The hydrothermal conversion of kaolinite to kalsilite: Influence of time, temperature, and pH

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ABSTRACT

Kalsilite (the low-temperature form of KAlSiO₄) is used as the precursor of leucite, an important component in porcelain-fused-to-metal and ceramic-restoration systems, and it has also been proposed as a high-thermal expansion ceramic for bonding to metals. The present study reports the hydrothermal synthesis and characterization of pure kalsilite from kaolinite in subcritical conditions, as well as the characterization of the intermediate products by means of XRD, ²⁹Si and ²⁷Al MAS NMR, IR, SEM, and TEM. Effects of time, temperature, and pH on the reaction products are analyzed. The experimental data indicate that pure kalsilite is obtained after hydrothermal treatment of kaolinite at 300 °C for 12 h in 0.5 M KOH solution. Longer reaction times increase the crystallinity of the structure, whereas lower reaction times give rise to the metastable ABW-type KAlSiO₄ polymorph. Lower temperatures are not sufficient to produce kalsilite, but zeolite W is obtained instead as the unique reaction product. Finally, the pH of the aqueous solution in contact with kaolinite is an important parameter for the synthesis of kalsilite, which must be ≥13.70.

Keywords: Kalsilite, kaolinite, hydrothermal synthesis, MAS NMR, XRD

INTRODUCTION

KAAlSiO₄ is a feldspathoid that, like zeolites, has a framework structure of linked (Si,Al)O₄ tetrahedra. KAAlSiO₄ exists in several polymorphic forms (Cellai et al. 1997): (1) low kalsilite (P6₃, known simply as kalsilite) (Perrotta and Smith 1965), which is a stuffed tridymite derivative occurring mainly in K-rich silica undersaturated volcanic rocks, and (2) its high-temperature form known as high kalsilite (space group P6₃mc) (Kawahara et al. 1986). Another high-temperature polymorph is the orthorhombic KAAlSiO₄-O1, which has an AlSiO₄ framework that is a topological variant of tridymite with space group P12₁1 (Gregorkiewitz et al. 2008) and undergoes a mineral transformation into KAAlSiO₄-O2 at >1450 °C (Cook et al. 1977). Another phase named kaliophilite has been described with a unit cell that is a multiple of the kalsilite cell (space group P6₃22; Cellai et al. 1992). Finally, a metastable polymorph of KAAlSiO₄ was prepared by Minor et al. (1978) by K⁺ exchange of orthorhombic RbAlSiO₄; it shows orthorhombic symmetry (Ccmm) and retains the ABW zeolite compatible unit cell of RbAlSiO₄ showing doubling of the b- and c-axes relative to the normal ABW-type cell; this polymorph transforms into normal “low kalsilite” at 1100 °C (Norby and Fjellvåg 1992).

Kalsilite has been studied as the precursor of leucite, an important component in porcelain-fused-to-metal (PFM) and ceramic dental-restoration systems (Zhang et al. 2007). Kalsilite has also been proposed as a high-thermal expansion ceramic for bonding to metals (Bogdanoviciene et al. 2008). Very recently, nano-kalsilite has been demonstrated to show an excellent and highly improved oxidation activity toward carbon in diesel soot combustion (Kimura et al. 2008). All of these uses require the production of single-phase kalsilite.

Reviews of related literature show very different methods for the synthesis of kalsilite: (1) cation exchange from nepheline (Dollase and Freeborn 1977; Stebbins et al. 1986; Sobrados and Gregorkiewitz 1993); (2) solid-state synthesis from oxides or zeolite (Smith and Tuttle 1957; Dimitrijevic and Dondur 1995; Heller-Kallai and Lapides 2003; Kosanović et al. 1997); (3) sol-gel methods using TEOS or SiO₂ as a Si source (Hamilton and Henderson 1968; Bogdanoviciene et al. 2007); (4) crystallization from molten salts (Sobrados and Gregorkiewitz 1993); and (5) hydrothermal methods from muscovite or oxides as substrates (Barrer et al. 1951, 1956, 1968, 1972; Kopp et al. 1961; Andou and Kawahara 1984). Many of these methods give rise to secondary products or to poorly ordered kalsilite.

Compared with other synthesis methods, the hydrothermal method is economical and convenient to prepare pure materials with fine particle size at low temperature. However, the hydrothermal methods referenced above to obtain kalsilite, use high pressures (1000 bars), relatively high temperatures (up to 600 °C), and long reaction times (15 days), with a consequent increase in the production cost. The present study reports the hydrothermal transformation of kaolinite, a natural and readily available precursor, into kalsilite at subcritical conditions with a full characterization of the intermediate and final reaction products by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), transmission electron microscopy (TEM), and energy dispersive X-ray spectrometry (EDX). Effects of time, temperature, and pH on the synthesis products are analyzed.

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