

METAKAOLINITE: Si & Al PRECURSORS FOR KALSILITE SYNTHESIS

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Metakaolinite has been used as a silica and alumina precursor to synthesise kalsilite via the hydrothermal method with the addition of potassium hydroxide (KOH) as the potassium source. The effects of the KOH concentrations and reaction temperatures have been investigated. X-ray diffraction (XRD) diffractograms and field emission scanning electron microscope (FESEM) images showed the formation of hexagonal kalsilite after the hydrothermal reaction of metakaolinite at 190 °C in 1.25 M KOH for 24 hours. Kalsilite formed as a minor crystalline phase at a KOH concentration of less than 1.0 M KOH, while, at a higher KOH concentration, the crystallinity of the product increases. On the other hand, 190 °C was sufficient to convert metakaolinite to kalsilite. Besides, zeolite F and muscovite have been found as the dominant products at a lower KOH concentration and temperature, respectively.

INTRODUCTION

Kaolin is a product commonly used in the manufacture of ceramics, catalysts, cement production, and in agriculture. It is also important for the paper, rubber and plastics industries. For certain applications, however, kaolin is converted into a metakaolinite form by calcining [1]. Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), the principal kaolin mineral, is a 1:1 layered phyllosilicate made of one tetrahedral sheet of silica and one octahedral sheet of alumina. There are smaller metal cations in the centre of the tetrahedrons and octahedrons and their apices are filled with oxygen atoms and groups of hydroxyls [2]. Thermal decomposition at 400 °C – 700 °C disrupts kaolinite's crystalline structure. The heating reaction breaks off the mineral's -OH chain and the kaolinite structure collapses, resulting in metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), an amorphous aluminosilicate structure. Here, the coordination number of the Al changes from a single six (Al^6) to a mixture of five (Al^5) and four (Al^4) during the thermal decomposition reaction of kaolinite [3].

Several studies on the synthesis of kalsilite using kaolin as a precursor have been reported upon [4-7]. Kaolin was chosen due to its high silica and alumina contents, having a theoretical composition of 46.54 % SiO_2 , 39.5 % Al_2O_3 and 13.96 % water [8]. Kalsilite,

KAlSiO_4 , is a type of basic mineral silicate and can be grouped into feldspathoids that typically co-exist with olivine, melilite, clinopyroxene, phlogopite, nepheline, and leucite, mainly formed in K-rich and silica under-saturated volcanic rocks [9]. Several methods are widely used to synthesise kalsilite from different types of Si and Al sources; however, hydrothermal [10,11] and solid state [12] synthesis methods are economical and have relatively simple steps to produce pure materials with smaller particle sizes.

Despite its availability in nature, only several works in the literature report the conversion of kaolinite/metakaolinite to kalsilite, particularly using the hydrothermal synthesis procedure. Brachold and Aneziris [12] successfully synthesized kalsilite, to be used as anti-corrosion materials, from kaolin at 200 °C using the hydrothermal method. However, the report used high concentrations of potassium hydroxide (KOH) (50 % w/w), which involved increased manufacturing costs and could influence the environment unless it was systematically treated. The effects of KOH molarity and the synthesis temperatures toward the kalsilite formation from metakaolinite via the hydrothermal treatment was followed by the product characterisation using X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM) and are described in the present research.

EXPERIMENTAL

Materials and method

Kaolin from Sibelco Co. was used as the principal source for Al_2O_3 and SiO_2 in all the synthesis sequences. Table 1 reflects the chemical composition of the kaolin. The additional source of Al_2O_3 comes from $\text{Al}(\text{OH})_3$ to achieve the desired ratio. Potassium hydroxide (Merck Ltd.) in the form of pellets and distilled water were used to prepare the alkali solution. The kaolin was calcined in a muffle furnace at 750°C for the dihydroxylation and formed metakaolinite.

Table 1. Main chemical compositions of the kaolinite. Oxide content in wt. %

Al_2O_3	SiO_2	Fe_2O_3	K_2O	TiO_2	MgO	L.O.I
34.20	49.60	1.01	1.80	0.55	0.55	12.10

1.0 g metakaolinite was mixed with 100 ml of various KOH solution concentrations from 0.50 M to 1.25 M in a stainless-steel hydrothermal reactor and heated from 170°C up to 250°C at $10^\circ\text{C}\cdot\text{min}^{-1}$ for 24 h, respectively. The reactor's pressure was approximately equal to that of the water vapour pressure at the corresponding temperature. After cooling to room temperature, the products were filtered and washed repeatedly using distilled water and dried at 80°C in an oven for 8 h.

Characterisation

The XRD diffractograms of the untreated kaolin and synthesis products were analysed using a Rigaku Smartlab X-ray diffractometer model, $\text{CuK}\alpha = 1.54056$, 50 mA, 40 kV. The data collection was carried out in the range of 2θ : $5 - 80^\circ$, with a step size of 0.01° under $\text{CuK}\alpha = 1.54056$, 50 mA and 40 kV. The phase identification was performed by searching the International Centre for Diffraction Data (ICDD) powder diffraction file database, with the help of JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds. The relative intensity yields were obtained from the normalised XRD intensities of the major reflection for each material. The average crystallite size, D , was determined using Scherrer's formula.

The solid phase morphologies were examined by a JEOL JSM-7900F FESEM, where the samples were coated with platinum. The samples were coated with a platinum layer to avoid charging effects from the free electrons and allowed for a clear image to be obtained. An inert element, such as platinum (Pt), will discharge the free electrons liberated from the electron beam's bombardment on the sample's surface. The coated samples were observed using the FESEM under a $5000 \times$ to $50000 \times$ magnification.

RESULTS AND DISCUSSION

The dehydroxylation of kaolin to form metakaolinite, which has an amorphous aluminosilicate structure, is based on the following reaction:



The effect of KOH molarity

The formation of kalsilite using metakaolinite as the Si and Al source in the KOH solution can be presented by the reaction:



By referring to the stoichiometry above, 2 mol of kalsilite are formed from 1 mol of metakaolinite and 2 mol KOH. A similar trend can be seen when kaolin is used as the Si and Al precursor with the addition of KOH as the K^+ source, according to the equation below:

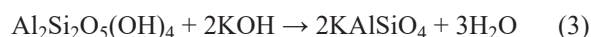


Figure 1 shows the XRD diffractograms when metakaolinite is added with various KOH concentrations for the kalsilite formation.

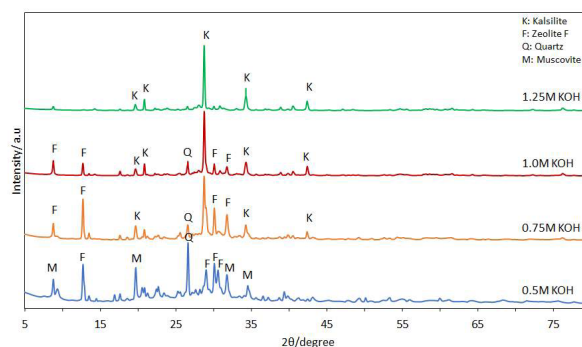


Figure 1. XRD diffractograms of the hydrothermal reaction products obtained at various KOH concentrations using metakaolinite as the precursor at 190°C .

The ICDD database PDF4+ 2020 was used for the phase identification. From the figure above, 1.25 M KOH shows the most significant kalsilite peaks (PDF file 00-011-0579) at 20.8° [002], 28.7° [102], 34.2° [110] and 42.3° [004]. A higher KOH concentration is required to produce highly crystalline kalsilite due to the Si and Al availability in the reaction media to bind with the K^+ ions in the nucleation process and subsequently lead to the growth of the KAlSiO_4 crystal. The argument is consistent with the findings of [13] after the researchers used a KOH concentration higher than 4.3 M when synthesising kalsilite using microcline as a precursor under hydrothermal conditions. Analogous results are also achieved by [14] when they used 4 M KOH added with an SiO_2 powder and $\text{Al}(\text{NO}_3)_3$ to obtain KAlSiO_4 .

after 336 hours using the hydrothermal reaction method. Compared with the above literature sources, this study shows metakaolinite can also be used as a precursor for the kalsilite synthesis under the hydrothermal reaction since it contains a high Si and Al composition with the Si:Al ratio close to 1. Moreover, this work utilised a much lower KOH molarity, lowering the manufacturing cost and appealing to the ecosystem protection.

On the other hand, a further reduction in the KOH concentration promotes several diffraction peaks corresponding to zeolite F, quartz and muscovite. It can be seen that the kalsilite crystal starts to form as a minor crystalline phase when 0.75 M KOH is used in the hydrothermal reaction while the main crystalline phase is zeolite F. The formation of zeolite F is in agreement with our expectations since its chemical formula is almost identical with kalsilite except with addition of a hydrated molecule ($\text{KAlSiO}_4 \cdot 1.5\text{H}_2\text{O}$) [15]. Based on the formula, the ratio of Si:Al is 1 and identical with the Si:Al ratio of kalsilite, hence providing the competition during the nucleation process as can be seen from the diffractograms when 0.75 M KOH and 1.0 M KOH were used, respectively. Besides, no kalsilite is formed at a concentration below 0.5 M. The existence of the muscovite and quartz peaks in the diffractograms suggests that the dissolution of Si and Al in metakaolin occurs ineffectively due to the lack of K^+ ions, leading to the recrystallisation of the precursor.

Effect of the reaction temperature

The XRD patterns of the products obtained after the hydrothermal treatment of metakaolinite in the 1.25 M KOH solution at various temperatures are shown in Figure 2. A sample of the product synthesised at 170 °C only presents the diffraction peaks of muscovite, quartz and zeolite F as the major phases, indicating that metakaolinite failed to incorporate the K^+ ion available effectively at the accurate Si and Al ratio. The formation of muscovite (potassium aluminium silicate hydroxide) occurred due to the precipitation of alumina and silica from metakaolinite with KOH [16]. However, after

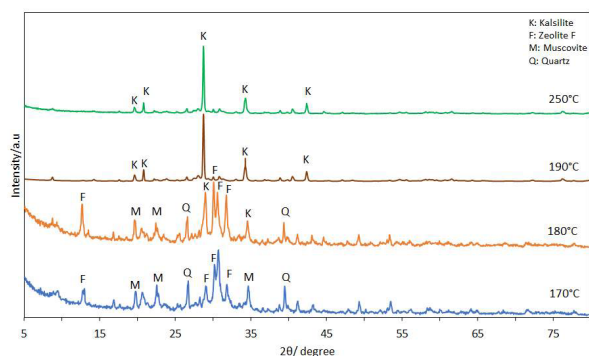


Figure 2. XRD diffractograms of the hydrothermal reaction products obtained at various temperature using metakaolinite as a precursor and 1.25 M KOH.

heating the sample at 180 °C, two new peaks at 28.7° [102] and 34.2° [110], in addition to the diffraction peaks of the other major crystalline phases, are observed. These new peaks belong to KAlSiO_4 (P6_3 space group, PDF file 00-011-0579). Figure 5 shows the crystal structure of the P6_3 space group kalsilite formed in this study modified from [17]. Each tetrahedron is connected with three O atoms in the plane perpendicular and by one O atom in the direction parallel to the c-axis, respectively. The hexagonal cell dimensions are $a = 5.23\text{\AA}$ and $c = 8.55\text{\AA}$.

The muscovite and quartz diffraction peaks gradually became weaker with each subsequent increase in temperature and disappear completely when the synthesis is carried out at 190 °C, most probably due to the topotactic reaction between the Si and Al successfully incorporating the K^+ ion to form KAlSiO_4 crystals. Further heating up to 250 °C of the sample shows identical KAlSiO_4 peaks and the unit cell parameters for the crystal are $a = 5.23299$ and $c = 8.55349$, which are slightly larger than those reported by [18].

Crystallite size

The average crystallite size calculated by the Scherrer equation is shown below:

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (4)$$

Where D is the crystallite size, K is a constant, λ is the X-ray wavelength, β is the peak width at half of its height (FWHM) and θ is the scattering angle. The average crystallite size of KAlSiO_4 is 220 nm. The theoretical result is line with the FESEM images showing an average particle size of the crystal around 250 nm. Comparing the results with Kimura et al. [19], a slightly bigger crystallite size is obtained in this study compared to the 100 nm crystal size reported by the researchers after the thermal treatment of nano-sodalite with K_2CO_3 .

FESEM morphologies

The morphological characterisations of the synthesised products with the effect of the KOH concentrations and reaction temperatures are illustrated in Figure 3 and 4, respectively.

Figure 3a shows square pillars-like shaped crystals corresponding to zeolite F when the metakaolinite was treated with 0.75 M KOH while Figure 3b shows hexagonal kalsilite crystals after 1.25 M KOH was used. Figure 4 presents the effect of the reaction temperatures on the product morphologies. Square pillar-like shaped crystals of zeolite F (Figure 4a) were observed when the reaction was carried out at the temperature 180 °C. On the other hand, by further heating to 250 °C resulted in hexagonal crystals corresponding to the kalsilite formation (Figure 4b).

CONCLUSIONS

In this work, kalsilite was successfully synthesised using metakaolinite and KOH as precursors via the hydrothermal method while the effect of the KOH concentrations and reaction temperatures towards the crystal formation have been studied. Metakaolinite transforms into kalsilite when treated with 1.25 M of KOH in a hydrothermal reaction at 190 °C for 24 hours. The average crystallite size of the formed KAlSiO_4 was 220 nm after being calculated by using Scherrer's equation. Higher KOH concentrations increase the product's crystallinity while, at lower KOH concentrations, zeolite F and muscovite were obtained as the dominant products. A lower reaction temperature, up until 180 °C, is not favourable for the kalsilite formation, instead, square pillar-like shapes of zeolite F and muscovite are formed. On the other hand, 190 °C was seen as adequate to fully transform metakaolinite to hexagonal kalsilite and is supported by the XRD and FESEM results.

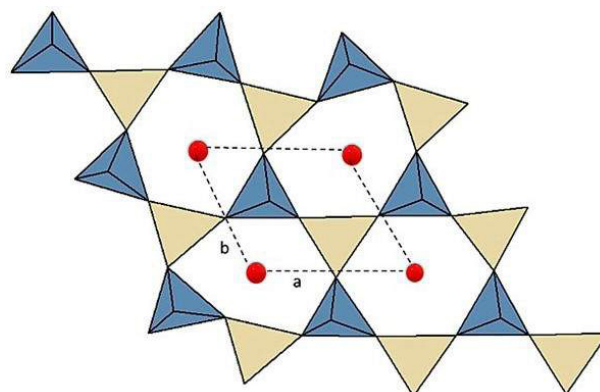
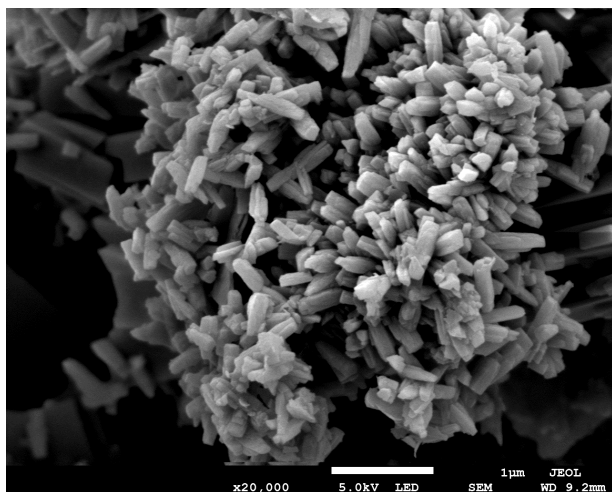
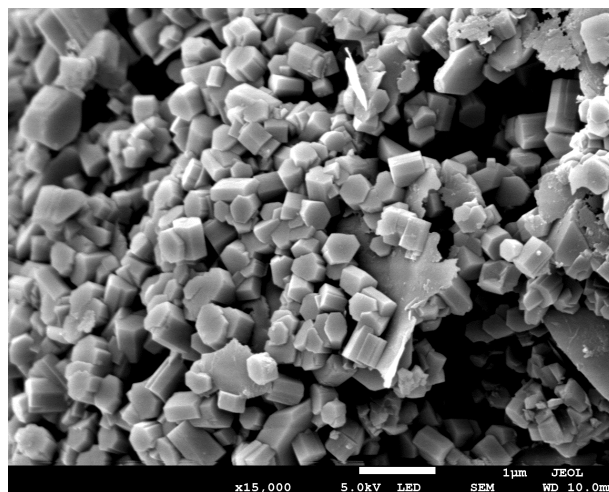


Figure 5. The crystal structure of the P6_3 kalsilite view along the c -axis. The red balls are K atoms, the Si-centred tetrahedra pointing downward (D) are brown, while the Al-centred tetrahedra pointing upward (U) are blue (modified from [20]).

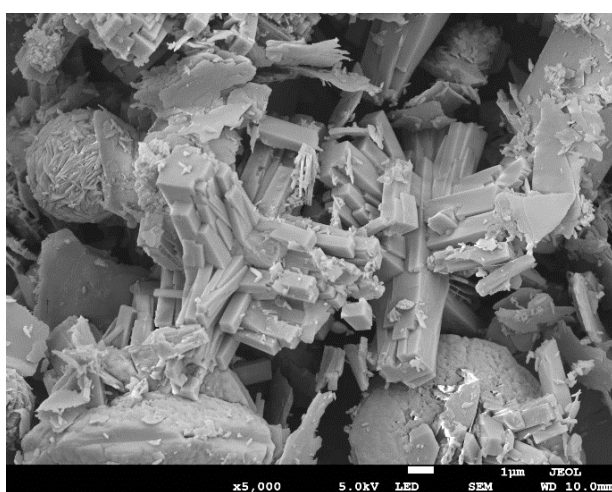


a) 0.75 M KOH

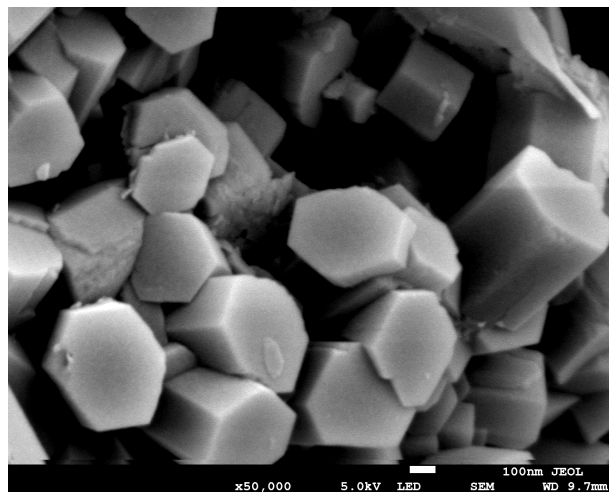


b) 1.25 M KOH

Figure 3. FESEM images of the products formed after being treated at 190 °C.



a) 180 °C



b) 250 °C

Figure 4. FESEM images of the products formed at different temperatures after being treated with 1.25 M KOH.

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