The Influence of Random Defect Density on the Thermal Stability of Kaolinites

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Abstract

The thermal stability of kaolinite and the microstructure of its thermal products strongly depend on random defects (R_2) rather than crystalline defects (HI). Kaolinite with lower random defect density is more stable than that with higher defect density during dehydroxylation and the derived metakaolinite can be directly transformed into orthorhombic mullite (3/2-mullite). However, for kaolinite with higher random defect density, there is a cubic phase occurring in the transformation from metakaolinite to primary mullite. Primary mullite will be transformed into orthorhombic mullite as temperature increases. Al^V is universally present in the metakaolinite and the relative amounts of Al^{VI}, Al^V and Al^{IV} vary with the random defect density of the parent kaolinite.

I. **Introduction**

The kaolinite-mullite reaction series is of importance in ceramic technology[1] and has been extensively studied by various methods including magic-angle-spinning nuclear magnetic resonance (MAS NMR),[2-10] transmission electronic microscopy (TEM),[11-13] infra-red spectroscopy (IR),[14,15] electron paramagnetic resonance (EPR),[16] X-ray diffraction (XRD) as well as controlled-rate thermal analysis (CRTA).[17] As we know, the properties and structure of the thermal products derived from kaolinite mainly depend on the characteristics of the parent kaolinite and the heat treatment conditions. Usually, the Hinckley Index (HI) is the most widely used index of kaolinite defect density and is sensitive to all the crystalline defects of kaolinite (i.e., ±nb/3 translations, ±nπ /3 rotations, and random defects).[18] Previous report suggested that the dehydroxylation temperature would be higher for kaolinite with high HI index.[8] Recently, another index, the R_2 index of Lietard,[19] was used to characterize the random defect density of kaolinite and provides some new insights of microstructure of kaolinite.[20] The R_2 index is only sensitive to random defects and is an independent index (no relation with HI) that decreases with the increase of the monoclinic character of kaolinite. Well-resolved (131) and ($1\bar{3}1$) reflections indicate triclinic character and correspond to a high R_2 value whereas the overlapping of the two peaks indicates monoclinic character and corresponds to a low R_2 value. The R_2 of natural kaolinites is in the range 1.2 (low defect) to 0.3 (high defect).[20] Fialips et al. (2001)[20] found that, although the R_2 values decreased with the increase of random defect density of the synthetic kaolinites, their HI indexes were almost constant. More recently, our study[21] demonstrated that the random defect density of parent kaolinite has an important effect on the microstructure and chemical composition of the resultant mullites. Based on our results, a systematic study of kaolinites with different random defect densities will provide more important information about the kaolinite-mullite reaction sequence. In most previous studies, only one or two samples have been studied, making it difficult to compare the experimental results as a function of the variation of experimental conditions and characteristics of the parent kaolinites. Hence, in this study, four kaolinite samples with different random defect densities were used as starting materials. The thermal treatments at 350 – 1400 °C were conducted under similar experimental conditions and the resultant thermal products were studied using XRD, FTIR, ^{29}Si and ^{27}Al MAS NMR spectroscopy. The objective of this study is to reveal the influence of the random defect density of parent kaolinite on the thermal stability and microstructure of the thermal products.

II. **Samples and Experimental Procedure**

Four kaolinite samples with different random defect density (K1, K2, K3 and K4) were used in this study. XRD and chemical analysis show that quartz is the main impurity (< 3%) in K1, K3 and K4. In addition, K1 contains minor anatase and K4 shows minor illite. K2 is a kaolinite taken from a coal bed and contains 3% organic materials.

The samples were ground in a mortar so as to pass through a 200 mesh sieve before thermal treatments and various analyses. Thermal treatments of the parent kaolinites were carried out on a LCT-2 differential thermobalance in the range 350 - 1200 °C at a heating rate of 20 °C /min and then kept at the appointed temperatures for one hour. The thermal treatments above 1200 °C were performed in a Pt muffle. The calcined samples were quenched in air and ground in a mortar so as

to pass through a 200 mesh sieve.

XRD patterns of the samples were acquired on unoriented samples with a D/MAX-IIIA diffractometer using Cu Kα radiation. FTIR spectra using KBr pressed disk techniques were conducted on a Perkin-Elmer 1725X spectrometer with 0.9 mg samples. The spectra were collected for each measurement over the spectral range of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1}. ^{29}Si and ^{27}Al MAS NMR spectra of the samples were measured with a Brüker MSL-300 NMR spectrometer at 59.6 MHz and 78.2 MHz, respectively, using TMS as external reference with a 2 μs pulse width and a 30 s recycle delay and using a solution of $AlCl_3$ as external standard reference with a 0.6 μs pulse width and a 0.2 s recycle delay, respectively. Rotors were spun in air at 4 - 5 kHz. The decompositions of ^{27}Al and ^{29}Si MAS NMR spectra were performed using the PEAKFIT simulation program.

III. Results and Discussion

The HI index and the R_2 index of Lietard of kaolinite used in the present study were calculated as the methods described in the literatures[19-21] and these results are shown in Figure 1. Figure 1 indicates that the change trend of the HI index for the four samples ($K1_{HI} > K3_{HI} > K2_{HI} > K4_{HI}$) is different from that of the R_2 index of Lietard ($K1_{R2} > K2_{R2} > K3_{R2} = K4_{R2}$).

Our XRD results (not shown) show that the (001) basal reflection of the parent kaolinite disappears at ca. 600 ^{o}C for K1, ca. 550 ^{o}C for K2 and ca. 500℃ for K3 and K4, and only an intense broad background at 18–28° (2θ) occurs. This reflects the transformation of kaolinite into metakaolinite[2] and is confirmed by observation of the disappearance of the O-H stretching vibration at 3620 – 3700 cm^{-1} of kaolinite in the FTIR spectra (not shown). Figure 1 displays the relationship between the HI index, the R_2 index of Lietard and the transformation temperature from kaolinite to metakaolinite. Figure 1 indicates that kaolinite with lower random defect density has better thermal stability than that with higher random defect density. However, this kind of relation does not exist between the HI index and the transformation temperature. Since the experimental conditions including particle size, thermal treatment and various analyses are similar in this study, therefore, we propose that the thermal stability of kaolinite strongly depends on the random defect density of parent kaolinite indicated by R_2 index rather than crystallinity indicated by HI.

After dehydroxylation, kaolinite is transformed into amorphous metakaolinite. At this stage, the chemical shift value of the main ^{29}Si signal indicates that the environment of Si atoms is still Q^3, i.e. the layered structure of kaolinite remains unchanged. The increased FWHH (full-width-at-half-height) of ^{29}Si signal to ca. 20 ppm from 2-3 ppm for parent kaolinite indicates the presence of amorphous materials[9-10] with the signal centered between –99 and –104 ppm being the characteristic of metakaolinite. There is no obvious difference between the ^{29}Si MAS NMR spectra of the thermal products derived from the four parent kaolinites. This is similar to previous studies.[2-10] However, ^{27}Al MAS NMR spectra demonstrate the prominent difference of the microstructure of aluminum in these metakaolinites. ^{27}Al MAS NMR spectra of metakaolinites indicate the extensive existence of Al^{IV} and Al^V, resulting from dehydroxylation of kaolinite, whereas Al^{VI} decreases. To elucidate the microstructural difference in the metakaolinites derived from different parent kaolinites, the relative contents of Al^{VI}, Al^V and Al^{IV} were calculated based on the simulated ^{27}Al spectra at 850 – 900 ^{o}C. This shows that the ratios of Al^{VI}, Al^V and

Al^{IV} are 27 : 50 : 23 and 29 : 50 : 21, for K1 and K2, respectively, in which the intensity of Al^V is the strongest and the intensity of Al^{VI} exceeds that of Al^{IV}. This is similar to the result of Sanz et al. (1988).[6] For K3, the ratio is 19 : 45 : 36, in which the intensity of Al^{IV} is stronger than that of Al^{VI}. For K4, the ratio is 27 : 30 : 43 and the intensity of Al^V is always lower than that of Al^{IV}. Although the Al content in the four parent kaolinites is similar as shown by the chemical analysis,[21] the current study reveals that the relative amounts of Al^{VI}, Al^V and Al^{IV} in the thermal products are significantly different. Furthermore, our calculation demonstrates that there is a relatively high amount of Al^V in metakaolinite derived from the parent kaolinite with a high R_2 value whereas metakaolinite, derived from parent kaolinite with a lower R_2 value, has a lower content of Al^V. Hence, we propose that the relative amounts of 4-, 5- and 6-coordinated aluminium atoms in metakaolinite depend on the random defect density of the parent kaolinite. This may assist interpretation of the prominent variation of the relative amounts of Al^{VI}, Al^V and Al^{IV} reported in the literature.

Another very interesting result observed during the transformation from metakaolinite to mullite is shown in Figure 2 (Only the XRD patterns of K1 and K4 are displayed.). For K2, K3 and K4, three broad reflections at d=1.39, 1.98 and 2.43 Å were recorded in the XRD patterns at 950 – 1050 °C, corresponding to the cubic phase (γ-alumina or Al-Si spinel).[1,3,6] As the temperature increasing to 1200 °C, these three reflections disappear and the peaks of mullite and cristobalite are particularly prominent and well resolved. At 1300 – 1350 °C, the splitting of (hk0) and (kh0) of mullite occurs. This indicates that the primary mullite transforms into orthorhombic mullite (3/2-mullite).[13,21] However, for K1, there is no cubic phase observed during the transformation from metakaolinite to mullite. The orthorhombic mullite (3/2-mullite) was directly formed from metakaolinite at 1250 – 1300 °C, which is 100 °C higher than the temperature of primary mullite formation for K2, K3 and K4. This suggests that the characteristics of the parent kaolinite have an important effect on the temperature of mullite formation and its microstructure.

Our previous ^{29}Si and ^{27}Al MAS NMR study has demonstrated that mullite derived from K3 and K4 is rich in aluminum whereas that from K1 and K2 is rich in silica.[21] For primary mullite derived from K2, its Al and Si contents are similar to that of orthorhombic mullite from K1 whereas its symmetry is similar to that of primary mullite derived from K3 and K4. This suggests that the Al and Si contents have little influence on the symmetry of primary mullite.

IV. Conclusions

Four kaolinite samples with different random defect density, indicated by the R_2 index of Lietard, were studied in this study. Our results demonstrate that the random defect density has a significant effect on the thermal stability of kaolinite and the formation of mullite. Kaolinite with lower random defect density is more stable than that with higher random defect density during dehydroxylation and the derived metakaolinite will be directly transformed into orthorhombic

mullite (3/2-mullite) at 1250 – 1300 °C, without forming the cubic phase (γ -alumina or Al-Si

spinel). However, for kaolinite with higher random defect density, a cubic phase occurs during the transformation from metakaolinite to primary mullite. With increasing temperature, primary mullite transforms into orthorhombic mullite. The Al and Si contents have little influence on the symmetry of mullite.

Al^V is universally present in metakaolinite and the relative amounts of Al^{VI}, Al^V and Al^{IV} in

metakaolinite vary with the random defect density of the parent kaolinite. Metakaolinte derived from kaolinite with lower random defect density usually contains more amount of Al^V than that derived from kaolinite with higher random defect density.

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Figure Captions

Fig. 1. The relation between HI index, R_2 index of Lietard and the transformation temperature from kaolinite to metakaolinite.

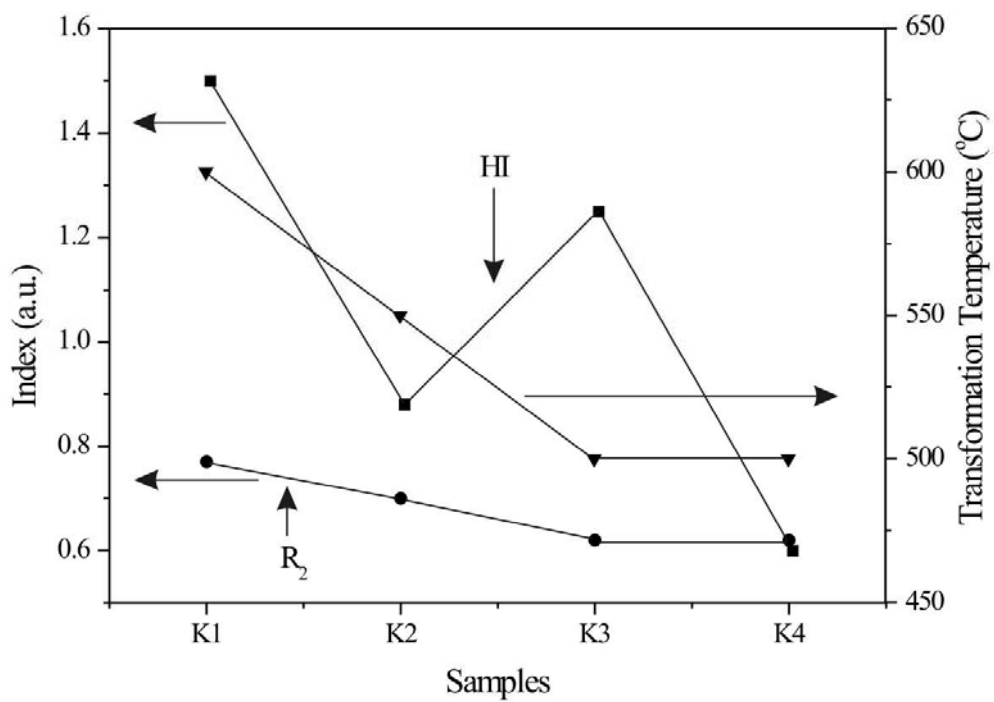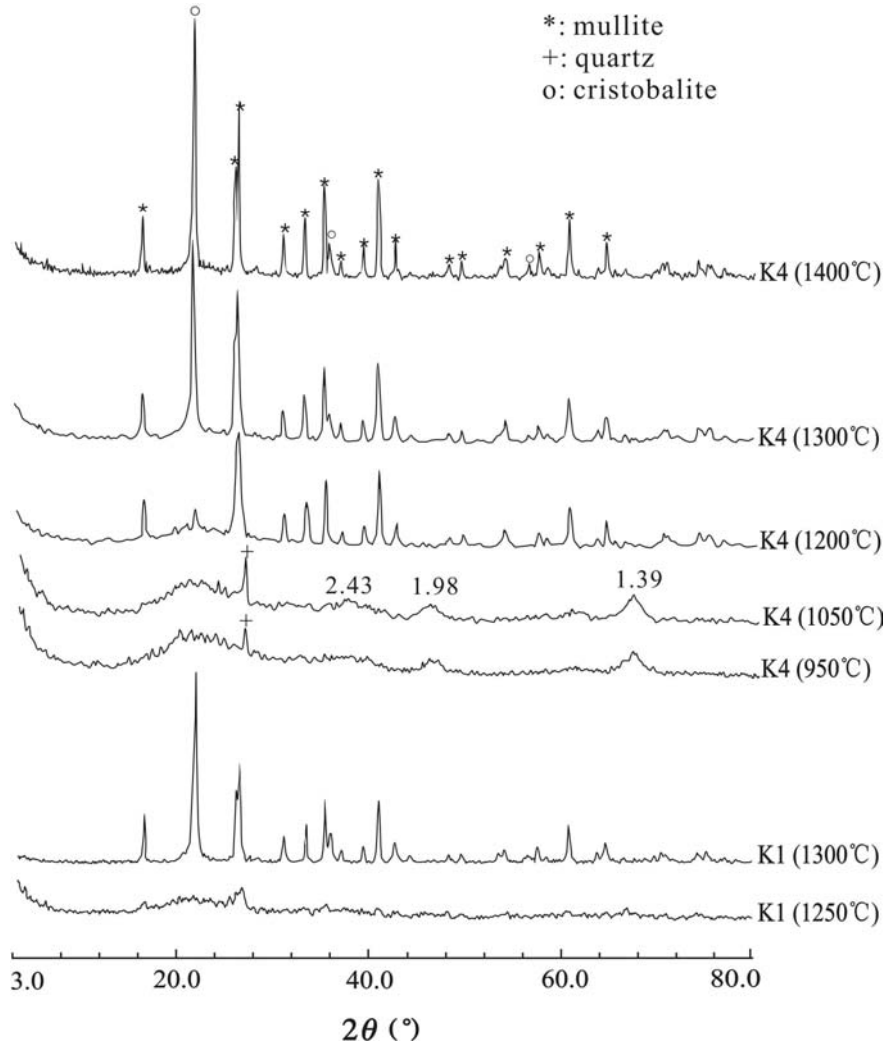Fig. 2. XRD patterns (Cu Kα) of K1 (1250 and 1300 ^{o}C) and K4 (950 - 1400 ^{o}C).

Figure –1

Figure-2