Engineering Chemistry
ISSN: 2813-6535, Vol. 6, pp 45-52
doi:10.4028/p-10dRdD

Submitted: 2023-02-08
Revised: 2023-08-12
Accepted: 2023-10-19
Online: 2024-03-05

Structural Order-Disorder Analysis of Thermally-Activated Water-Washed Kaolin Particles Using Fourier Transform Infrared Spectroscopy

Shahrul Azwan SHAKRANI[1,a*], Afizah AYOB[1,b], Mohd Asri AB RAHIM[1,c] and Salina ALIAS[2,d]

[1]Faculty of Civil Engineering & Technology, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

[2]School of Civil Engineering, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia

[a]shahrulazwan@unimap.edu.my, [b]afizah@unimap.edu.my, [c]asrirahim@unimap.edu.my, [d]salina346@uitm.edu.my

*corresponding author

Keywords: Calcination, Clay Minerals, FTIR, Kaolin, Structural Order

Abstract. During the calcination of kaolin particles, kaolinite is thermally activated at high temperatures, causing the crystal structure to collapse and yielding amorphous metakaolinite through dehydroxylation. This metakaolinite is used as a supplementary cementitious material, and one of the most important factors influencing the pozzolanic properties is calcination conditions. Fourier transform infrared spectroscopy (FTIR) has become useful in distinguishing and obtaining information about structural order-disorder and phase transformation following the calcination process. In this study, water-washed kaolin particles were thermally activated at elevated temperatures ranging from 600 to 800 °C for 3–4 h at a rate of 10 °C/min before being analyzed with FTIR to determine the optimum conditions for calcining kaolin particles by examining functional groups, and also to study structural order-disorder or crystallinity of calcined kaolin particles. The most reactive metakaolinite state of water-washed kaolin particles was achieved after 3 h of calcination at 800 °C. Using both empirical and numerical approaches, variations in the position and relative intensity of O-H stretching and deformation of hydroxyl groups in the infrared spectrum can be used to classify the degree of structural order of water-washed kaolin particles. By increasing the calcination temperatures and period, the well-ordered and partially-ordered structures of kaolin particles were transformed into well-ordered, partially-ordered, and poorly-ordered structures. These structural disorder and crystallinity have a significant impact on pozzolanic activity because well-ordered kaolinite can be transformed into less reactive metakaolinite, whereas poorly-ordered kaolinite with high defects can be transformed into more reactive metakaolinite. However, in this study, the structure of water-washed kaolin particles that achieved complete dehydroxylation was discovered to be partially-ordered to poorly-ordered and can be transformed into highly reactive pozzolans.

Introduction

Kaolin is a mineral composed of sheet silicates or phyllosilicates that form as a result of chemical weathering in sedimentary rocks. Kaolin minerals normally comprise aluminosilicate minerals, including pure kaolinite, as well as mineral impurities, such as feldspars, quartz, smectites, and micas [1]. Kaolin has been widely used as raw material in different industrial applications, such as agriculture, ceramic, construction, cosmetics, materials, manufacturing, and pharmaceutics.

In material science and engineering, calcination is a process of removing unwanted compositions in solids at very high temperatures in the absence of oxygen or air at the desired phase using thermal activation. The calcination period is a critical parameter that can significantly influence kaolin mineralogical changes. Kaolin minerals subjected to calcination at temperatures ranging from 600 to 900 °C displayed improved pozzolanic reactivity [2]. Calcined kaolin can accelerate cement hydration and replace between 5% and 10% of the mass of ordinary Portland cement in concrete mixtures. During calcination, the dehydroxylation of kaolin produces an amorphous phase known as metakaolin. Metakaolin, depending on the degree of dehydroxylation and the accessible surface for reaction, provides reactive silica and alumina that can react with calcium hydroxide via pozzolanic activity [3].

Fourier transform infrared spectroscopy (FTIR) is a technique that has been used for the characterization of structure, bonding, chemical properties, and functional groups in kaolin minerals using very small quantities of samples. Besides, FTIR can also determine the structural disorder of kaolin by detecting changes in the position and relative absorbance intensity of O-H stretching and bending bands in the IR spectrum [4-6]. There are two approaches to investigate the kaolin structural order using FTIR as recommended in Vaculíková et al. [7]: (1) an empirical approach that relies on the resolution and relative intensities of O-H stretching and bending vibrations of the hydroxyl group in kaolin and (2) a numerical approach that relies on crystallinity indices calculated from the intensities of selected O-H bands of the hydroxyl group in kaolin. The resolution of the IR spectra of structural O-H groups of kaolin particles can be useful for a better understanding of the modifications that occur in the stretching modes related to crystallinity [5].

In the present study, thermally-activated water-washed kaolin particles prepared under various temperatures and duration were analyzed using FTIR in order to determine the optimum conditions for kaolin particles subjected to calcination by examining the functional groups. The structural disorder or crystallinity of calcined kaolin particles was also determined using both empirical and numerical approaches in the FTIR analysis. These calcined water-washed kaolin particles are ideal for the FTIR analysis of structural disorder because (1) grinding effects are minimized due to no mechanical treatment required and (2) particle size effects are minimized by having similar particle size distribution [4].

Methodology

Water-washed kaolin particles were procured from Kaolin (Malaysia) Sdn. Bhd. under the label of KM65. The elemental analysis indicates a high percentage of SiO_2 and Al_2O_3 at 64.16% and 28.59%, respectively, which are close to pure kaolinite composition. These water-washed kaolin particles were calcined at elevated temperatures of 600, 700, and 800 °C for a duration of 3 and 4 h and a heating rate of 10 °C/min using a laboratory furnace, as presented in Table 1. The uncalcined water-washed kaolin particles were assigned as sample WK as a control sample, while calcined (thermally-activated) water-washed kaolin particles were assigned as samples TWK 6003, TWK 6004, TWK 7003, TWK 7004, TWK 8003, and TWK 8004 based on various elevated temperatures and calcination periods.

Table 1. Calcination of water-washed kaolin particles under various elevated temperatures and durations.

Sample	WK	TWK 6003	TWK 6004	TWK 7003	TWK 7004	TWK 8003	TWK 8004
Temperature (°C)	0	600	600	700	700	800	800
Duration (h)	0	3	4	3	4	3	4
Heating Rate (°C/min)	0	10	10	10	10	10	10

Calcined water-washed kaolin particles were left overnight to cool in the furnace and kept in a container for further testing. By using the potassium bromide (KBr) pellet method, about 1 mg of calcined water-washed kaolin particles was homogenized with 100 mg of solid KBr at a ratio of 1:100. This technique is widely used in FTIR sample preparation and suitable for kaolin particles due to solid and powder sample conditions [8]. Besides, this method is also useful for routine characterization and examination of clay mineral modification like kaolin particles. The IR spectra were obtained using a spectrophotometer (Perkin-Elmer Spectrum 65, USA) at 4 cm^{-1} resolution with 100 scans in the scanning range of 4000–450 cm^{-1} under a controlled ambient temperature. FTIR analysis was performed to determine the degree of structural disorder of calcined water-washed kaolin particles using empirical and numerical approaches. In the empirical approach, the attributes and classification of structural order were determined based on the resolution and relative intensities of the O-H stretching and bending absorption bands, as described in Table 2. Calcined water-washed kaolin particles were classified into three categories: well-ordered, partially-ordered, and poorly-ordered.

Table 2. Attributes and classification of structural disorder using empirical approach [6-7].

Attributes	Position (cm^{-1})	Description
1st	3695, 3670, 3650, 3620	Four distinguishable O-H bands are observed
2nd	-	O-H broadening bands are not observed
3rd	938, 916	O-H deformation bands are observed
4th	795, 758	Two weak O-H bands of equal intensity are found
Classification	Position (cm^{-1})	Description
Well-ordered	-	O-H stretching and bending bands are resolved
Partially-ordered	3670, 3650, 938	Individual O-H bands are identified at low intensity
Poorly-ordered	3660	One of O-H bands is observed (at/near inflexions)
	3670, 3650, 938	

Meanwhile, the crystallinity indices for CI_1 and CI_2 were determined using Eq. 1 and Eq. 2 in the numerical approach from the intensities of absorption bands in the spectra, respectively.

$$CI_1 = \frac{I(\nu 1)}{I(\nu 3)} \tag{1}$$

$$CI_2 = \frac{I(\nu 4)}{I(\nu 1)} \tag{2}$$

Where $I(\nu_1)$ and $I(\nu_4)$ are the intensities of O-H stretching bands at 3695 and 3620 cm^{-1}, while $I(\nu_3)$ is the intensity of O-H bending band at 915 cm^{-1}. Two-point baseline method was performed to determine the O-H band intensity. The structural disorder of water-washed kaolin can be further classified in accordance with the crystallinity indices described in Table 3.

Table 3. Classification of structural disorder using numerical approach [9-10].

Classification		Well-ordered	Partially-ordered	Poorly-ordered
Crystallinity Indices Ranges	CI_1	$CI_1 > 0.8$	$0.7 < CI_1 < 0.8$	$CI_1 < 0.7$
	CI_2	$CI_2 < 0.9$	$0.9 < CI_2 < 1.2$	$CI_2 > 1.2$

Results and Discussion

Thermally-Activated Water-Washed Kaolin Particles. The IR band positions and assignment of water-washed kaolin particles under various elevated temperatures and calcination periods are described in Fig. 1 and Table 4. Without thermal activation in the WK sample, the Al-O-H stretching of inner-surface hydroxyls and the stretching of inner hydroxyls were formed at absorption bands of 3697 and 3620 cm^{-1}, respectively, while Al-O-H deformation of inner hydroxyls and translation mode were discovered at absorption bands of 913 and 796 cm^{-1}, respectively. The H-O-H stretching and the bending of absorbed and coordinated water were evidenced at absorption bands of 3446 and 1635 cm^{-1}, respectively. At absorption bands of 1115, 1031, and 1007 cm^{-1}, the Si-O stretching out-of-plane and in-plane vibration modes were observed. The Si-O perpendicular deformation was found at the absorption band of 698 cm^{-1}, while the Si-O-Al and Si-O-Si deformation modes were witnessed at 536 and 471 cm^{-1}, respectively. Thermal activation at 600 °C is insufficient to break the crystalline structure of water-washed kaolin particles from samples TWK 6003 and TWK 6004. When the temperature in the samples TWK 7003 and TWK 7004 was raised to 700 °C during calcination, the peaks of Si-O stretching were transformed and broadened. However, stretching of the inner surface and inner hydroxyls of Al-O-H revealed evidence of incomplete dihydroxylation. At the temperature of 800 °C in the TWK 8003 and TWK 8004 samples during calcination, all Al-O-H stretching and deformation of inner-surface and inner hydroxyls have disappeared, implying that kaolinite has been completely dehydroxylated and converted to metakaolinite with the presence of a new band at 559 cm^{-1} associated with the stretching of AlO_6 octahedral. The increase in calcination temperature from 600 °C to 800 °C over a period of 3–4 h increased the absorbance intensity of the IR spectra due to the manifestation of thermal expansion. This causes the opposite shifts of the low- and high-frequency components of the absorption bands of the structural O-H groups in kaolin particles, as stretching and deformation vibrations of hydroxyls are particularly sensitive to changes in hydroxyl surfaces.

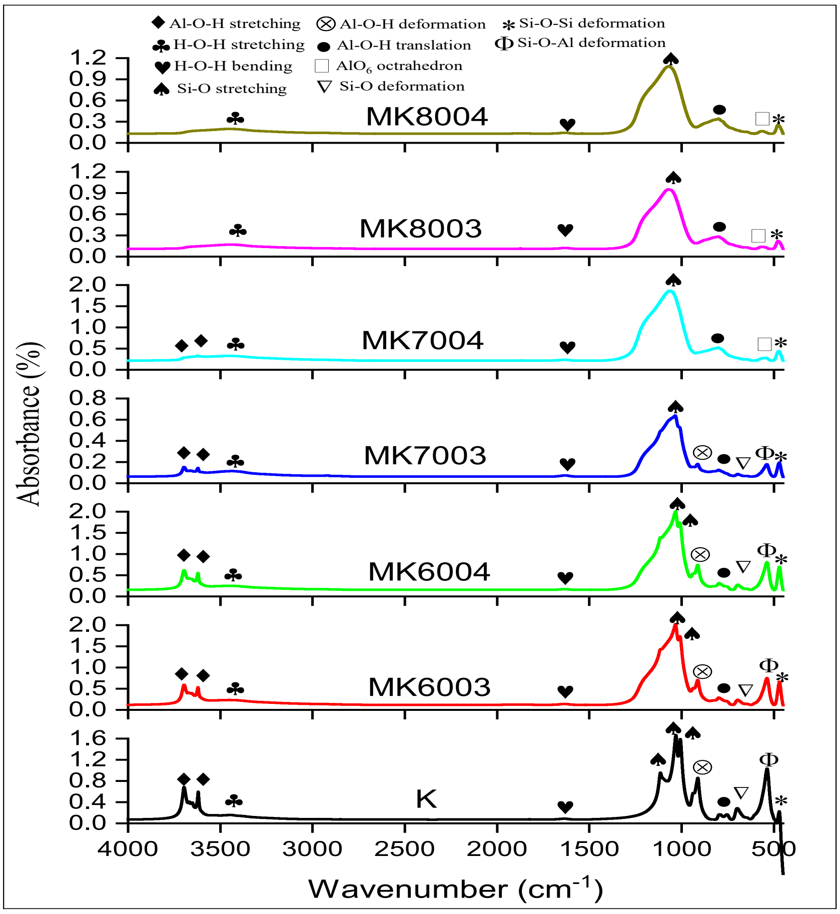

Fig. 1. The IR spectra of water-washed kaolin particles under various elevated temperatures and calcination periods (4000–450 cm^{-1}).

Table 4. Infrared band positions and assignment of water-washed kaolin particles under various elevated temperatures and calcination periods.

WK (cm^{-1})	TWK 6003 (cm^{-1})	TWK 6004 (cm^{-1})	TWK 7003 (cm^{-1})	TWK 7004 (cm^{-1})	TWK 8003 (cm^{-1})	TWK 8004 (cm^{-1})	Assignment
3697	3697	3697	3697	3694	-	-	Al-O-H stretching of inner-surface hydroxyls
3620	3621	3622	3622	3622	-	-	Al-O-H stretching of inner hydroxyls
3446	3449	3448	3436	3466	3466	3447	H-O-H stretching of absorbed and coordinated water
1635	1630	1631	1628	1634	1629	1631	H-O-H bending of absorbed and coordinated water
1115	-	-	-	-	-	-	Si-O stretching out-of-plane
-	-	-	-	1071	1060	1072	Broadening of Si-O stretching
1031	1032	1032	1035				Si-O stretching in-plane
1007	1011	1011	-	-	-	-	Si-O stretching in-plane
913	913	913	913	-	-	-	Al-O-H deformation of inner hydroxyls
796	798	798	799	800	800	800	Al-O-H translation
698	696	695	695	-	-	-	Si-O deformation at perpendicular
-	-	-	-	559	564	563	AlO_6 octahedron stretching
536	539	539	539				Si-O-Al deformation
471	471	471	471	475	476	476	Si-O-Si deformation

Structural Order-Disorder Analysis. The degree of structural order of water-washed kaolin particles under various elevated temperatures and calcination periods can be determined by the differences in the position and relative intensity of the O-H stretching and deformation of hydroxyl groups in the IR spectrum. Water-washed kaolin particles under various elevated temperatures and calcination periods have absorption bands between 3750 and 3550 cm^{-1} and between 1200 and 450 cm^{-1} corresponding to the O-H stretching and deformation of hydroxyl groups, respectively, as described in Fig. 2 and Fig. 3.

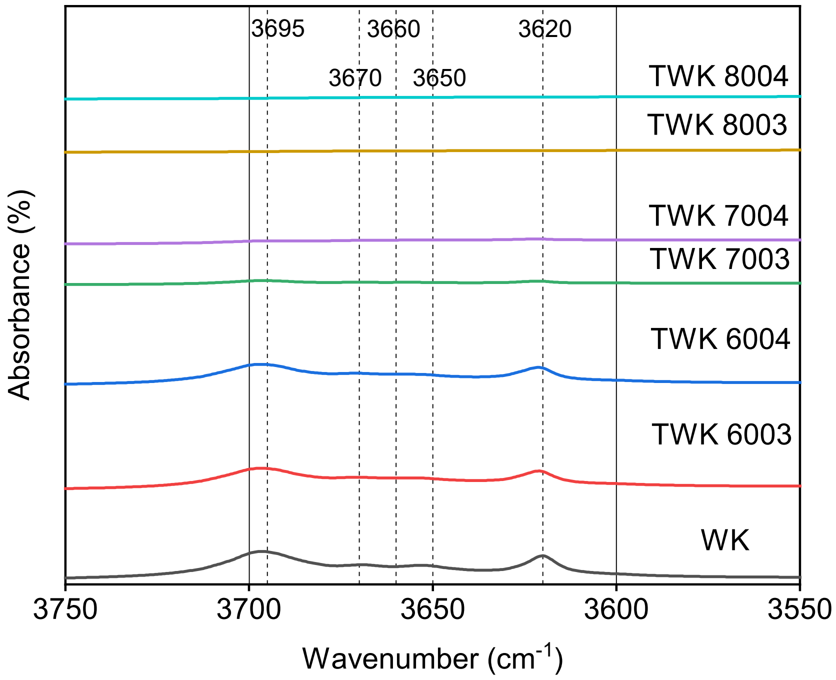

Fig. 2. The IR spectra of water-washed kaolin particles under various elevated temperatures and calcination periods (3750–3550 cm^{-1}).

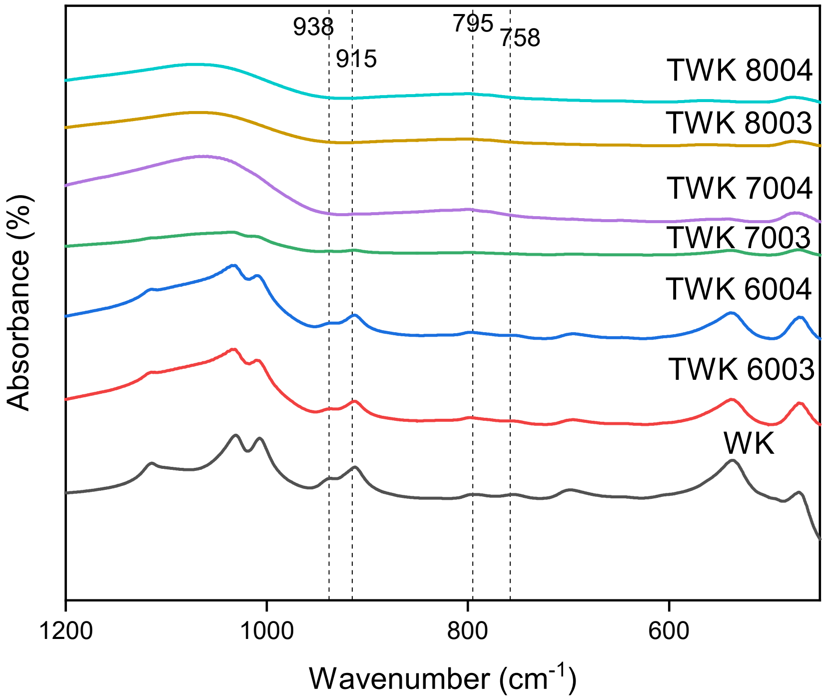

Fig. 3. The IR spectra of water-washed kaolin particles under various elevated temperatures and calcination periods (1200–450 cm^{-1}).

Using both empirical and numerical approaches, the degree of structural order of water-washed kaolin particles subjected to various elevated temperatures and calcination periods can be classified in relation to variations in position and relative intensity of O-H stretching and deformation of hydroxyl groups in the IR spectrum, as described in Table 5. Through the empirical approach, the structure of water-washed kaolin particles under various elevated temperatures and calcination periods was classified as partially-ordered for WK, TWK 6003, and TWK 6004 samples, and poorly-ordered for TWK 7003, TWK 7004, TWK 8003, and TWK 8004 samples. On the other hand, the structure of water-washed kaolin particles under various elevated temperatures and calcination periods was classified as well-ordered for samples WK, TWK 6003, and TWK 6004; well-ordered to partially-ordered for sample TWK 7003; partially-ordered for sample TWK 7004; and partially-ordered to poorly-ordered for TWK 8003 and TWK 8004 samples using the numerical approach.

Table 5. Classification of the degree of structural order of water-washed kaolin particles under various elevated temperatures and calcination periods using empirical and numerical approaches.

Sample	Empirical Approach					Numerical Approach		
	Attributes				Classification	Crystallinity Indices		Classification
	1st	2nd	3rd	4th		CI_1	CI_2	
WK	Yes	Yes	Yes	Yes	Well-ordered	0.81	0.88	CI_1 & CI_2: Well-ordered
TWK 6003	Yes	Yes	Yes	Yes	Well-ordered	0.85	0.90	CI_1 & CI_2: Well-ordered
TWK 6004	Yes	Yes	Yes	Yes	Well-ordered	0.84	0.89	CI_1 & CI_2: Well-ordered
TWK 7003	No	No	No	Yes	Poorly-ordered	0.84	0.92	CI_1: Well-ordered CI_2: Partially-ordered
TWK 7004	No	No	No	No	Poorly-ordered	0.72	1.13	CI_1: Partially-ordered CI_2: Partially-ordered
TWK 8003	No	No	No	Yes	Poorly-ordered	0.66	1.16	CI_1: Poorly-ordered CI_2: Partially-ordered
TWK 8004	No	No	No	Yes	Poorly-ordered	0.66	1.17	CI_1: Poorly-ordered CI_2: Partially-ordered

By increasing the calcination temperatures and periods, the well-ordered and partially-ordered structure of water-washed kaolin particles is transformed into well-ordered, partially-ordered, and poorly-ordered structures. This is because the structure of kaolinite would be disordered because the hydroxylation process is done more readily, as reported by Souri et al. [11]. Structural order and crystallinity have a significant effect on pozzolanic activity. During calcination, well-ordered kaolinite is transformed into less reactive metakaolinite, while poorly-ordered kaolinite with high defects is transformed into more reactive pozzolans. As a result, there is a tendency for these kaolin and metakaolin particles to be grouped into highly reactive pozzolans.

Conclusions

In conclusion, FTIR has proven to be a very useful spectroscopic technique in the study of kaolinite dehydroxylation of water-washed kaolin particles. This technique differentiates between different water-washed kaolin samples and provides basic information on their chemical composition, surface properties, and structural changes caused by surface modification using thermal activation. Based on the IR spectral resolution, the results presented here provide a new method of assessing the structural disorder of water-washed kaolin particles and determining the transformation of kaolinite into metakaolinite in kaolin samples. By using the empirical approach, the O-H stretching and bending vibrations are accurate enough to differentiate between well-ordered, partially-ordered, and poorly-ordered kaolinite based on the resolution and relative intensity of kaolin samples. During thermal treatment, the O-H bands of hydroxyl groups in kaolinite were gradually removed. However, thermal treatment has no effect on Si-O vibrations but has a significant effect on Al-O vibrations. For the numerical approach, the crystallinity indices can be easily determined based on the intensity of the O-H bands to further classify the structural disorder into well-ordered, partially-ordered, and poorly-ordered kaolinite. The structure disorder of water-washed kaolin particles changed from well-ordered to partially-ordered and poorly-ordered as calcination temperatures and periods increased. As structural disorder and crystallinity have a significant effect on pozzolanic activity, the water-washed kaolin particles have a tendency to be highly reactive pozzolans.

Acknowledgements

The first author gratefully acknowledges the financial assistance provided by Universiti Malaysia Perlis and the Ministry of Higher Education Malaysia through the SLAB scholarship. The authors would also like to thank the Faculty of Chemical Engineering & Technology (formerly known as the School of Bioprocess Engineering), Universiti Malaysia Perlis for providing the FTIR research facility.

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