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Thermal dehydroxylation in surface modified kaolinite

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Metakaolinite with increased surface area has been prepared by a thermal decomposition–hydration–redecomposition technique. An attempt has been made to characterize the new phase using solid state nuclear magnetic resonance (NMR) and Raman spectroscopy, and transmission electron microscopic (TEM) studies, and to compare with the metakaolinite obtained by normal heating. Raman and solid state NMR spectral data indicate that additional vacuum treatment procedure removes further hydroxyls from the metakaolinite. TEM studies show the changes in shape and size of particles during the dehydroxylation treatments. Dielectric properties measured on samples of kaolinite, metakaolinite and the vacuum-treated kaolinite showed distinct evidence of the dehydroxylation reactions taking place as a result of the thermal treatments.

1. Introduction

Kaolinite has found a variety of applications in industry for many years. For all high-temperature uses of kaolinite, the removal of the hydroxyl groups and conversion to the metakaolinite state before passing to spinel and mullite phases is very important and has been the subject of detailed study [1–5]. The major techniques involved in such studies have been thermogravimetry and differential thermal analysis, infrared spectroscopy and X-ray diffraction. However, the results from these studies were rather inadequate to explain fully the dehydroxylation reactions and the structure of metakaolinite, because the infrared (IR) spectra showed diffuse and broad bands and the X-ray diffractograms (XRD) of metakaolinite did not show any powder pattern [6]. Recent studies by Mackenzie *et al.* [7] were able to establish the sequence of kaolinite dehydroxylation by studying the atomic environments of both silicon and aluminium through ^{29}Si and ^{27}Al solid state nuclear magnetic resonance (NMR) using magic angle spinning by involving the remaining hydroxyls in metakaolinite. Raman spectral data were also used effectively in the identification of the hydroxyls present in kaolinite minerals [8, 9] and this technique has certain advantages over using IR spectra alone because the latter are based mainly on the change in dipole moments [10]. However, both these techniques could be used complementary to one another to interpret the thermal dehydroxylation reactions in kaolinite.

Normally metakaolinite is prepared by calcining kaolinite above the dehydroxylation temperature. A modified heat treatment procedure reported earlier [11, 12] was found to result in a dehydroxylated kaolinite with increased surface area and was used in our study on the clay–polymer composites [13]. In the present investigation an attempt is made to characterize this surface-modified powder and compare it with the metakaolinite prepared by simple calcination, using various techniques such as DTA, IR, Raman and solid state NMR spectroscopy. An electron microscopic study was conducted to investigate the change in particle size and shape due to thermal modification. The dielectric properties of kaolinite, metakaolinite and the sample prepared by modified heat treatment have been interpreted based on the extent of dehydroxylation, because the hydroxyl groups contribute towards the electrical conduction in such powders [14].

2. Experimental details

Kaolinite clay was collected from Trivandrum District, Kerala State, India, and it was washed and dried to pure kaolinite (WC). About 10 g clay were heated to 650° C for 5 h, immediately dispersed in cold water under vigorous stirring, dried and again heated in vacuum at 450° C for 4 h (VT). Similarly a 10 g sample was heated at 650° C for 5 h to obtain the metakaolinite (MK). The kaolinite (WC), metakaolinite (MK) and the vacuum-treated kaolinite (VT), were used for further investigation.

The DTA was taken in Du Pont thermal analyser at a heating rate of $10^\circ \mathrm{C\,min}^{-1}$ using alumina as standard. The surface areas of the samples were measured by the BET method. XRD patterns were taken in a Philips diffractometer with a copper target and IR spectra were taken in a Perkin Elmer instrument by the KBr pellet method. Raman spectra were recorded with a Spex Ramalog instrument using the 488 nm line of a spectra-physics 165 Ar$^+$ laser for excitation. The solid state magic angle spinning NMR spectra of samples were obtained on a XL 200 Varian spectrophotometer at magic angle spinning speeds upto 2600 r.p.s. The transmission electron microscope used was Jeol JEM 100 B. The dielectric measurements were conducted on a precision capacitance

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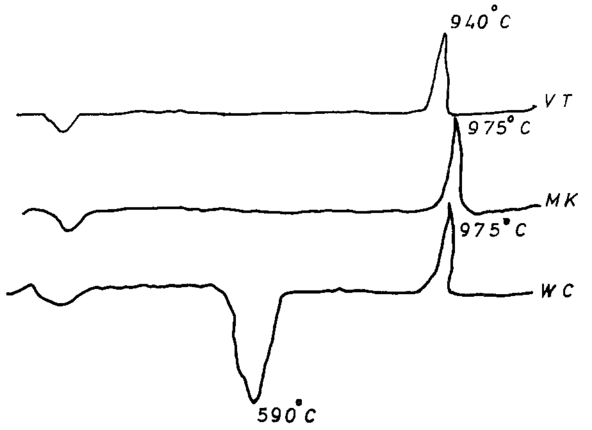


Figure 1 DTA curves of WC, MK and VT.

bridge (GR 716) in the frequency range 10^2 to 10^5 Hz and on a Marconi circuit magnification meter (TF 329 G) in the range 10^5 to 10^7 Hz by applying the resonance curve method.

3. Results and discussion

3.1. Chemical composition

Table I gives the chemical constituents of the starting kaolinite sample. Being high in alumina and low in iron and alkalies this sample should behave as true kaolinite during thermal treatment.

3.2 Thermal analysis

The DTA curves of WC, MK and VT presented in Fig. 1 show a small endothermic peak due to the loss of adsorbed water at 110° C. The endothermic peak at 590° C for WC corresponds to dehydroxylation leading to formation of metakaolinite [15]. The endothermic peak is absent in both MK and VT. The exothermic peak at 975° C in kaolinite due to the spinel formation [4] is present in MK at the same temperature, which has been shifted down to 940° C in the case of the VT sample. Possibly the reactivity of the particle was enhanced by the hydration–redecomposition process.

3.3. Surface area

Table II shows the results of BET surface area measurements on WC, MK and VT. WC had a surface area of $15\,\mathrm{m^2\,g^{-1}}$ which was not appreciably changed due to simple calcination to metakaolinite (MK). However, the surface area of WC after the thermal decomposition–hydration–redecomposition treatment was found to increase to $29\,\mathrm{m^2\,g^{-1}}$. As has already been reported [12] scanning electron microscopy of the treated powder has shown some sort of surface porosity and this could be the reason for the increased surface area.

TABLE I Chemical analysis of the kaolinite

Constituent	(%)
SiO_2	46.02
Al_2O_3	37.3
Fe_2O_3	0.9
TiO_2	0.67
MgO	0.28
CaO	Trace
K_2O	0.45
Na_2O	0.18
Loss on ignition	14.2

3.4. IR and Raman spectra

The appearance of a band in the Raman spectrum is dependent on a derivative of the polarizability of a system in the time of duration of a vibration responsible for a band. From the selection rule it emerges that bands of highly symmetrical vibrations are weak in infrared and strong in Raman spectra [16]. Hence a comparison of IR and Raman spectra provides scope for evaluating the degree of depolarization of a band to distinguish a symmetrical vibration from an asymmetrical one. In short, for a complete analysis of a vibrational spectrum, the IR and Raman spectra should be involved and conclusions drawn such that they are complementary to each other [8].

Fig. 2 shows the IR spectrum of WC, MK and VT samples. The IR spectrum of WC shows characteristic peaks for OH stretching modes between 3705 and $3620\,\mathrm{cm^{-1}}$ [17, 18]. There are well-defined peaks in the range 1100 to $400\,\mathrm{cm^{-1}}$ responsible for Si–O, Si–O–Al and Al–OH linkages [18]. However, the IR spectra of MK and VT are broad and not individually sharp in the range 3620 to $3705\,\mathrm{cm^{-1}}$, possibly due to the overlap of symmetrical group vibrations. Further, the bands in the range 1100 to $400\,\mathrm{cm^{-1}}$ are diffuse, probably because of the effect of the heat treatment of kaolinite and the subsequent removal of hydroxyls.

Figs 3 to 5 present the Raman spectra corresponding to WC, MK and VT. In the range of hydroxyl groups, the Raman spectrum of WC shows five characteristic peaks similar to these reported for kaolinite [8, 9] at 3626, 3654, 3667, 3686 and $3692\,\mathrm{cm^{-1}}$. However, MK and VT retained the peaks appearing at 3686 and $3692\,\mathrm{cm^{-1}}$ in WC at almost the same position, whilst there was a slight shift for the $3692\,\mathrm{cm^{-1}}$ peak to $3694\,\mathrm{cm^{-1}}$ in MK and VT. The peaks at 3626 and $3654\,\mathrm{cm^{-1}}$ in kaolinite, although retained in MK, are surprisingly absent in VT. This could be clear evidence of the further removal of hydroxyls reported to be retained in metakaolinite.

The reduction in the intensity of the peak at $3667\,\mathrm{cm^{-1}}$ and subsequent shift to $3663\,\mathrm{cm^{-1}}$ are also indicative of the partial removal of the hydroxyls from metakaolinite as a result of the vacuum treatment. However, the peak at $3686\,\mathrm{cm^{-1}}$ observed in WC has been retained in MK with reduced intensity, and is still retained in VT. Reduction of the intensity of this peak indirectly indicates the removal of inner hydroxyls. The OH bending vibration at $911\,\mathrm{cm^{-1}}$ [17] in WC, being shifted to a higher range in MK, also indicates the involvement of the OH group in the dehydroxylation reactions. A large number of additional peaks

TABLE II Surface area of WC, MK and VT

	Surface area ($\mathrm{m^2\,g^{-1}}$)
WC	15
MK	14
VT	29

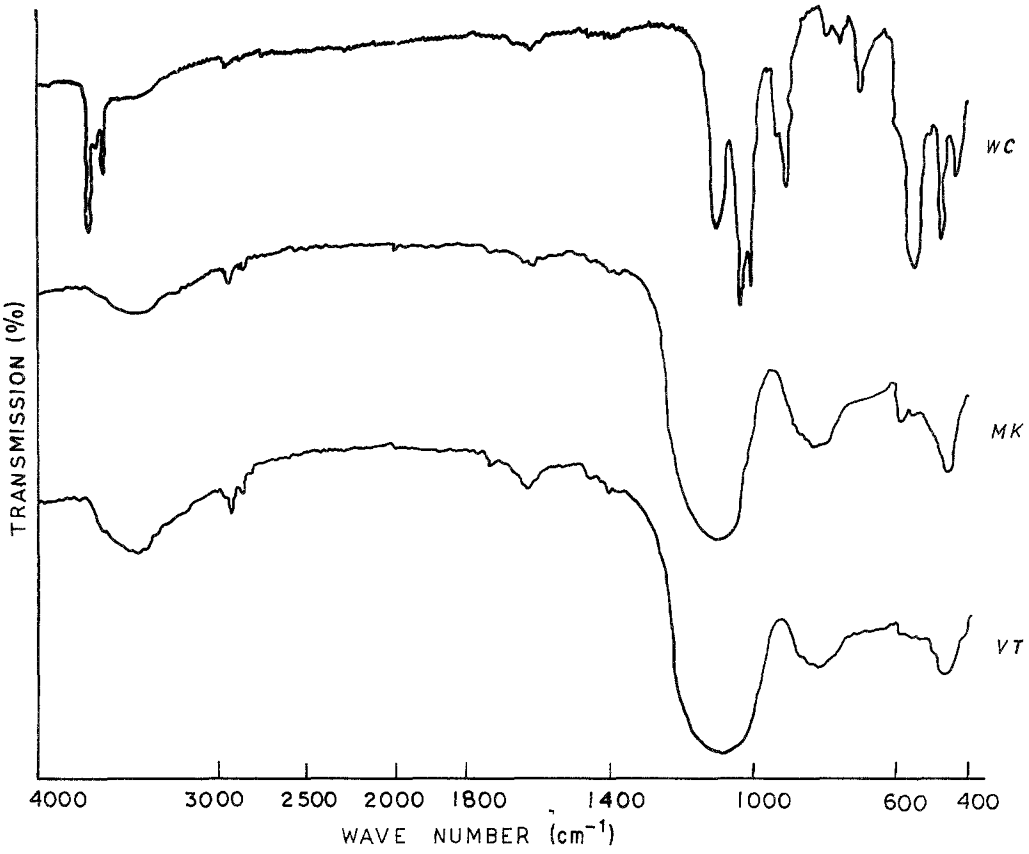


Figure 2 IR spectra of WC, MK and VT.

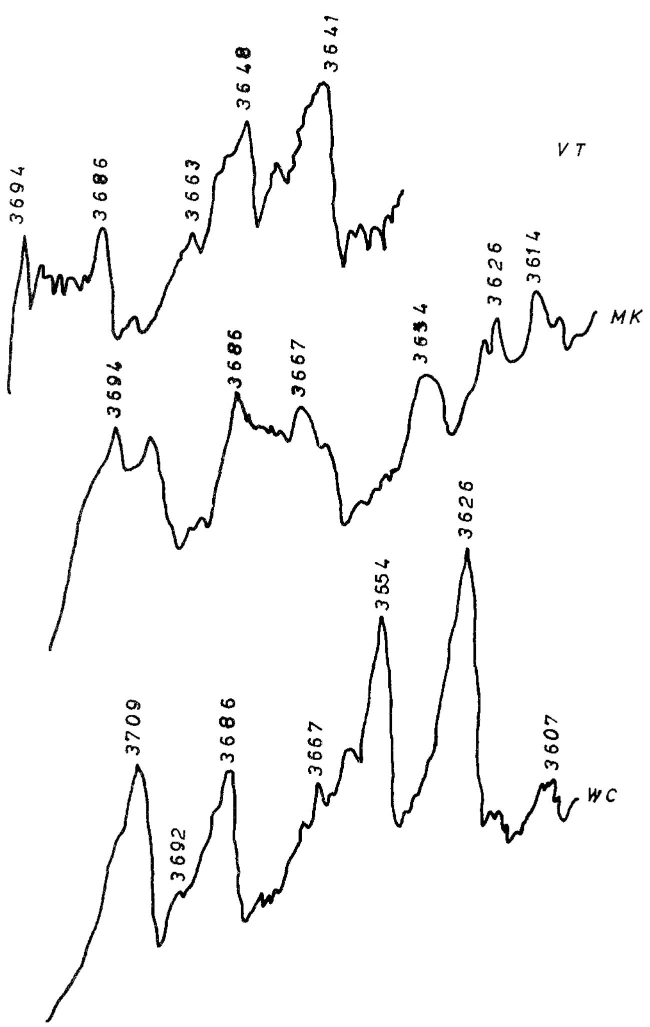


Figure 3 Raman spectra of WC, MK and VT in the 3620 to 3725 cm^{-1} region.

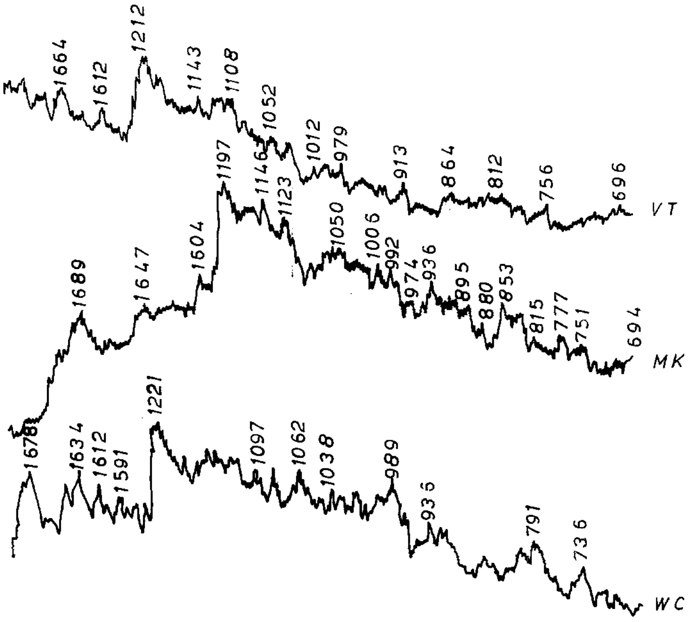


Figure 4 Raman spectra of WC, MK and VT in the 1700 to 690 cm^{-1} region.

have appeared in the Raman spectra when compared with IR spectra. Once these peaks are identified, which is difficult on the basis of the present level of information, it will be much easier to interpret the effect of heat treatment on kaolinite. On the other hand, this indicates the possibility of involving the Raman spectra combined with IR spectra for explaining the thermal transformation in kaolinite.

3.5. Solid state NMR

The ^{29}Si and ^{27}Al NMR spectra of the three samples WC, MK and VT are shown in Fig. 6. The ^{29}Si spectrum for kaolinite shows a single resonance at about −91.47 p.p.m., but the clay heated to 650° C shows a single broad resonance centred at about −98.6 p.p.m. with respect to TMS. This is identical with the spectrum of metakaolinite already reported [7]. The metakaolinite is reported to retain about 12% of its original hydroxyls which even after heating at 800° C, could not be completely eliminated [7]. The NMR spectrum of VT as seen from Fig. 6c shows the shift of the broad peak to −102 p.p.m., similar to that observed by Mackenzie *et al.* [7] on kaolinite heated to 800° C. This phenomenon is probably due to the Si–O–Si (Al) bond angles, as calculated from Si–O and Al–O distances [7]. Further an additional shoulder appeared in VT at −80 p.p.m. which is absent in MK and this provides evidence confirming Si–O layers or the formation of Si–O bonds from early spinel precipitation.

Figs 6d to f show the ^{27}Al NMR spectra of the three different samples. The principal resonance in WC is in the expected position for octahedral aluminium coordinated to hydroxyl groups; splitting may be due to the presence of more than one silicon site or to the effect of an electric field gradient at the quadrupolar aluminium nucleus [7]. MK shows an octahedral aluminium resonance at about −0.8 p.p.m. and tetrahedral signals at about 65 p.p.m. An additional peak at 34.6 p.p.m. can be detected in Fig. 6e as reported for

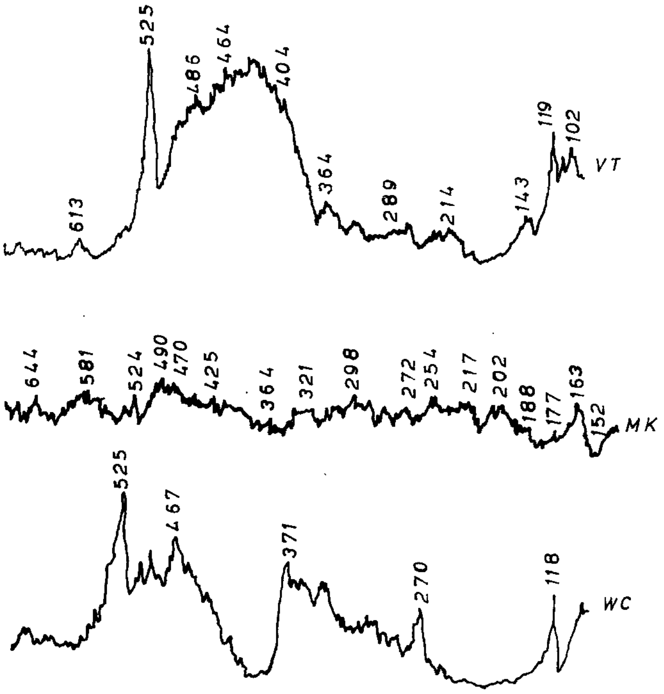


Figure 5 Raman spectra of WC, MK and VT in the 650 to 100 cm^{-1} region.

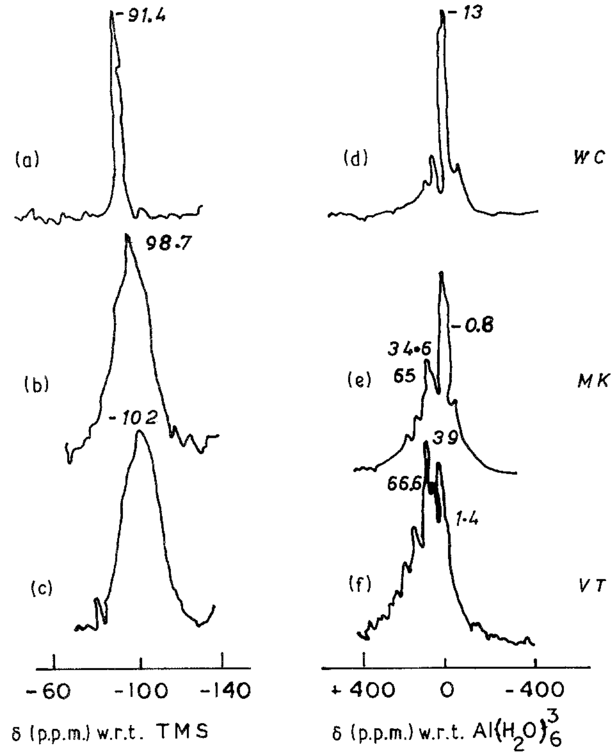


Figure 6 High resolution solid state NMR spectra of WC, MK and VT. Spinning speed 2600 r.p.s. (a) to (c) ^{29}Si spectra, (d) to (f) ^{27}Al spectra.

metakaolinite and dehydroxylated pyrophyllite [19]. The tetrahedral signal has shifted to 66.6 p.p.m. in the case of VT (Fig. 6f), as was observed for kaolinite heated to 800° C [7]. However, no recrystallization takes place by additional vacuum treatment as presented in Fig. 7. XRD patterns of VT are similar to that of MK (Fig. 7).

3.6. Microscopic observations

Figs 8a to c show the TEM of WC, MK and VT particles. WC, as seen from Fig. 8a reveals the flaky nature of kaolinite with an average particle size of about 0.37 μm. On heating metakaolinite to 650° C, the powder acquired an agglomerated structure, as was reported earlier (20), with an average particle size of about 0.75 μm (Fig. 8b). However vacuum treatment resulted in considerable deagglomeration of MK to fines of average size 0.25 μm (Fig. 8c) with a regular shape and irregularities on the surface which would have caused an increase in surface area and hence the higher reactivity [13, 20].

3.7. Dielectric behaviour

Dielectric measurements at 32° C on the WC, MK and VT presented in Figs 9, 10 and 11 reveal the decrease in dielectric constant (K) and dielectric loss (tan δ) with frequency in accordance with the normal trend for dielectrics [21]. The sharp decrease of K at low frequencies has been attributed to space charge polarization in this frequency range [21, 22]. At higher frequencies, K becomes practically frequency independent. The K value of 2.8 at a frequency of 10^6 Hz agrees with that reported by Bhattacherjee *et al.* [23] for kaolinite. The frequency-independent low values of K indicate that the space charge polarization effect is negligible in kaolinite at these frequencies [23]. Dielectric loss (tan δ) measurement also shows similar variations with frequencies in WC similar to those reported [23]. As seen from the above results, it is assumed that ionic contribution is very pronounced in WC.

The K and tan δ values of MK and VT follow similar trends as in WC, as is clear from Figs 10 and 11. However, the decrease here is not that steep, because of the prior hydroxyl removal, the absolute values of K and tan δ in VT being still less than that in MK essentially due to further removal of hydroxyls from metakaolinite by the vacuum treatment procedure. The dielectric measurements as explained

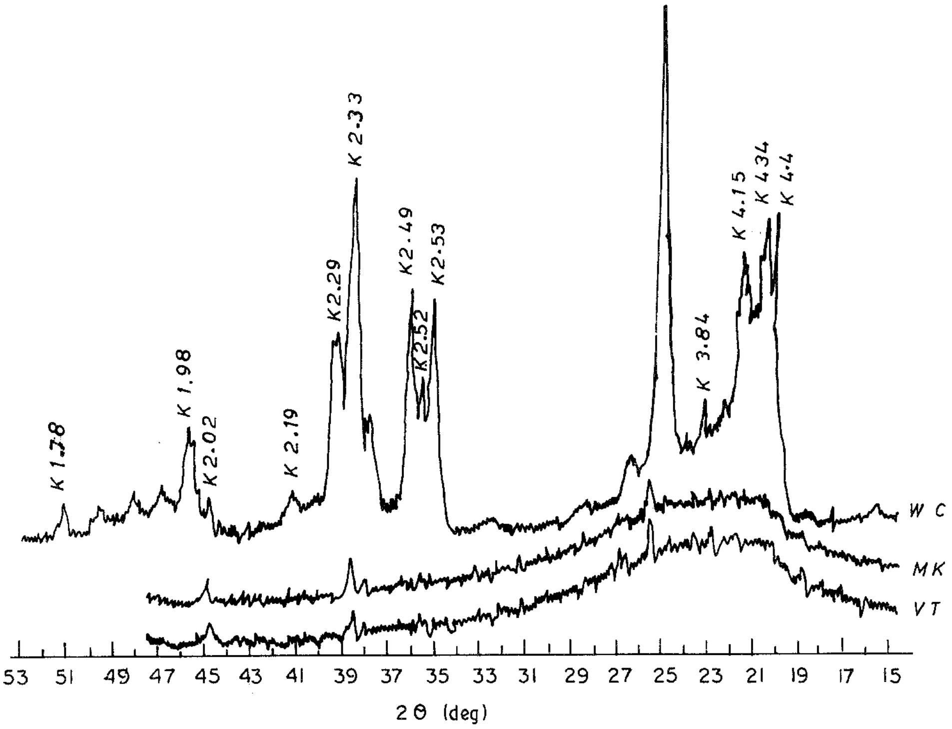
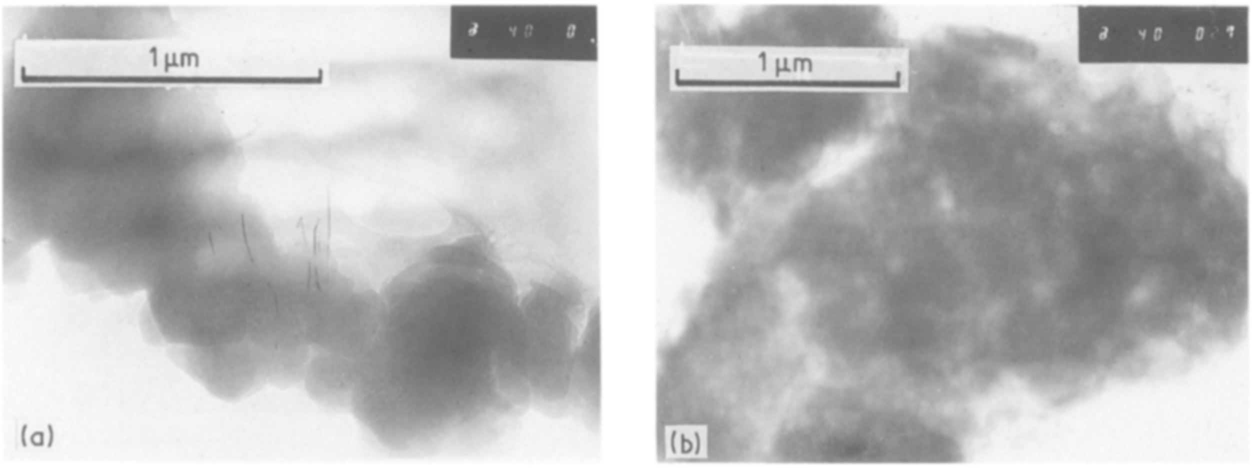


Figure 7 XRD pattern for WC, MK and VT.



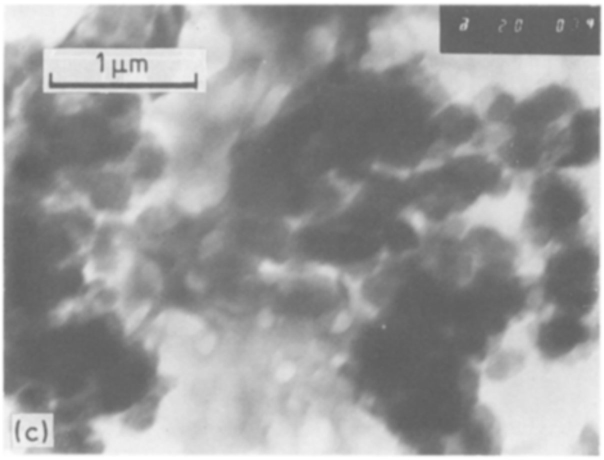


Figure 8 Transmission electron micrographs of (a) WC, (b) MK and (c) VT.

based on the dehydroxylation could be supported by NMR and Raman spectra and TEM studies.

To sum up, the observations made from the thermal analysis curve and surface area measurements that dehydroxylation followed by the vacuum treatment adopted to prepare VT have resulted in a type of metakaolinite with increased activation and surface area, compared to the corresponding metakaolinite prepared by simple calcination. However, the IR spectra and XRD of MK and VT probably do not explain the characteristics of these particles. Recent techniques such as Raman spectra and solid state magic angle spinning NMR have indicated the extent of hydroxyl removal. Raman spectra could be used as an effective tool to study the transformation in kaolinite, as was found in the present investigation, especially when coupled with the IR spectral data. Similarly, the increasing resonance value in ^{29}Si NMR from WC to VT through MK indirectly indicates the removal of further hydroxyls from the metakaolinite which has been reported to retain 12% of the hydroxyls from kaolinite [7]. The transmission electron microscopic pictures show that a total change in the particle size and shape has taken place due to thermal treatments. The dielectric properties are in line with the assumption of decreasing K and tan δ values with increasing frequencies.

4. Conclusions

1. Dehydroxylation of kaolinitic clay could be achieved by the dehydroxylation vacuum treatment technique.

2. Raman and IR spectra, when used jointly, could reveal adequate information on the extent of dehydroxylation in kaolinite.

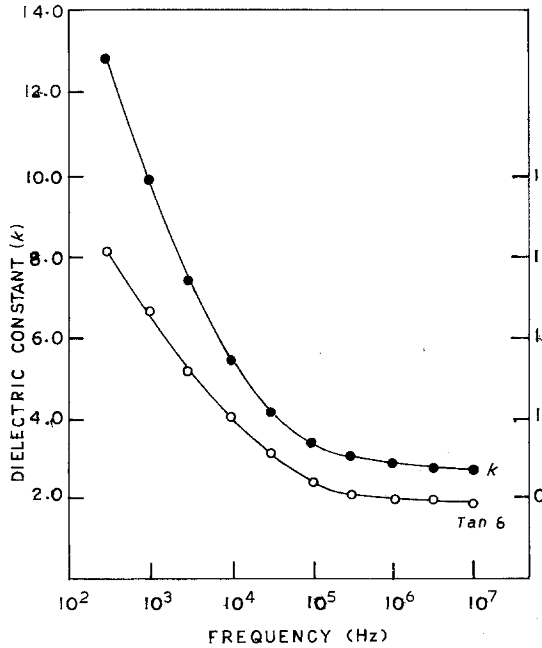


Figure 9 Variation of dielectric constant and dielectric loss (tan δ) with frequency of WC at room temperature.

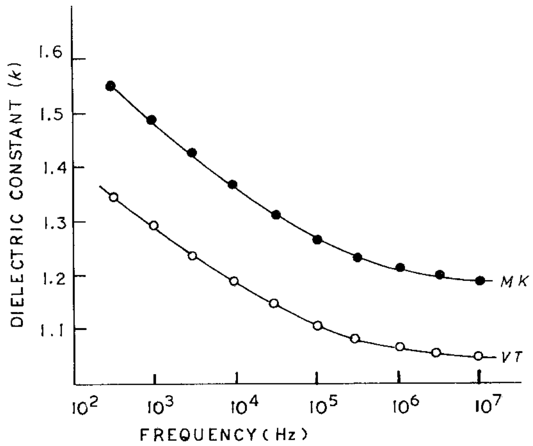


Figure 10 Variation of dielectric constant (k) with frequency of MK and VT at room temperature.

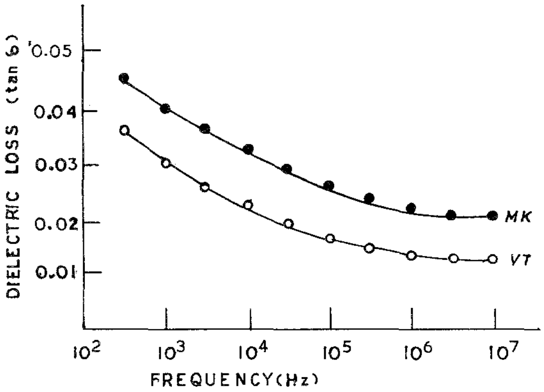


Figure 11 Variation of dielectric loss (tan δ) with frequency of MK and VT at room temperature.

3. ^{29}Si and ^{27}Al magic angle spinning NMR spectra could be used to study the environment of aluminium and silicon atoms in the kaolinite as well as in the dehydroxylated forms.

4. The dielectric property of kaolinite with and without dehydroxylation can be explained based on the information jointly obtained from the instrumentation techniques such as Raman and NMR spectroscopy.

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