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THERMAL REACTIONS OF KAOLINITE WITH POTASSIUM CARBONATE

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Abstract

It was previously established that kaolinite reacts with K_2CO_3 on heating to form products of $KSiAlO_4$ composition. In the present study we investigated the solid state reactions with K_2CO_3 of four kaolinites of different thermal stability. The mixtures were calcined at temperatures ranging from 400–700°C and washed before or after boiling with the remaining K_2CO_3. FTIR spectra indicated that the X-ray amorphous material formed after calcining the mixtures at 500–590°C had a $SiAlO_4$ tetrahedral framework. Attempts to convert the products to zeolites gave promising results. After calcining at 700°C under atmospheric pressure synthetic kaliophilite ($KSiAlO_4$) was obtained. These conditions are appreciably milder than previously reported for kaliophilite syntheses. Conversion to kalsilite increased with decreasing thermal stability of the original kaolinite.

In similar reactions with KCl much less K was incorporated into the amorphous phase and kaliophilite was not obtained. The reactions of the four kaolinites with K_2CO_3 or with KCl were similar in trend, but differed in detail.

Keywords: kaliophilite, kalsilite, kaolinite, potassium carbonate, thermal reactions, zeolite

Introduction

Reactions of kaolinite at elevated temperatures have found many applications. In recent years there has been considerable interest in the use of metakaolinite, obtained by heating kaolinite, as a starting material in zeolite syntheses [1–13]. High temperature reactions of kaolinite have long been of interest due to their importance in ceramics. The kaolinite–mullite reaction series has been studied exhaustively. High temperature changes that occur on heating kaolinite in the presence of various salts are less well documented.

To obtain zeolite from metakaolinite, this is reacted with alkali, usually NaOH. Kaolinite is a layer silicate composed of sheets of SiO_4 tetrahedra and AlO_6 octahedra. On heating to metakaolinite the Al changes from 6- to 4- and 5-coordination. The silicate sheets are preserved in a distorted form. Rocha and Klinowski [14] compared various properties of metakaolinite with the coordination of Al determined by solid-state NMR.

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They showed that the reactivity was greatest when 6-coordinated Al was lowest and 4- and 5-coordinated Al predominated. This occurred at 750–800°C. At higher temperatures 6-coordinated Al reappeared. The temperature range of 750–800°C is therefore favoured for preparing the most reactive metakaolinite, which is used as a starting material for zeolite synthesis.

Zeolites have a framework structure composed of linked (Si,Al)O_4 tetrahedra. The question whether transformation of metakaolinite to zeolites involves complete breakdown of the structure and nucleation of monomers in solution or whether structural elements are inherited is still under discussion. In his summary of some problems of zeolite crystallization from heterogeneous aluminosilicate systems, Zhdanov [15] suggested that nucleation occurs in the liquid phase, but that structural blocks are transferred from the aluminosilicate skeleton of the gel to the liquid phase. According to this view both structural inheritance and polymerization of dissolved species play a part in the second stage of zeolite crystallization. Gualteri *et al*. [9] attributed the greater reactivity of metakaolinite compared with that of kaolinite to its short-range structural similarity to zeolite nuclei. Several authors observed that the products obtained from variously preheated kaolinite differ from those derived from a mixture of aluminosilicates of similar chemical composition [3–5]. This may be regarded as support of the concept of structural inheritance, though it may also be attributed to differences in solubility of the reactants. Rocha *et al*. [2] concluded that a direct solid state transformation of metakaolinite to a zeolite precursor cannot be ruled out, and this appears to summarize the evidence to date.

Felspathoids are high temperature phases of composition $MSiAlO_4$, (M=Li, Na or K). Like zeolites they have framework structures of linked (Si,Al)O_4 tetrahedra. They were obtained from kaolinite by heating with the appropriate alkali carbonate [16–18]. Kubo and coworkers showed that such conversions of kaolinite to felspathoids are at least partly topotactic, with some structural continuity throughout. Felspathoids were also formed by heating zeolites of corresponding chemical composition and these transformations too were topotactic [19].

If the transformations from kaolinite to zeolites or to felspathoids involve structural inheritance, it may be reasoned that they would be facilitated by reactions which reduce the coordination of Al from 6 to 4 and result in a network of linked (Si,Al)O_4 tetrahedra. In previous studies [18, 20] it was shown that kaolinite reacts with alkali halides and other alkali salts on heating, according to the equation

$$2SiO_2\cdot Al_2O_3\cdot 2H_2O+2y\mathrm{MA}\rightarrow 2SiO_2\cdot Al_2O_3\cdot y\mathrm{M}_2O+(2-y)H_2O+2y\mathrm{HA} \qquad (1)$$

where M is a Li, Na or K ion. In the course of this reaction Al ions became 4-coordinated and were incorporated into the tetrahedral sheets. The value of y differed greatly for the various salts used. It is linearly correlated with the solubility of the salt in hot water (Fig. 1a). The course of these reactions can be monitored by the shifts in the position of the Si–O stretching vibrations, which shift to lower frequencies as the SiO_4 network is converted into a Si,AlO_4 network (Fig. 1b).

It may be expected that thermal reactions forming Si,AlO_4 tetrahedral networks rather than metakaolinite may facilitate conversion of kaolinite to zeolites or fels-

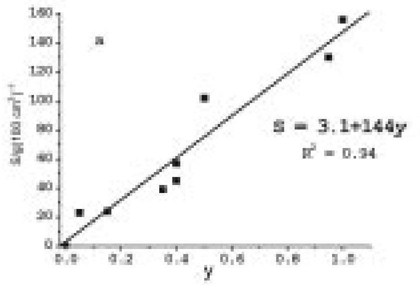

Fig. 1a Correlation between solubility (*S*) of salt in hot water and *y* ($2SiO_2{\cdot}Al_2O_3{\cdot}yM_2O$)

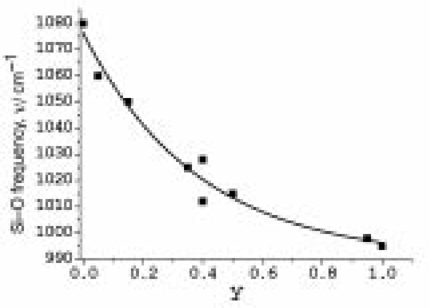

Fig. 1b Correlation between stretching frequency (ν) of T–O (*T*=Si,Al) and *y* in ($2SiO_2{\cdot}Al_2O_3{\cdot}yM_2O$). Graphs are based on data of Table 1 in [18]

pathoids. K_2CO_3 is very soluble. In the previous studies it was shown that *y* in Eq. (1) reached a value of 1 after heating mixtures of kaolinite with K_2CO_3 at 590°C for only 30 min at atmospheric pressure. On more prolonged heating kaliophilite, $KSiAlO_4$, began to crystallize.

The objective of the present study was to establish whether pretreatment by heating with K_2CO_3 would promote conversion of kaolinite to zeolites or felspathoid under milder conditions than are otherwise required. Kaolinites vary in their reactivity and thermal stability. The previous experiments on kaolinite – salt interactions – were carried out with one kaolinite only. In the present study the reactions of four kaolinites of different thermal stability were compared.

Experimental

Materials

Four kaolinites were used KGa1, well crystallized, CMS reference clay, Georgia; KGa2, poorly crystallized, CMS reference clay, Georgia; EC, English China Clay ‘Supreme’, Cornwall; UB, well crystallized, Umm Bogmah, Sinai.

The coarse fraction was separated by sedimentation. X-ray diffraction showed the following crystalline impurities: KGa1, KGa2 and UB – anatase, EC – muscovite.

The reagents used were of Analar quality.

Method

The clay fractions were mixed with the reagents in the ratio 1:10 by mass and ground manually in an agate mortar for 5 min. The ground mixtures were maintained at the temperatures indicated for 1 h. After cooling in air they were 1) washed free of excess carbonate (samples marked w); or 2) water was added and the suspension was boiled for 1 h and subsequently washed (samples marked b, w).

FTIR spectra of the samples in KBr pellets were obtained with a Bruker Tensor 27 spectrometer. XRD patterns were recorded on a Philips automatic powder diffractometer (PW 1710), CuK_α radiation.

Results

Thermal stability of the samples

The four kaolinites studied differ in their thermal stability. The IR spectra of samples calcined at 500°C were largely unchanged, but a broad shoulder appeared at about 1200 cm^{-1} in the spectrum of sample KGa2. It was weaker in the spectrum of sample EC, very weak in that of UB and absent in the spectrum of KGa1. After heating to 590°C some unchanged kaolinite was still detected in the XRD pattern of KGa1, barely in that of UB, but not in that of either EC or KGa2. Kaolinite was converted to metakaolinite, which is amorphous to X-rays, giving rise to a broad hump with a maximum that extends from ~3.8–3.5A. The IR spectra of metakaolinite derived from samples KGa1, KGa2 and UB correspond to those extensively described in the literature, with broad absorption bands at about 1086, 814 and 458 cm^{-1} (Fig. 2a). The spectrum of heated EC differs slightly, with absorption maxima at 1076, 802 and 476–458 cm^{-1}. This is due to the overlap of the spectrum of the muscovite impurity, which remains unchanged on heating up to 700°C.

In summary, the thermal stability of the kaolinites studied decreases in the order KGa1>UB>EC>KGa2. No crystalline phases were produced by heat treatment up to 700°C.

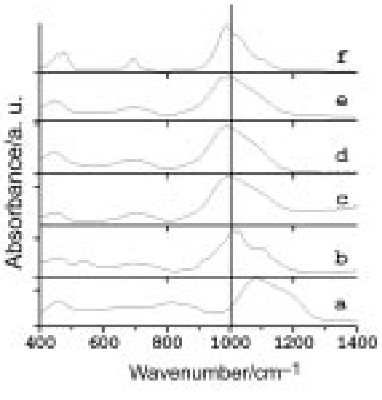

Fig. 2 FTIR spectrum of KGa2 a – heated 700°C; b – to f – +K_2CO_3, heated, w: b – 400°C; c – 500°C; d – 550°C; e – 590°C; f – 700°C

Reactions with K_2CO_3

XRD traces of all the kaolinite–K_2CO_3 mixtures calcined at 400°C showed the characteristic reflections of kaolinite, but it is evident from the background that part of the material was X-ray amorphous (Fig. 3). The diffuse background increased in the order KGa1<UB<EC<KGa2, which corresponds to the order of decreasing thermal stability of the original kaolinites.

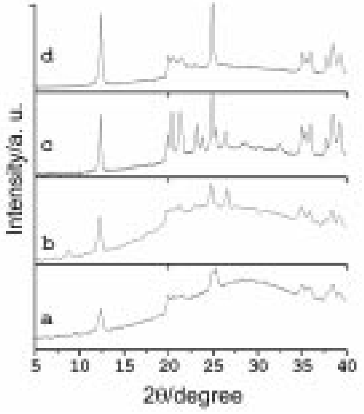

Fig. 3 XRD patterns of kaolinite +K_2CO_3 mixtures heated 400°C, w: a – KGa2; b – EC; c – UB; d – KGa1

Reflections due to unchanged kaolinite were absent in the XRD pattern of the KGa2–K_2CO_3 mixture calcined at 500°C, but could still be discerned after heating mixtures of the other samples at 550°C. After heating at 590°C kaolinite peaks persisted only with the KGa1–K_2CO_3 mixture. All the samples contained much amorphous material. The spacing of the maximum of the broad hump is less than that of metakaolinite. It differed slightly for the four kaolinites and changed with temperature, which indicates that some short-range order was preserved.

Figures 2b–f show FTIR spectra of KGa2–K_2CO_3 mixtures calcined at various temperatures. The corresponding spectra of the other kaolinites were similar, but the temperatures at which the thermal changes commenced and the exact positions of the absorption bands differed.

After heating at 400°C all the mixtures after washing showed IR absorptions characteristic of kaolinite. The spectra of the amorphous phase obtained after calcining kaolinite–K_2CO_3 mixtures at 500°C and above differed from the spectrum of metakaolinite, as previously reported [18, 20]. The maxima of the absorptions at ~1080 and 802 cm^{-1} of metakaolinite were shifted to ~990–1000 and ~690–700 cm^{-1}, respectively, and the absorption at about 458 cm^{-1} was reduced to 444 cm^{-1}. The frequency of the stretching vibrations at ~1000 and ~700 cm^{-1} differed by a few cm^{-1} for the four samples and changed with temperature. The frequency of the principal absorption at ~1000 cm^{-1} decreased by 5–10 cm^{-1} between 500 and 550°C and remained almost unchanged on further heating to 590°C for each series of samples. Absorptions attributed to unmodified metakaolinite were not detected in any of the calcined kaolinite–K_2CO_3 mixtures. From Fig. 1b it can be inferred that the value of y (Eq. (1)) approaches 1 after heating to only 500°C.

Samples boiled with the remaining K_2CO_3 after dry heating gave rise to FTIR spectra with bands that were shifted slightly to higher wavenumbers, as shown for sample UB in Fig. 4. Small shifts also occurred in the maximum of the broad hump observed in the corresponding X-ray patterns. These changes may be due to selective leaching of some Al at the prevalent pH of the suspension (~9.5). Mixtures with KCl did not show this effect (see later).

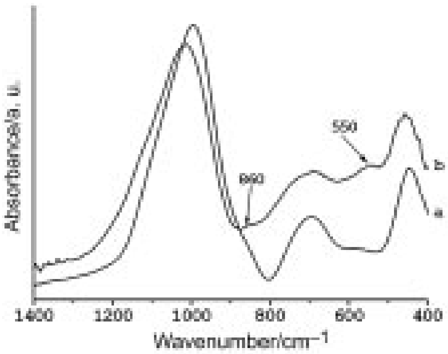

Fig. 4 FTIR spectrum of UB+K_2CO_3 mixture heated 590°C: a – w; b – b,w

In samples heated at 590°C and boiled, additional absorptions appeared at ~860 and ~550 cm^{-1} (Fig. 4b). Moreover, some XRD patterns of mixtures heated at 590°C showed a small peak at about 8A, which became more pronounced after boiling (Fig. 5a). These features indicate the development of a new, as yet undefined phase, possibly zeolite.

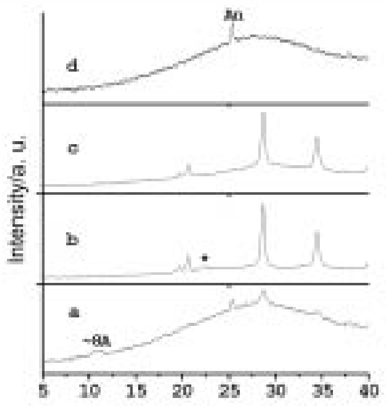

Fig. 5 XRD patterns of KGa2+K_2CO_3 mixture: a – heated 590°C, b,w; b – heated 700°C, w; c – KGa1+K_2CO_3 mixture, heated 700°C, w; d – KGa2+KCl mixture, heated 700°C, w; An=anatase, *=kalsilite

After heating the mixtures at 700°C a FTIR spectrum similar to that of synthetic kaliophilite [21] was obtained (Fig. 2f). The XRD pattern of these samples also corresponded to that of synthetic kaliophilite [22]. With the KGa2–K_2CO_3 mixture a distinct additional reflection appeared, which corresponds to kalsilite (Fig. 5b). Most of the other reflections of kalsilite overlap those due to kaliophilite [22]. Kalsilite was barely detectable in the diffractograms of the other kaolinite–K_2CO_3 mixtures (Fig. 5c). A weak absorption that may be attributed to kalsilite was observed in the IR spectrum of the KGa2–K_2CO_3 mixture after heating at 700°C.

The strongest reflection of synthetic kaliophilite is at 3.10A. Before distinct peaks were obtained, the maximum of the broad hump corresponding to the amorphous phase shifted to ~3.1A. This occurred at 550°C with the KGa2–K_2CO_3 mixture and at 590°C with the other samples. After heating at 590°C the KGa2 mixture already showed the strongest reflections of kaliophilite (Fig. 5a).

It is noteworthy that the reflections of anatase that were present in the XRD patterns of KGa2 (Fig. 5b), KGa1 (Fig. 5c) and UB disappeared after heating the kaolinite–K_2CO_3 mixtures at 700°C. They persisted in diffractograms of similarly treated kaolinites without additives and in mixtures with KCl (Fig. 5d, see later).

Reactions with KCl

The FTIR spectra and diffractograms of samples heated with KCl were similar to those previously described [18, 20]. After heating at 590°C the maxima of the broad T–O stretching vibrations occurred at ~1030 and 740 cm^{-1}. The exact positions differed with the four samples and changed with temperature. These absorptions correspond to a value of y of approximately 0.3 (Fig. 1b), much less than for similarly heated samples with K_2CO_3. With all the samples except for sample KGa1, part of the mixture was converted to an X-ray amorphous phase after heating at 500°C. However, some kaolinite still persisted in all the samples except KGa2 after calcining at 590°C. In fact more kaolinite was preserved in these mixtures than in similarly heated kaolinites without additives. In contrast to the K_2CO_3 treated samples, boiling the preheated specimens with the remaining salt did not affect the spectra. After heating at 700°C the IR absorptions were shifted to 1010–1015 and 705–720 cm^{-1}, respectively (Fig. 5d), corresponding to y=0.6. Kaliophilite was not formed and anatase persisted.

Discussion

The FTIR spectra of the products obtained with the four kaolinite–K_2CO_3 mixtures heated at 500–590°C show strong absorptions at ~1000, 690 and 450 cm^{-1}. Similar spectra were obtained with a different kaolinite in a previous study. The chemical composition of the anhydrous amorphous phase was $KSiAlO_4$ [18, 20].

Absorptions at ~1000, 690 and 450 cm^{-1} are characteristic of the Si,AlO_4 tetrahedral framework of zeolitic structures. In most of the spectra obtained after calcining the kaolinites with K_2CO_3 at 500–590°C these were the only absorptions observed in the 1400–400 cm^{-1} range. However, in some of the samples preheated at 590°C and subsequently boiled, weak absorptions appeared at ~850 and 600–550 cm^{-1} (Fig. 4) and a weak XRD reflection was observed in the vicinity of 8A. The IR spectra resemble those of the precursor phase obtained in the synthesis of a type A zeolite by alkali treatment of metakaolinite ([2], Fig. 4; [4], Fig. 3; [7], Fig. 5) as well as the spectrum of an amorphous phase obtained after ball milling and heating K-exchanged Linde 4A zeolite, ([23], Fig. 2). The ball-milled zeolite was transformed to kaliophilite and kalsilite on further heating. It may be speculated that the features observed after heating and boiling kaolinite–K_2CO_3 mixtures indicate incipient crystallization of a zeolite precursor. Although the evidence is not conclusive, it suggests that it may be feasible to find suitable, mild conditions for a successful zeolite synthesis. This requires further study.

After heating mixtures of kaolinites with K_2CO_3 at 700°C they were converted to a well crystallized phase, denoted 'synthetic kaliophilite' by Smith and Tuttle [22]. Some synthetic kaliophilite was even formed after heating the poorly crystallized kaolinite KGa2 at 590°C. On heating at 700°C some kalsilite was formed in addition to synthetic kaliophilite.

At least 7 polymorphs with chemical composition $KSiAlO_4$ have been identified [24]. The relationship between them is complex and identification is not always unambiguous. They crystallize with a 'stuffed tridymite structure', with K as stuffing ions. Si–Al ordering and distortion of the structure account for most of the transitions. Tuttle and Smith [25] asserted that synthetic kaliophilite is a metastable phase formed from appropriate precursors at all temperatures under atmospheric pressure. This is borne out in studies of zeolite transformation to $KSiAlO_4$ (e.g. [21]) and by the results presented here. Under hydrothermal conditions kalsilite was formed [22, 26, 27]. Conversion of zeolites to a $KSiAlO_4$ phase requires temperatures above 950°C [21, 23]. Synthetic kaliophilite crystallizes in the system $P6_3/m2/m2/c$ or $P6_3mc$. Kalsilite has similar cell-dimensions, but the symmetry is lower. Due to ubiquitous twinning it is uncertain whether the spacegroup is $P6_3$ or whether the symmetry is orthorhombic, pseudohexagonal [26]. The spacegroup $P6_3/m2/m2/c$ implies complete Si–Al disorder and an undistorted structure. The lower symmetry of kalsilite requires some Si–Al ordering and distortion of the structure [26, 28]. As pointed out by Abbot [29] it is unusual for the polymorph with highest symmetry to form at low temperatures. He therefore assumed that the polymorph with spacegroup $P6_3/m2/m2/c$ is, in fact, the hypothetical stable polymorph at high temperatures (>850°C). It follows that, in agreement with Tuttle and Smith [25], the synthetic kaliophilite obtained in the present series of experiments is metastable. The appearance of some kalsilite in samples heated at 700°C indicates a transition from complete Si–Al disorder to partial ordering. The fact that under the conditions of the experiments this was much more pronounced with KGa2 than with the other kaolinites shows that the structure of the starting material affects the kinetics of Si–Al ordering of the high temperature products. The conditions of formation of kaliophilite and kalsilite in the present series of experiments are much milder than those reported in the literature for syntheses from different starting materials, e.g. hydrothermally from a gel at 800°C [22] or from a zeolite at 950–1060°C under atmospheric pressure [21, 23]. Whether anatase participates in these kaolinite–K_2CO_3 reactions remains to be investigated.

In summary, kaolinites heated with excess K_2CO_3 at 500–590°C produce an amorphous phase, which may act as a precursor of either a zeolitic structure or of synthetic kaliophilite. Different kaolinites reach different stages of the precursor formation at any specific time. Appropriate conditions for further treatment must therefore be established individually for each sample.

Reactions of kaolinite with KCl under similar conditions produce an amorphous phase with T–O stretching bands at higher frequencies than those obtained after corresponding reactions with K_2CO_3. As was shown previously, much less K was incorporated into the KCl treated samples and this was well correlated with the relative solubilities of the salts in hot water. With alkali carbonates an additional factor should be considered. Gal [30] noted that K_2CO_3 underwent a phase transition at about 400°C, converting it into an active phase. This increased its reactivity with various oxides, including SiO_2 and Al_2O_3. Reaction with such activated K_2CO_3 could explain the ease with which all the kaolinites reacted with K_2CO_3. However, Gal observed a similar phase transition with $Na_2CO_{3,}$ which also promoted reactions with the various oxides, but nevertheless the reaction of kaolinite with Na_2CO_3 was very much more limited than with $K_2CO_{3,}$ in agreement with its lower solubility (Table 1 in [18]). A phase transition to an active phase can therefore, at most, be a contributing actor to the high reactivity of K_2CO_3 with kaolinite on heating. It appears that a common feature affects the solubility of the salts and their reactivity with kaolinite at elevated temperatures.

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