HYDROTHERMAL FORMATION OF A KAOLINITE-LIKE PRODUCT FROM NONCRYSTALLINE ALUMINOSILICATE GELS

C. R. De Kimpe, H. Kodama, and R. Rivard

Abstract—Noncrystalline aluminosilicate gels with Al$_2$O$_3$/(Al$_2$O$_3$ + SiO$_2$) weight ratios from 0.3 to 0.5 were reacted in 0.1 N KOH at temperatures varying from 125°C to 175°C. The pH of the solutions dropped sharply with increasing gel:solution ratios, indicating that the coordination number of Al in the products changed from IV to VI. The degree of hydrolysis appeared to be higher with KOH than with NaOH. X-ray powder diffraction and infrared spectroscopy showed that disordered kaolinite was the only crystalline product formed. Thermal data and surface area measurements indicated that the kaolinite was formed by a condensation process.

Key Words—Aluminosilicate, Gel, Infrared spectroscopy, Kaolinite, Synthesis, X-ray powder diffraction.

INTRODUCTION

In a previous investigation (De Kimpe, 1969) the mild hydrothermal treatment (at 175°C for 8 days) of a noncrystalline aluminosilicate gel with a Al$_2$O$_3$/(Al$_2$O$_3$ + SiO$_2$) weight ratio (hereafter simply called weight ratio) of 0.4 in the presence of NaOH produced kaolinite. The success of the synthesis was attributed to the fact that the gel was hydrolyzed in the alkali metal hydroxide solution and, consequently, the pH dropped close to neutrality. Treatment of the same gel in the presence of HCl or H$_2$O (Rodrique et al., 1973) produced kaolinite at ≈200°C, whereas at lower temperatures, pseudoboehmite was formed. Therefore, it appeared that not only pH conditions but also hydrolysis processes were important for the formation of kaolinite in this system.

In a more extensive study (130°C–176°C, 8–30 days, weight ratio of the gels = 0.3–0.5) of aluminosilicate gels and NaOH (De Kimpe, 1976), zeolites and phyllosilicates were produced. Zeolites of the harmotome-philippsite and chabazite-gmelinite groups were preferentially formed at pH > 9, whereas kaolinite and beidellite were formed at pH < 9. The crystallization of phyllosilicates was greatly influenced by the initial composition of the gel: the best results were obtained from a gel with a weight ratio of 0.4. Kaolinite and beidellite did not crystallize from a gel with a weight ratio of 0.3 and only very poorly from a gel with a weight ratio of 0.5. On the contrary, zeolites formed regardless of the gel composition. pH, one limiting factor in the system, was controlled by the initial gel:solution ratio and the degree of hydrolysis of the gel. Thus, the system involving aluminosilicate gel and NaOH differed from other systems in which sodium aluminate, alumina + silica, crystalline compounds, etc. have been used as starting materials for the formation of zeolites. In the latter systems, no hydrolysis is involved, and it is likely that the pH of the system does not vary beyond the conditions of formation of zeolites (Breck, 1974). The nature of the cation present in the metal alkali hydroxide plays also a role in the nature of the end products (Colella and Aiello, 1975).

The purpose of the present study was to investigate the effect of KOH on the hydrolysis of an aluminosilicate gel and on the crystallization products from this gel, and to compare the results with those obtained in the presence of NaOH.

EXPERIMENTAL

Preparation of gels

Gels were prepared in plastic beakers by the simultaneous hydrolysis of ethylorthosilicate (Si(OC$_2$H$_5$)$_4$) and aluminum isopropoxide (AI(OCH(CH$_3$)$_2$)$_3$) in deionized water at 25°C, according to the following reaction:

$$2m \text{Al(OCH(CH$_3$)$_2$)$_3$} + n \text{Si(OC$_2$H$_5$)$_4$} \rightarrow 2m \text{Al}_2O_3(n-m)SiO_2(m+n)H_2O + 4n C_2H_5OH + 6m (CH$_3$)$_2CHOH$$

For a given weight ratio, one sixth of the required volume of ethylorthosilicate and of the required weight of aluminum isopropoxide was added every hour to a beaker containing 300 ml of deionized water with continuous stirring. After all portions of both components...
were mixed, the solution was further agitated overnight. The precipitate formed by evaporating the solution to dryness at 60°C was ground and then dried in an oven at 105°C.

The Al₂O₃/(Al₂O₃ + SiO₂) weight ratio of kaolinite is 0.46; thus, for these tests gels with weight ratios of 0.3, 0.4, and 0.5 were prepared. X-ray powder diffraction examination indicated that all precipitates were X-ray amorphous. According to structural models suggested by Cloos et al. (1969), gels with weight ratios from 0.3 to 0.5 have a structure in which an internal core of a network of Si-Al⁴⁺ tetrahedra is neutralized, at least partially, by polymerized hydroxyaluminum (Al⁵⁺) cations.

Hydrothermal aging

Ten milliliters of 0.1 N KOH was added to 300, 900, 1500, and 2100 mg of each of the three different gels in Pyrex glass tubes. The tubes were sealed and agitated end-over-end in an oven for 30 days at 125°C and 150°C and for 15 days at 175°C (±2°C). The corresponding internal pressure in the tubes was 2.3, 4.7, and 8.8 atm, respectively. After aging, the tubes were opened, and the pH of contents was measured after centrifugation and recorded as final pHs. The products were then washed three times with distilled water and dried at 60°C.

Analytical procedures

Crystalline phases were detected in the products by X-ray powder diffraction (XRD) with a Philips diffractometer using Ni-filtered CuKα radiation. Specific surface area was measured by a nitrogen gas adsorption method (Nelsen and Eggertsen, 1958) on a Quantasorb instrument. Differential thermal analysis (DTA) was carried out on a Stone DTA apparatus. Thermogravimetric (TGA) data were obtained with a Cahn thermobalance under vacuum. Infrared absorption (IR) spectra were recorded on a Beckman IR12 spectrophotometer.

RESULTS AND DISCUSSION

Final pH values

The final pH depended on the amount of gel used for aging (Figure 1). For the gels with weight ratios of 0.3 and 0.4, the final pH was not influenced by temperature, whereas for the gel having a weight ratio of 0.5, higher temperatures (150°C and 175°C) lowered the pH 0.4–0.6 units, compared to the pH at 125°C. As compared with the results in the presence of NaOH (De Kimpe, 1976), pH values were similar for the 300-mg samples, 2 to 3 units lower for the 900-mg samples, and 1 to 2 units lower for the 1500- and 2100-mg samples. The lower values measured in the presence of KOH indicate that hydrolysis had progressed further in the latter case; thus, K⁺ appears to have favored the reorganization of gels into structures containing more six-fold coordinated aluminum (De Kimpe et al., 1964).

X-ray powder diffraction and infrared spectroscopy

Three successive stages of crystallization were recognized based on differences in the XRD patterns (Figure 2). In the first stage, the patterns showed only a broad maximum at ~3.5 Å (curve 1). In the second stage, additional bands at ~4.45 and ~2.4 Å developed.
which are related to hk bands of phyllosilicates (curve 2). In the third stage, sharp peaks at 7.1 and 3.55 Å appeared, and the hk bands became stronger (curves 3, 4, and 5). The d value of the 006 reflection was 1.489 Å which corresponds to 8.94 Å for the b parameter. In the first and second stages, the IR spectra (Figure 3, curves 1 and 2) did not differ from that of the starting material, except for the lattice-deformation absorption bands between 450 and 800 cm⁻¹. In the third stage (Figure 3, curves 3, 4, and 5), distinct OH-vibration absorption bands at 3620 and 3700 cm⁻¹ and a band at 920 cm⁻¹ due to Al–OH deformation developed, and Si–O–Al deformation bands at 450–800 cm⁻¹ became stronger. The XRD characteristics and the presence of IR absorption bands at 3700 cm⁻¹ and 920 cm⁻¹ indicate that the crystalline component in the products was a kaolinite-like material, and the poorly defined hk bands indicate a high degree of disorder. The amount of crystalline material, as assessed by the intensity of the 7.1-Å peak, decreased with increasing weight ratio of the starting gels (Table 1). Thus, a kaolinite-like product was formed more readily in systems containing excess silica with respect to the composition of the mineral. This observation agrees with the conclusions of Rodrique.

![Figure 3](image_url)

**Figure 3.** Infrared spectra: same products as in Figure 2.

![Figure 4](image_url)

**Figure 4.** Differential thermal analysis curves: same products as in Figure 2.

<table>
<thead>
<tr>
<th>Amount of gel (mg) per 10 ml of 0.1 N KOH</th>
<th>0.3 weight-ratio gel</th>
<th>0.4 weight-ratio gel</th>
<th>0.5 weight-ratio gel</th>
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<td>Aging temperature (°C)</td>
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<td>300</td>
<td>Am (64)  Am (66)  Am (66)</td>
<td>Am (108)  Am (103)  Am (107)</td>
<td>hk (139)  Am (150)  Am (166)</td>
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<td>900</td>
<td>Am (103)  Ka (20)  n.d.</td>
<td>hk (321)  hk (396)  Ka (10)</td>
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<td>2100</td>
<td>Am (136)  Ka (100)  Ka (40)</td>
<td>(hk) (249)  Ka (55)  Ka (80)</td>
<td>(hk) (277)  Ka (20)  Ka (20)</td>
</tr>
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</table>

1 Am = amorphous; hk = amorphous with hk bands; Ka = contains kaolinite; (hk) = weakly developed; Ka (50) = relative intensity of the 7.1-Å line, with respect to the most intense line; n.d. = not determined. Surface areas shown in parentheses on line below X-ray diffraction data.

| Table 1. Crystallization products and specific surface areas. |
|---------------------------------------------------------|-----------------|-----------------|-----------------|
| Amount of gel (mg) per 10 ml of 0.1 N KOH | 0.3 weight-ratio gel | 0.4 weight-ratio gel | 0.5 weight-ratio gel |
|                                          | Aging temperature (°C) | Aging temperature (°C) | Aging temperature (°C) |
|                                          | 125  150  175          | 125  150  175          | 125  150  175          |
| 300                                      | Am (64)  Am (66)  Am (66) | Am (108)  Am (103)  Am (107) | hk (139)  Am (150)  Am (166) |
| 900                                      | Am (103)  Ka (20)  n.d. | hk (321)  hk (396)  Ka (10) | (hk) (287)  hk (485)  hk (479) |
| 1500                                     | Am (121)  Ka (50)  Ka (30) | hk (359)  Ka (30)  Ka (40) | (hk) (276)  Ka (10)  Ka (15) |
| 2100                                     | Am (136)  Ka (100)  Ka (40) | (hk) (249)  Ka (55)  Ka (80) | (hk) (277)  Ka (20)  Ka (20) |

1 Am = amorphous; hk = amorphous with hk bands; Ka = contains kaolinite; (hk) = weakly developed; Ka (50) = relative intensity of the 7.1-Å line, with respect to the most intense line; n.d. = not determined. Surface areas shown in parentheses on line below X-ray diffraction data.
et al. (1973) on the importance of a silica subtraction process in the kaolinitization of noncrystalline aluminosilicate gels.

Unlike the reactions in the presence of NaOH, where both zeolites and phyllosilicates formed, the kaolinite-like product was the only crystalline phase formed in the presence of KOH. It is interesting to compare the products obtained in the presence of KOH with those obtained at similar pHs in the presence of NaOH. For example, in the pH range 9.0–10.2, the former products were amorphous to X-rays and showed no trace of zeolites, whereas the latter products contained various zeolites. The presence or absence of zeolites in the product apparently is a function of the nature of the cation involved in the transformation. Such a cation effect also has been noted to some extent for systems involving other types of starting materials from which the products have been crystallized (Breck, 1974; Colella and Aiello, 1975).

**Thermal data and specific surface area**

Based on XRD data (Table 1), the 35 reaction products can be divided into four groups: (1) amorphous, (2) amorphous with hk bands, (3) low kaolinite content (relative intensity of the 7-Å peak < 40), and (4) high kaolinite content (relative intensity of the 7-Å peak ≥ 40). From TGA data between 105° and 900°C, the average water content of these groups was found to be 15.4 ± 2.3%, 20.7 ± 3.1%, 18.0 ± 1.8% and 15.7 ± 0.8% for groups 1 to 4, respectively. The water content increased between stage 1 and stage 2 and subsequently decreased with an increase in kaolinite content (stages 3 and 4). This change in water content may be explained by assuming a hydrolysis process wherein the dense three-dimensional network of noncrystalline aluminosilicate broke into segments followed by the condensation of these segments into a two-dimensional structure (De Kimpe and Fripiat, 1968). The DTA curves (Figure 4) demonstrate to some extent the condensation process. Samples showing hk bands gave a small endotherm at 425°C (curve 3), which became more pronounced and displaced towards higher temperature (curves 4 and 5) as kaolinite developed.

Surface areas of hydrothermal products are reported in Table 1. A relationship between surface area and stage of crystallization was considered for the products at various stages. The surface areas obtained for the four groups defined above are: Group 1 (amorphous), 64–166 m²/g; Group 2 (amorphous with hk bands), 249–485 m²/g; Group 3 (low kaolinite content), 92–510 m²/g; and Group 4 (high kaolinite content), 97–376 m²/g. The large increase in surface area from Group 1 to Group 2 can be explained by assuming a structural modification with increasing water content from 15.4% for Group 1 to 20.7% for Group 2. The wide range of surface areas for Groups 3 and 4 reflects the complex mixture of a crystalline phase and residual noncrystalline material.

**CONCLUSIONS**

The results obtained by treating noncrystalline aluminosilicate gels in the presence of KOH differed from those in the presence of NaOH, which had been reported previously, in that the KOH system provided a higher degree of hydrolysis. The greater hydrolysis resulted in a more complete transformation of the starting gel into hydrated segments, such as Si-O-Al-OH, which subsequently condensed to form a phyllosilicate under neutral pH conditions.

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**REFERENCES**


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Resimme—Nichtkristalline Aluminosilikat-Gele mit Al$_2$O$_3$/($\text{Al}_2\text{O}_3 + \text{SiO}_2$)-Gewichtsverhältnissen von 0,3 bis 0,5 wurden in 0,1 N KOH bei Temperaturen von 125° bis 175°C zur Reaktion gebracht. Der pH-Wert der Lösungen nahm mit zunehmenden Gel/Lösung-Verhältnissen sehr stark ab. Dies deutet darauf hin, daß sich die Koordinationszahl von Aluminium in den Produkten von IV nach VI veränderte. Der Hydrolysegrad schien bei KOH höher zu sein als bei NaOH. Röntgenpulverdiffraktometrie und Infrarotspektroskopie zeigten, daß ein ungeordneter Kaolinit das einzige kristalline Produkt war. Thermische Daten und Oberflächenmessungen deuteten darauf hin, daß der Kaolinit durch einen Kondensationsprozeß gebildet wurde. [E.C.]

Résumé—Des aluminosilicates non cristallins, de rapport moléculaire Al$_2$O$_3$/($\text{Al}_2\text{O}_3 + \text{SiO}_2$) variant de 0,3 à 0,5, ont été traités en présence de KOH 0,1 N à des températures de 125° à 175°C. La forte diminution du pH des solutions pour des rapports gel:solution croissants indique un changement du nombre de coordination de l'aluminium de IV à VI dans les produits de réaction. L'hydrolyse des gels est plus prononcé en présence de KOH que dans NaOH. La diffraction des rayons-X et la spectroscopie infrarouge ont permis d'identifier une kaolinite peu ordonnée comme seul produit de réaction cristallin. L'analyse thermique et les mesures de surface spécifique ont montré qu'un mécanisme de condensation était à l'origine de la cristallisation de la kaolinite.