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Transformation of Kaolin to Kalsilite: Effect of KOH Concentration and Reaction Temperature

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Kalsilite was synthesized *via* a hydrothermal method using kaolin as a silica and alumina precursor and potassium hydroxide (KOH) as a potassium source. The effects of KOH concentration and reaction temperature were investigated. X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses indicated that kalsilite was formed as a result of the hydrothermal reaction of kaolin at 190 °C in 0.75 M KOH for 24 hours. Higher KOH molarity was found to increase the crystallinity of the product while 190 °C was sufficient to convert kaolin to kalsilite. However, zeolite W was the dominant product at lower KOH concentrations and temperatures.

Key words: Kaolinite; hydrothermal; zeolite

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Kalsilite, $KAlSiO_4$, is a basic mineral silicate of the feldspathoids group that typically co-exists with olivine, melilite, clinopyroxene, phlogophite, nepheline, and leucite, which are mainly formed in K-rich and silica undersaturated volcanic rocks [1]. It has a framework structure of linked $(Si,Al)O_4$ tetrahedra and exists in several polymorphic forms. Recently, kalsilite has been found to be suitable for use in a bioactive glass composite for dental veneering, due to its high thermal expansion coefficient [2]. Kalsilite has also been studied as precursor of leucite which is an essential component in porcelain-fused-to-metal (PFM) and ceramic dental-dental restoration systems [3].

Several methods for the synthesis of kalsilite have been reported in the literature, such as cation exchange from nepheline [4,5], solid-state synthesis reaction from zeolite, kaolinite or other silicate compounds [6,7] and hydrothermal methods from muscovite and syenite [8,9]. Despite the fact that several techniques are available for kalsilite synthesis, mixtures of kalsilite polymorphs are produced by cation exchange and solid-state reactions. Of these available methods, hydrothermal synthesis is an economical and relatively simple method to produce pure materials with micro- to nano-size particles at low temperature. However, relatively high pressure (up to 1000 bars), a longer reaction time (15 days) and a higher temperature (up to 600 °C) are needed to obtain kalsilite with a hydrothermal method where muscovite is used as a precursor [7]. Kaolin is a clay mineral that is abundant in nature, and is used in numerous industries such as catalysis, plastics, and cement production. Its main component is the mineral kaolinite ($Al_2Si_2O_5(OH)_4$). It is a phyllosilicate which comprises alternating sheets of SiO_4 tetrahedra and Al octahedra of O and OH, with a theoretical composition of 46.54% SiO_2, 39.5% Al_2O_3 and 13.96% water [10].

Despite its wide availability, only a small number of studies have reported the conversion of kaolin to kalsilite, particularly using a hydrothermal synthesis procedure. Brachold and Aneziris, (2012) [11] successfully synthesized kalsilite from kaolin at 200 °C using a hydrothermal method, to produce heat insulation materials. However, the study used high concentration KOH (50% w/w), which increases production costs and could have negative effects on the environment if not handled appropriately. The present study reports the effects of KOH concentration and reaction temperature on the formation of kalsilite from kaolin by hydrothermal treatment, followed by characterization of the products by XRD and SEM.

MATERIALS AND METHOD

Kaolin purchased from Sibelco Co. was used as the main Al_2O_3 and SiO_2 sources. Its chemical composition is presented in Table 1. To achieve the desired composition, the additional Al_2O_3 was sourced from $Al(OH)_3$. KOH in the form of pellets (Merck Ltd.) and distilled water were used for the preparation of the alkaline solution.

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Table 1. Chemical composition of the purchased kaolin

Oxide content in wt.%							
SiO_2	Al_2O_3	K_2O	Fe_2O_3	MgO	TiO_2	CaO	L.O.I
49.60	34.20	1.80	1.01	0.55	0.52	0.22	12.10

1.0 g kaolin was mixed with 100 mL of KOH solution of various concentrations from 0.50 M to 1.25 M in stainless-steel hydrothermal reactors and heated from 170 °C up to 220 °C at 10 °C/min for 24 h. The pressure of the reactor was approximately equal to that of the vapour pressure of water 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.

Characterization

X-ray diffractograms of the untreated kaolin and synthesized products were obtained using a Philips X'pert Pro PW3040 XRD from PANalytical. Data collection was carried out in the range of 2θ: 5 – 80°, step size of 0.02° under Cu-Kα = 1.54056, 30 mA and 40 kV. Phase identification was performed by searching the 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 normalized XRD intensities of the major reflection for each material.

The morphologies of the solid phases were examined using an SEM by ZEISS (MA10) where the samples were coated with gold. Each sample was coated with a gold layer to avoid charging effects from free electrons and to obtain a clear image. An inert element such as gold (Au) discharges the free electrons liberated when the electron beam bombards the sample surface. Coated samples were observed by SEM under 5000x to 30000x magnification.

RESULTS AND DISCUSSION

The effect of KOH concentration and reaction temperature on the formation of kalsilite from kaolin was investigated to determine the optimum conditions for the reaction. The influence of these parameters is discussed below.

Effect of KOH Concentration

The decomposition reaction of kaolinite in KOH solution can be represented by the following equation:

$$Si_2Al_2O_5(OH)_4 + 2KOH \longrightarrow 2KAlSiO_4 + 3H_2O$$

The stoichiometry above shows that every 1 mole of kaolinite requires 2 moles of KOH in order to obtain 2 moles of kalsilite. However, in this study, the formation of kalsilite from kaolinite required almost 10 times more KOH compared to the theoretical value for the reaction. This result is consistent with the findings reported by Beccero *et al*. (2009) [12]. Results for the synthesis of kalsilite using various KOH concentrations are shown in Figure 1.

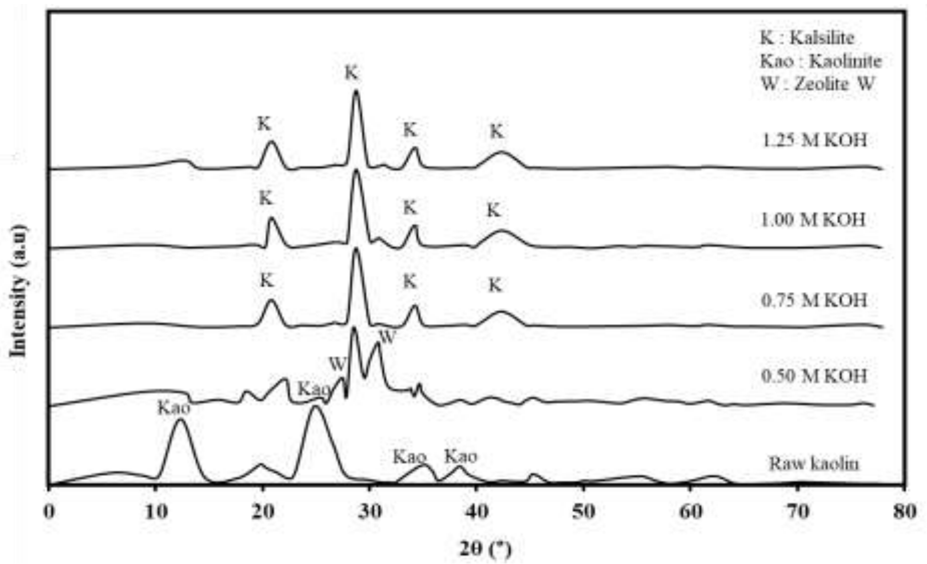

Figure 1. XRD diffractograms of hydrothermal reaction products obtained with various KOH concentrations at 190 °C.

In Figure 1, 0.75 M KOH shows the most significant peaks at 20.8°, 28.8°, 34.2° and 42.4°. These observations are also supported by findings from Kakutani *et al.* (2017) [13] after the hydrothermal reaction of silica powder with 4 M KOH and aluminium nitrate for 336 h. Compared with the values in the literature [11,14,15], the present study uses much lower KOH concentrations, which reduces production costs as well as helps to conserve the environment. It is suggested that 0.75 M of KOH is optimal for the transformation of kaolin into kalsilite. A further reduction in KOH concentration promotes several diffraction peaks corresponding to zeolite W and quartz, indicating the precursor was not completely decomposed due to a lack of K^+ ion available for kalsilite formation.

Effect of Reaction Temperature

Kalsilite transformation reactions were carried out at different temperatures with 0.75 M KOH and a reaction time of 24 hours. Figure 2 shows that the transformation of kalsilite from kaolin increases steadily with the increase in reaction temperature from 170 °C to 220 °C.

Several diffraction peaks associated with quartz and zeolite W were observed at lower reaction temperatures, suggesting an incomplete transition to the metastable phase. This is most likely due to the activation energy barrier for the nucleation process. The formation of a metastable form of kalsilite began at 170 °C. The diffraction peaks of quartz and zeolite W disappeared at 190 °C and three new peaks assigned for kalsilite can be observed due to the complete transformation of the metastable phase to kalsilite. Further increases in temperature up to 220 °C showed identical peaks of kalsilite. A similar trend has been reported by Meng *et al.* (2018) [16], where zeolite W was obtained at 180 – 190 °C due to the incomplete decomposition of potassic rocks. It was also reported that microcline and albite peaks appeared at the same temperature range.

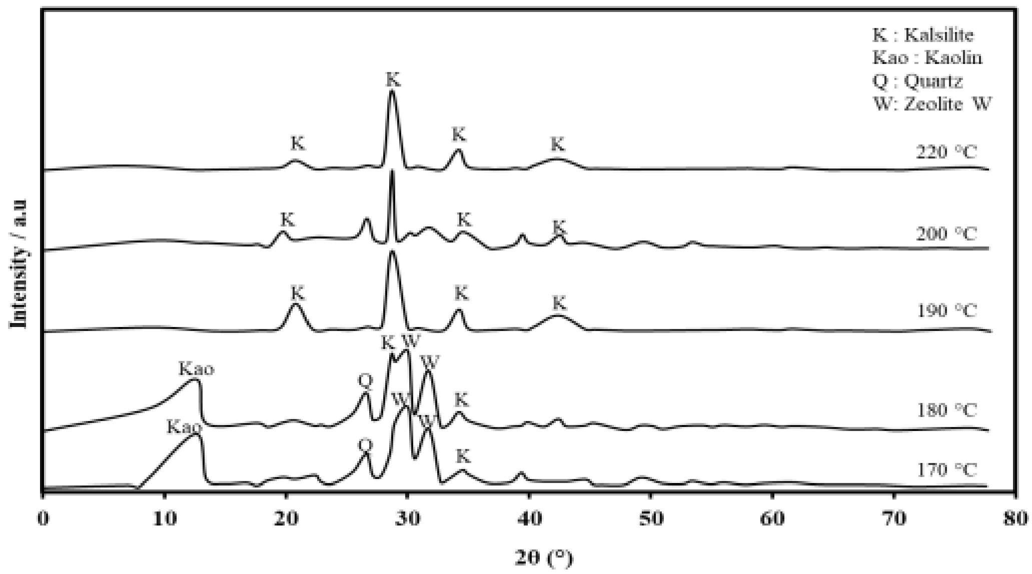

Figure 2. XRD diffractograms of hydrothermal reaction products obtained with 0.75 M KOH at various reaction temperatures.

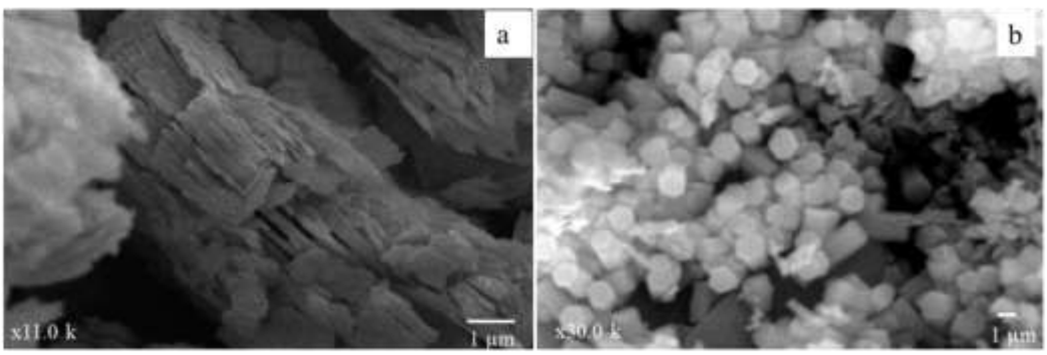

Figure 3. SEM images of a) kaolin precursor and b) kalsilite synthesized at 190 °C using 0.75 M KOH

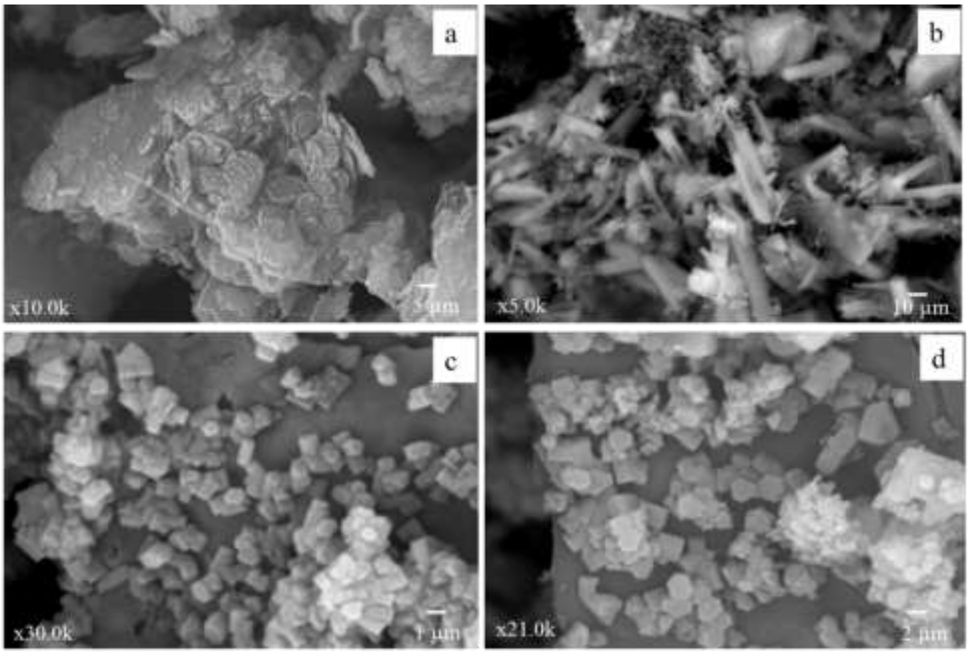

Figure 4. SEM images of the products after treatment with a) 0.25 M KOH, b) 0.50 M KOH, c) 0.75 M KOH and d) 1.0 M KOH at 190 °C.

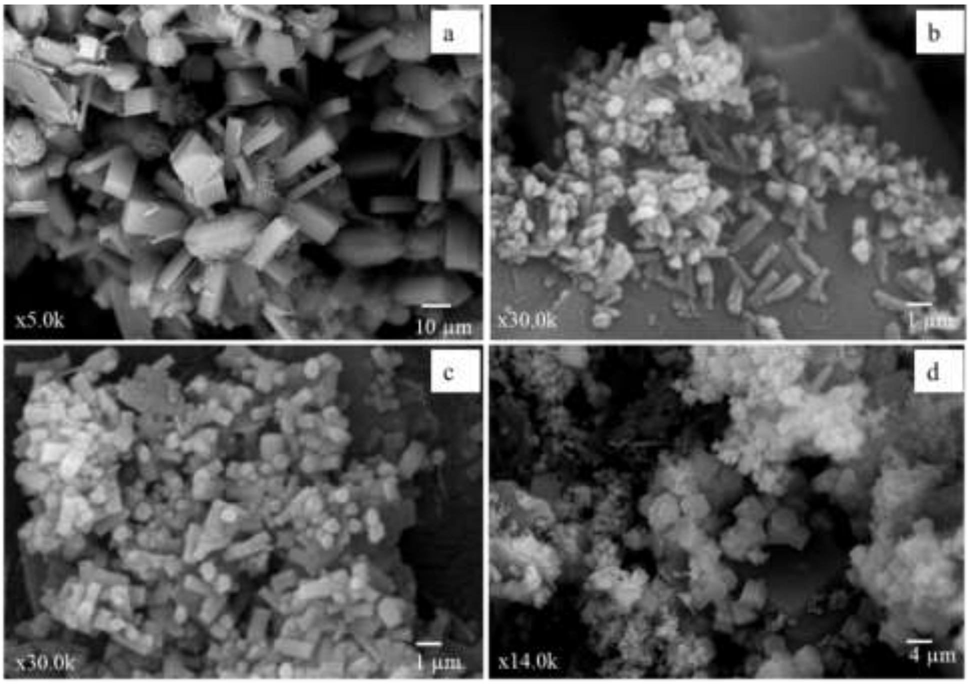

Figure 5. SEM images of the products obtained when treated with 0.75 M KOH at different temperatures a) 170 °C, b) 180 °C, c) 190 °C and d) 200 °C .

SEM Morphologies

The SEM images of kaolin and synthesized kalsilite are shown in Figure 3. Kaolin can be described as having a flake-like structure while kalsilite has hexagonal platelets with clean edges. Morphological characterizations of the synthesized products with the effect of KOH concentration and reaction temperature are illustrated in Figures 4 and 5, respectively.

Figure 4(a) shows the rough and scraggy morphology of the product which corresponds to the incomplete transformation of kaolin to kalsilite/zeolite W. On the other hand, Figure 4(b) shows square pillar-shaped crystals corresponding to zeolite W. The same morphology was reported in several previous studies [16,17]. The hexagonal crystals of kalsilite were observed both in figure 4(c) and 4(d) while the latter shows an enhanced version of it.

Figure 5 presents the effect of reaction temperature on the morphology of the product. Square pillar-shaped crystals of zeolite W were observed when the reaction was carried out at temperatures below 190 °C (5(a) and 5(b)). In comparison, hexagonal crystals of kalsilite can be seen when the reaction was carried out at 190 °C and 200 °C, respectively.

CONCLUSION

In this work, kalsilite was successfully synthesized using kaolin and KOH as precursors *via* a hydrothermal method, and the effects of KOH concentration and reaction temperature on the crystal formation were studied. Kaolin transformed into kalsilite when treated with 0.75 M of KOH in a hydrothermal reaction at 190 °C for 24 h. Higher KOH concentrations increased the crystallinity of the kalsilite formed, while at lower KOH concentrations, zeolite W was the dominant product. Reaction temperatures of 180 °C and below were not favourable for kalsilite formation, whereby zeolite W was formed instead. However, 190 °C was sufficient to convert kaolin into kalsilite. These results were supported by XRD and SEM analyses.

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