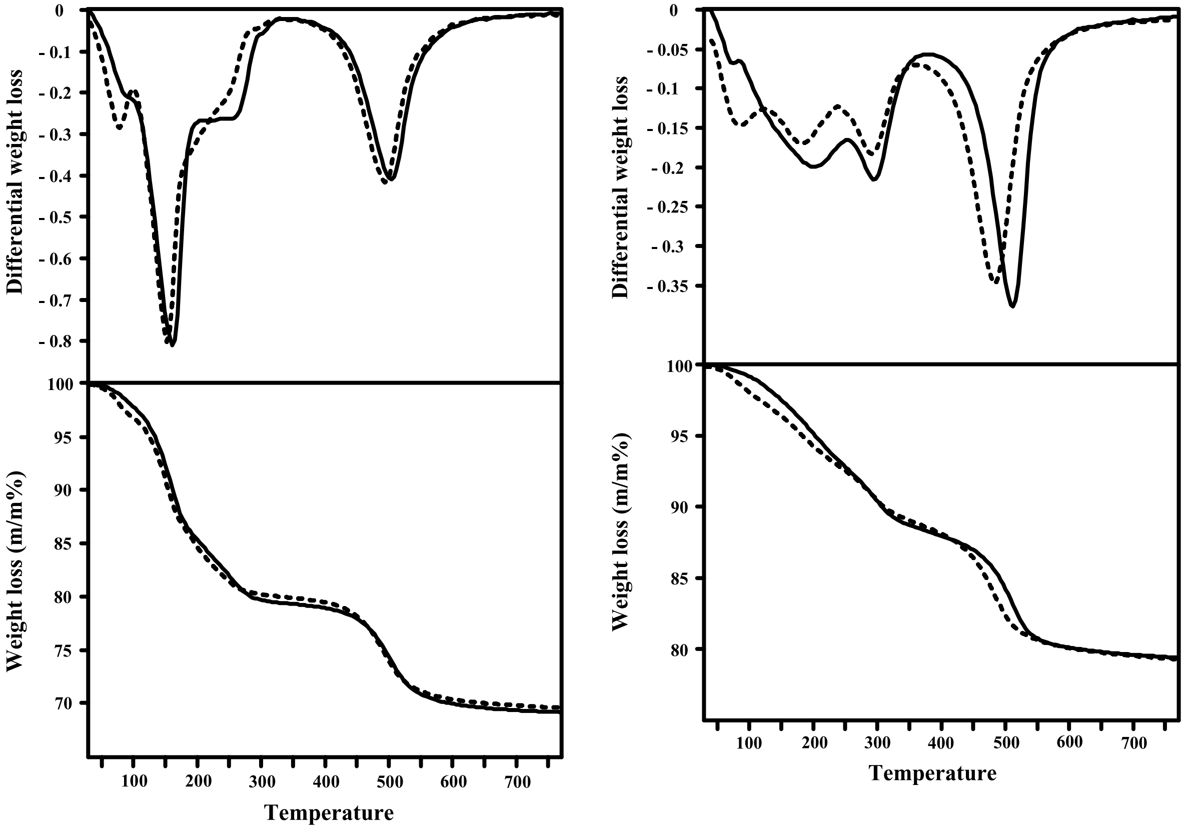

Fig. 4. TG and DTG curves for mechanochemically activated kaolinite after grinding for 0, 3 and 6 h and intercalating with formamide: (- -) non-aged and (—) aged 6 months.

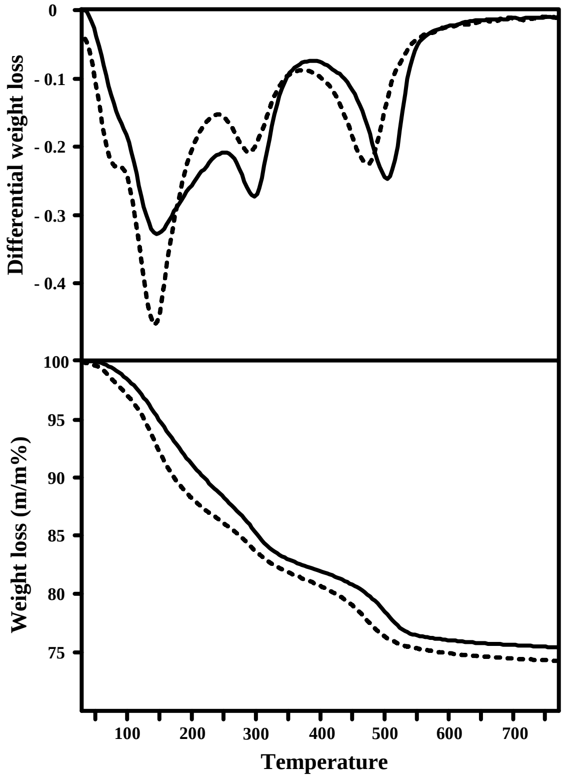

Fig. 4. (*Continued*).

3.3. DRIFT spectroscopy

Kaolinite as with the other kaolin clay minerals contains two types of hydroxyl groups: (i) the outer hydroxyl groups or so called inner surface hydroxyls; and (ii) the inner hydroxyl groups designated. The inner surface hydroxyl groups are situated in the outer upper, unshared plane, whereas the inner hydroxyl groups are located in the plane shared with the apical oxygens of the tetrahedral sheet. Kaolinite has four infrared active and five Raman active modes centred at 3695 (ν_1), 3684 (ν_4), 3670 (ν_2), 3650 (ν_3) and 3620 (ν_5) cm^{-1}. The four higher frequency vibrations (ν_1, ν_4, ν_2, ν_3) are assigned to the stretching vibration of the three inner surface hydroxyl groups and the ν_5 band at 3620 cm^{-1} is assigned to OH stretching vibration of the inner hydroxyl group. The intensity of these bands depends on the defect structure of the kaolinite and the degree of substitution into the aluminium layers. In highly ordered kaolinites, the Raman active band (ν_4) at 3684 cm^{-1} may also be observed in the infrared spectra albeit by band component analysis. Upon intercalation, changes in the intensities of the inner surface hydroxyl groups are observed as the hydrogen bonding patterns are regenerated. Such changes may be observed by vibrational spectroscopic techniques such as infrared spectroscopy.

The DRIFT spectra of the hydroxyl stretching region of the high defect kaolinite is shown in Fig. 5. The figure shows the DRIFT spectrum of the untreated kaolinite, the DRIFT spectra of the formamide-intercalated mechanochemically activated high defect kaolinite and the 1-year aged formamide-intercalated 6 h mechanochemically activated kaolinite. Upon intercalation of the kaolinite with formamide, additional bands are observed at 3606 and 3626 cm^{-1}. These bands are attributed to

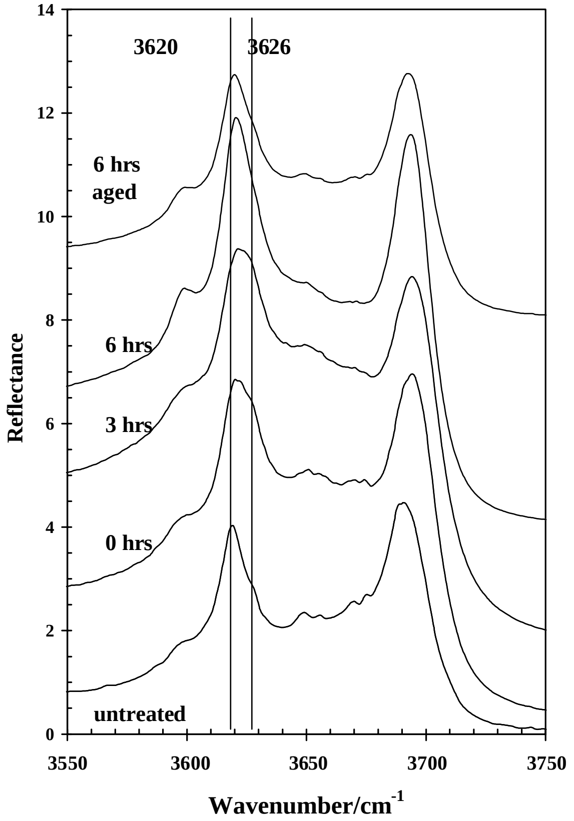

Fig. 5. The DRIFT spectra of the hydroxyl stretching region of kaolinite mechanochemically activated for 0–3 and 6 h followed by intercalation with formamide.

the intercalated water and to the inner surface hydroxyl groups hydrogen bonded to the formamide, respectively. The difference in the spectra between the intercalated and non-intercalated high defect kaolinite is the appearance of a band at 3626 cm^{-1}. The intensity of this band is diminished in the aged 6 h mechanochemically activated kaolinite. In fact, the spectrum of the aged 6 h sample strongly resembles that of the non-treated kaolinite. Importantly, the ageing of the mechanochemically activated kaolinite has enabled this metakaolinite to return to the original kaolinite structure.

The DRIFT spectrum of the high defect kaolinite and its formamide-intercalate show strong resemblance to the spectrum of the untreated kaolinite. Bands are identified for the non-intercalated high defect kaolinite at 3693, 3669, 3650, 3629, 3619 and 3600 cm^{-1} with relative intensities of 33.0, 11.2, 12.6, 9.5, 18.9 and 10.6%. Upon intercalation, hydroxyl stretching bands are observed at 3697, 3675, 3653, 3627, 3620 and 3606 cm^{-1} with relative intensities of 19.7, 14.0, 17.5, 19.9, 4.8 and 21.3%. Just as for the formamide-intercalated low defect kaolinite additional infrared bands are observed at 3626 and 3606 cm^{-1}.

The DRIFT spectrum of the high defect kaolinite before any treatment in the 1500–1800 cm^{-1} region is illustrated in Fig. 6. Mechanochemically activated

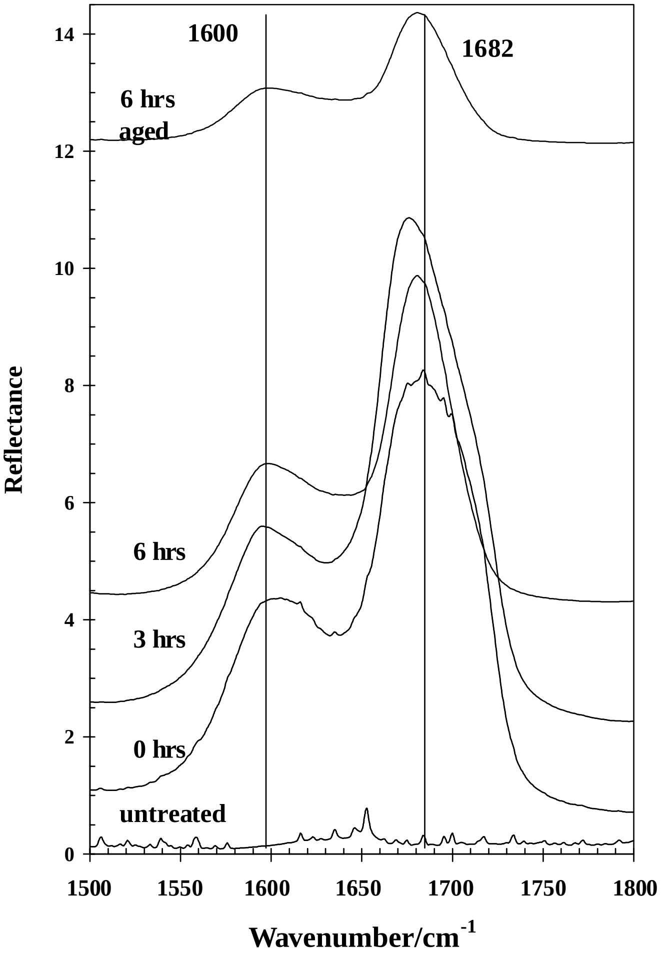

Fig. 6. The DRIFT spectra of the water bending and amide region of kaolinite mechanochemically activated for 0–3 and 6 h followed by intercalation with formamide.

kaolinite followed by intercalation with formamide results in increased intensity in bands centred around 1600 and 1682 cm^{-1}. The first band is attributed to weakly hydrogen bonded water deformation modes. This band is the bending mode of water and the hydroxyl stretching mode appears at around 3695 cm^{-1}. The second band at 1682 cm^{-1} is assigned to an amide II type vibration and is principally ascribed to the C=O stretching band. In the aged kaolinite both bands are present, suggesting some of the formamide has been retained in the structure. However, the intensity of the 1682 cm^{-1} band has been reduced by some 80%. The intensity of the water band has also been reduced. This suggests that the water and formamide are closely associated in the intercalated kaolinite structure. Such a conclusion fits well with the XRD data where some 20% of the intercalated kaolinite remains after 1 year of ageing.

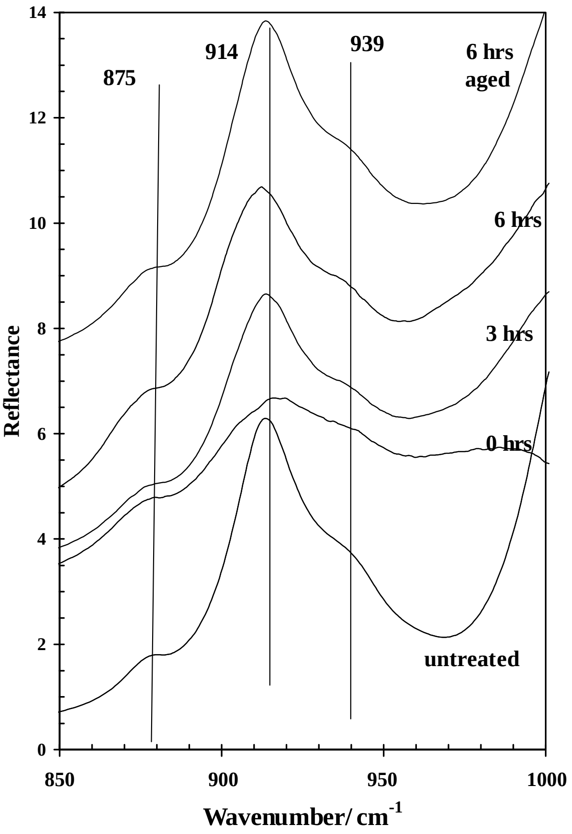

Fig. 7. The DRIFT spectra of the hydroxyl deformation region of kaolinite mechanochemically activated for 0–3 and 6 h followed by intercalation with formamide.

Another means of studying the changes in the structure of kaolinite upon intercalation is the study of the hydroxyl deformation modes (Fig. 7). These bands are centred on 915 and 939 cm^{-1}. For the Szeg high defect kaolinite, bands are observed at 876, 913, 925 and 939 cm^{-1} with relative intensities of 5.0, 73.0, 2.0 and 20.0%, respectively. Thus, as with the hydroxyl stretching frequencies, the intensity of the hydroxyl deformation vibrations of the inner surface hydroxyls has been reduced to minimal intensity. An additional band at 905 cm^{-1} with 48.2% of the total intensity is attributed to the hydroxyl deformation vibration of the inner surface hydroxyls hydrogen bonded to the C=O of the formamide. The band at 974 cm^{-1} is attributed to an out-of-plane CH wag. Upon intercalation of the high defect kaolinite with formamide, infrared bands are observed at 936, 915, 907 and 876 cm^{-1} with relative intensities of 13.7, 33.0, 41.8 and 8.8%. Significant intensity remains in the 936 cm^{-1} band indicating that the high defect kaolinite was not fully intercalated even after mechanochemical activation. What is clear (as compared with the 1500–1800 cm^{-1} region) is that the infrared spectrum of the aged kaolinite strongly resembles that of the untreated material. In other words, the kaolinite structure has re-ordered and the kaolinite has reformed from the mechanochemically activated kaolinite.

4. Conclusions

The mechanochemical treatment of kaolinite results in the dehydroxylation of the kaolinite through point heating. It is proposed that this dehydroxylation occurs through a homogenous process involving proton transfer. The amount of dehydroxylation increases with grinding time. The effect of this point heating results in a decrease in the dehydroxylation temperature with grinding time and an increase in the amount of adsorbed/coordinated water.

Ageing of the formamide-intercalated mechanochemically activated kaolinite results in de-intercalation of the formamide and the de-intercalated kaolinite returns to its original *d*-spacing. Mechanochemical activation is a means of synthesising kaolin-hydrogel. This material reformed into kaolinite after 1 year.

Acknowledgements

The Inorganic Materials Research Program, in the School of Physical and Chemical Sciences of the Queensland University of Technology is gratefully acknowledged for financial and infra-structural support for this project. The Australian Research Council is thanked for funding of the thermal analysis facility.

References

[1] D.K. Arkhipenko, E.A. Plekhanova, Izvest. Sibir. Otdel. Akad. Nauk. S.S.S.R. (1961) 109.
[2] F. Freund, Ber. Deut. Keram. Ges. 37 (1960) 209.
[3] F. Freund, Ber. Deut. Keram. Ges. 44 (1967) 392.
[4] A.M. Kalinina, Zh. Neorgan. Khim. 8 (1963) 2675.
[5] V.I. Lebedev, N.V. Kotov, Izvest. Akad. Nauk. S.S.S.R., Seriya Geologicheskaya (1967) 75.
[6] J. Rocha, J. Klinowski, J. Chem. Soc., Chem. Commun. (1991) 582.
[7] J. Rocha, J.M. Adams, J. Klinowski, J. Solid State Chem. 89 (1990) 260.
[8] F. Gonzalez Garcia, M.T. Ruiz Abrio, M. Gonzalez Rodriguez, Clay Miner. 26 (1991) 549.
[9] S.J. Gregg, K.J. Hill, T.W. Parker, J. Appl. Chem. (London) 4 (1954) 631.
[10] H. Takahashi, Clays, Clay Minerals, in: Proceedings of the Sixth National Conference on Clays, Clay Minerals, Berkeley, 1959, p. 279.
[11] J.G. Miller, T.D. Oulton, Proc. Natl. Conf. Clays Clay Miner. 18 (1970) 313.
[12] S. Yariv, S. Shoval, Proc. Natl. Conf. Clays Clay Miner. 23 (1975) 473.
[13] S. Yariv, Powder Technol. 12 (1975) 131.
[14] S. Yariv, Proc. Natl. Conf. Clays Clay Miner. 23 (1975) 80.
[15] S. Yariv, H. Cross, Geochemistry of Colloid Systems for Earth Scientists, Springer–Verlag, Berlin, 1979.
[16] F. Freund, Ber. Deut. Keram. Ges. 44 (1967) 5.
[17] R.L. Frost, J. Kristof, E. Mako, W.N. Martens, Langmuir 18 (2002) 6491.
[18] R.L. Frost, E. Mako, J. Kristof, E. Horvath, J.T. Kloprogge, Langmuir 17 (2001) 4731.
[19] J. Kristof, R.L. Frost, J.T. Kloprogge, E. Horvath, E. Mako, J. Therm. Anal. Calorimet. 69 (2002) 77.
[20] R.L. Frost, A.M. Vassallo, Clays Clay Miner. 44 (1996) 635.