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FORMATION OF PHYLLOSILICATES AND ZEOLITES FROM PURE SILICA–ALUMINA GELS

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Abstract—The hydrothermal aging of pure silica–alumina gels in presence of 10 ml of 0.1 N sodium hydroxide solution at 175, 150 and 130°C for 8–30 days led to the synthesis of zeolites and the phyllosilicates, beidellite and kaolinite. The solution was neutralized by a partial hydrolysis of the gel which readily reorganized into a prezeolitic material. At pH values $\geqslant 9$, with 300 or 600 mg of gel, it evolved towards the crystalline zeolites *P* and *S*, with low surface area (7–100 m^2/g) but high exchange capacity (300–475 m-equiv./100 g). With gel amounts of 600–2400 mg, and pH values of 8–5.5, the prezeolitic material provided rows of O–Si–O–Al–OH which recombined to form the phyllosilicate structures. Surface area increased (170–325 m^2/g) but exchange capacity decreased (100–250m-equiv./100 g). The results obtained by various techniques (XRD, DTA, IR) indicated a moderate degree of crystallinity of these phyllosilicates; in addition, X-ray powder diffraction suggested that *hk* bands were the first to develop.

The positive results obtained with a 0.40 ratio Al_2O_3 gel compared with the negative results obtained with 0.30 or 0.50 Al_2O_3 gels indicate that the gel composition is very important for the formation of phyllosilicates under the experimental conditions.

INTRODUCTION

The occurrence of kaolinite in nature indicates that this mineral is stable under acid and desaturated soil conditions which explains why much of the synthesis work leading to the formation of kaolinite from pure silica–alumina sources was conducted in the acid or neutral pH range (De Kimpe, Gastuche and Brindley, 1964; Poncelet and Brindley, 1967; De Kimpe and Fripiat, 1968; Rodrique, Poncelet and Herbillon, 1973). Low pH favors six-fold coordination of aluminum (De Kimpe, Gastuche and Brindley, 1964) and the low solubility of silica in such environments may prevent the precipitation of an amorphous phase in which Al would be four-fold coordinated. However, the hydrothermal aging of pure silica–alumina gels failed to produce kaolinite at low temperature, whereas more success was obtained when complexes such as aluminum-oxalate (Wey and Siffert, 1962) or aluminum–fulvic acids (Linares and Huertas, 1971) were used to stabilize the six-fold coordination of aluminum. In the presence of Fe_2O_3 and TiO_2 and under a CO_2 atmosphere, some kaolinite was also produced at room temperature (Grubb, 1969) and a boehmitic or pseudoboehmitic phase appeared to be a precursor in the transformation. This possibility was also mentioned by Oberlin and Couty (1970).

From work on the synthesis of kaolinite from H-exchanged zeolites, De Kimpe and Fripiat (1968) concluded that O–Si–O–Al–OH rows were the elements required to form the phyllosilicates. This was further emphasized by Rodrique, Poncelet and Herbillon (1973) who reported the synthesis of kaolinite from pure silica-rich silica–alumina gels. They considered that in these gels, the depolymerized state of Al was an important factor of success. The progressive subtraction of silica would produce O–Si–O–Al–OH rows from which kaolinite microcrystals grow. However, the lowest temperature at which kaolinite was obtained in their experiments was 200°C.

Hydrothermal aging of pure silica–alumina gels at high pH and in the presence of alkali leads to the synthesis of various zeolites (Barrer *et al*., 1959; De Kimpe, 1967; Breck, 1974). De Kimpe (1967) observed that a partial hydrolysis of the gel acidified the solution and that increasing the gel/solution ratio caused the pH to approach neutrality. Under these conditions, the transformation of the gel into kaolinite was obtained at 175°C (De Kimpe, 1969).

The present study therefore was undertaken to determine the domains of existence of phyllosilicates and zeolites but especially to identify the conditions under which kaolinite would form from silica–alumina gels in the presence of a sodium hydroxide solution.

EXPERIMENTAL

Pure silica–alumina gels were prepared at 25°C by slow cohydrolysis of aluminum isopropoxide and ethyl orthosilicate with $Al_2O_3/Al_2O_3 + SiO_2$ relative weight ratios of 0.30, 0.40 and 0.50 (Léonard *et al*., 1964). After overnight hydrolysis under continuous agitation, the products were dried at 60°C, ground and then oven-dried at 105°C. These gels are amorphous to X rays and the 0.40 ratio gel, used in most of the experiments, is constituted by an internal Si–Al^{IV} core which is neutralized, at least partially, by Al^{VI}-hydroxypolymers (Cloos *et al*., 1969).

Contribution No. 79.

Table 1. Crystallization products in the aging of 0.40 ratio Al_2O_3 gel in the presence of 10 ml 0.1 N NaOH†

Starting sample weight (mg)	175°C		150°C	130°C	
	8 days	15 days	15 days	15 days	30 days
300	$P_2 + Ch_2$	P_1	$P_3 + Ch_3$	P_1	$P_3 + Ch_1$
600	$P_2 + Sm_3$	$P_2 + Sm_3$	⑤P_1	Am	P_1
900	①Sm_2	Sm_2	②Am*	Am	Am*
1200		①$Sm_2 + Ka_3$	Ka_3	Am	Am*
1500		$Sm_1 + Ka_2$	Ka_2	Ka_2	Ka_1
1800		③$Ka_1 + Sm_2$	Ka_1	Ka_2	②Ka_1
2100				Ka_2	Ka_1
2400				Ka_3	Ka_2

* With *hk* bands.

† P: Zeolite in the Harmotome–Phillipsite group; Ch: Zeolite in the Chabazite-gmelinite group; Am: Amorphous; Sm: Smectite; Ka: Kaolinite; 1: Strong; 2: Medium; 3: Weak.

① The numbers refer to Figs. 6 and 7.

Various amounts of gel (300–2400 mg) were put in Pyrex glass tubes in the presence of 10 ml of 0.1 N NaOH. The tubes were then sealed and aged in an oven fitted with end-over-end agitation for periods of 8, 15 or 30 days at temperatures of 130, 150 or 175°C ± 2°C according to the rate of reaction. The corresponding internal pressure in the tubes was 2.7, 4.7 or 8.8 atm., respectively.

After aging, the final pH was measured and the samples were recovered by centrifugation, washed with water and dried at 60°C.

The following analyses were carried out: (1) X-ray powder diffraction, on a Philips diffractometer using Ni-filtered, Cu Kα radiation; (2) i.r. spectroscopy, on a Beckman IR12 spectrograph, using KBr pellets; (3) cation exchange capacity, by saturation with N NH_4OAc at pH 7 and distillation; (4) specific surface area, on a Quantasorb sorption instrument (Quantachrome Corp., U.S.A.) applying the continuous flow method of Nelsen and Eggertsen (1958); (5) DTA, on a Stone instrument fitted with direct contact between thermocouple and sample and an air flow of 0.075 SCFH; (6) TGA, on a Cahn electrobalance under vacuum (10^{-2} mm Hg).

RESULTS AND DISCUSSION

Aging of various amounts of the 0.40 ratio Al_2O_3 gel in the presence of NaOH at different temperatures allowed two types of minerals to be formed. As summarized in Table 1, zeolites crystallized at all temperatures with 300 or 600 mg of gel and phyllosilicates were obtained with 600 mg or greater amounts of gel. The result of the synthesis was affected by several factors:

1. *Variation of pH*. The amount of gel in the tube and consequently the gel/solution ratio had a strong influence on final pH values (Fig. 1). At any temperature, the decrease of pH correlates directly with the amount of gel. However, the position of the 130 and 150°C lines suggests that the process is not completely temperature-controlled. In the structures proposed by Cloos *et al.* (1969) for pure silica–alumina gels and at a ratio of approximately 0.40 Al_2O_3, mono- and

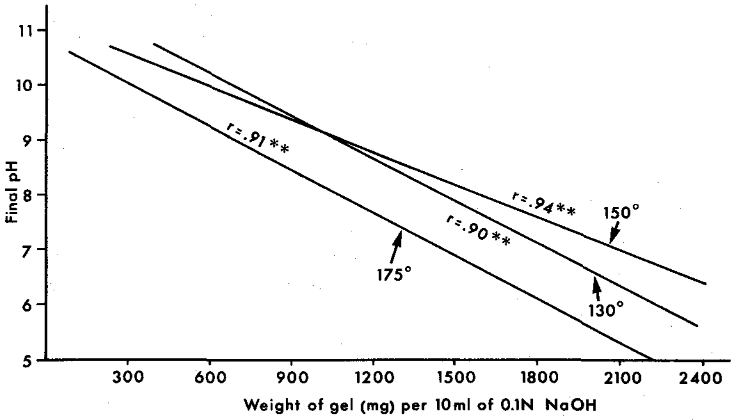

Fig. 1. Variation of final pH as a function of the weight of gel in the aging of the 0.40 ratio Al_2O_3 gel.

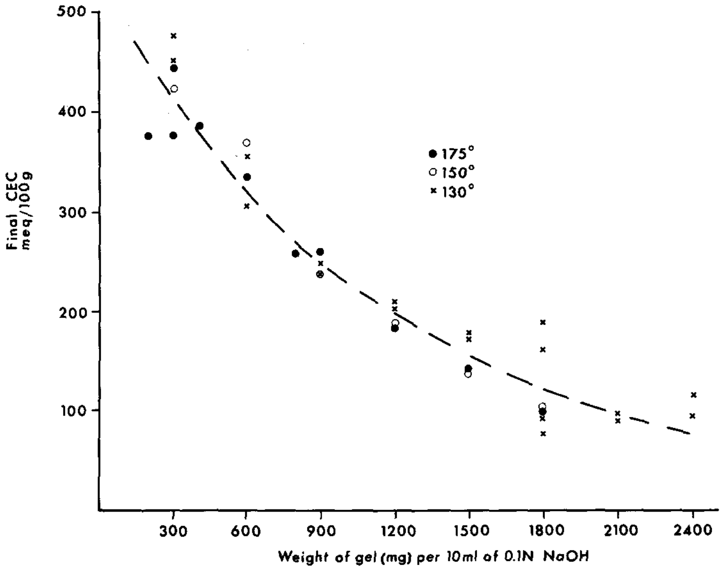

Fig. 2. Variation of the final CEC value with the weight of 0.40 Al_2O_3 gel.

polymeric hydroxyaluminum cations partly compensate the negative charge of the Si–Al^{IV} core. Some protons may also be included. In the presence of a hydroxide solution, dissolution of the gel presumably occurs to some extent and this hydrolysis acidifies the solution. The range of the final pH values thus extended approximately from 6 to 11.

2. *Variation of CEC.* After hydrothermal aging, the cation exchange capacity values ranged from 75 to 475 m-equiv./100 g (Fig. 2). Compared to the starting gel exchange capacity, about 120 m-equiv./100 g, there is a large increase for the products obtained at low gel/solution ratios. It is due to the great number of exchange sites in the zeolites, although the specific surface area measured with nitrogen is low (7–100 m^2/g). It is also related to an increase of four-fold coordinated Al atoms. At very alkaline pH conditions, some silica is extracted from the Pyrex tubes, as verified in tubes containing the hydroxide solution only. This silica probably combines with the hydroxyaluminum cations while the negative charges are compensated by Na^+. Sodium was measured in the NH_4OAc solution used when saturating the samples for the CEC determination and it was found that 1 m-equiv. $NH_4^+ = 0.98$ m-equiv. $Na^+ + 6.34$ ($r = 0.97^{**}$). In the neutral pH range, for high gel/solution ratios, the specific surface area of the products (170–325 m^2/g) is greater than in the starting gel (120 m^2/g) but the high content of six-fold coordinated Al explains the low cation exchange capacity.

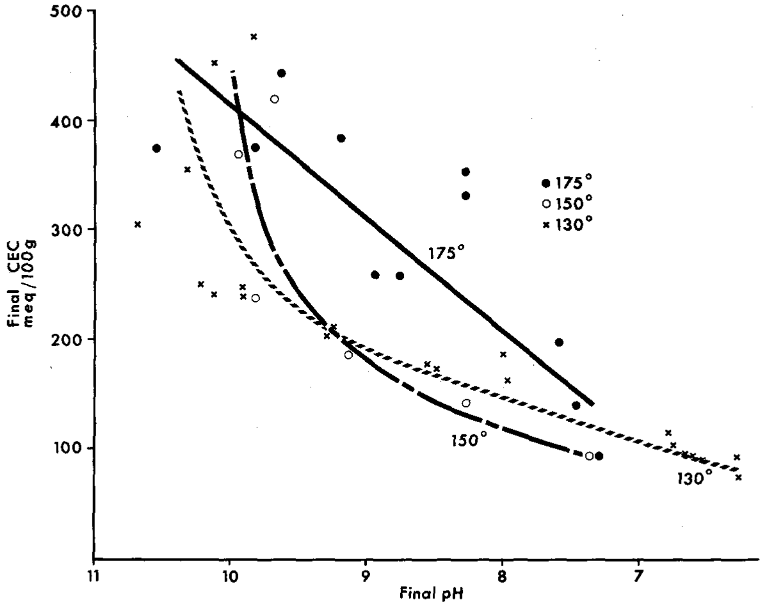

Fig. 3. Relationship between final CEC value and final pH in the aging of the 0.40 Al_2O_3 gel.

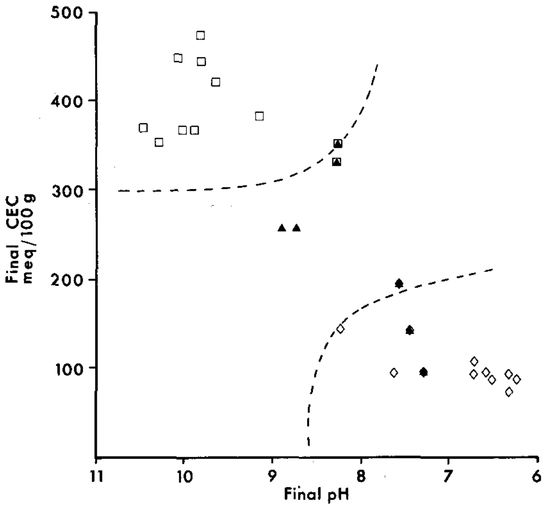

Fig. 4. Domains of occurrence of zeolites (□), smectite (▲) and kaolinite (◇) as a function of final CEC and final pH in the aging of the 0.40 Al_2O_3 gel.

Although the relationship between final CEC and pH values is not clear (Fig. 3) a graphical plot of the data allows a definition of the domains of occurrence for the various minerals that were formed in these experiments (Fig. 4). Zeolites exist in the domain at very alkaline pH and large cation exchange capacity. Kaolinite was formed in the domain of neutral pH and low exchange capacity. Smectite formed in a domain intermediate between these two. This is in agreement with the expected variation of the coordination number of Al with pH (Grubb, 1969). Finally, the relatively large CEC values of the kaolinitic products also suggest that the transformation was not complete.

Minerals crystallization

X-ray powder diffraction. Zeolites from two different groups were produced (Table 1), zeolite *S* in the chabazite–gmelinite group and zeolite *P* (gismondine) in the harmotome–phillipsite group. This is in line with the results of other workers (Barrer *et al.*, 1959; Breck, 1974). Zeolite *S* was obtained only with 300 mg of gel, in the presence of an excess of alkali. It also required more alkaline pH conditions than zeolite *P* which was obtained with 300 and 600 mg of gel. At 175 and 150°C, zeolite *P* crystallized in the cubic form (Fig. 5, curve 2) while at 130°C, pairs of lines at 5.02–4.94, 3.18–3.11 and 2.68–2.65A suggest a mixture of cubic and tetragonal crystals (Barrer *et al.*, 1959).

The composition of the starting gel had a pronounced influence on the crystallization of zeolite *P*. Aging of various amounts of 0.30 and 0.50 ratio Al_2O_3 gels in 0.1 N NaOH was conducted at 130°C for 30 days. The 300 mg samples remained amorphous but zeolite formation took place in some samples as indicated in Table 2. Because of the differences in the gel composition, final pH values were two or three units higher than with the 0.40 ratio

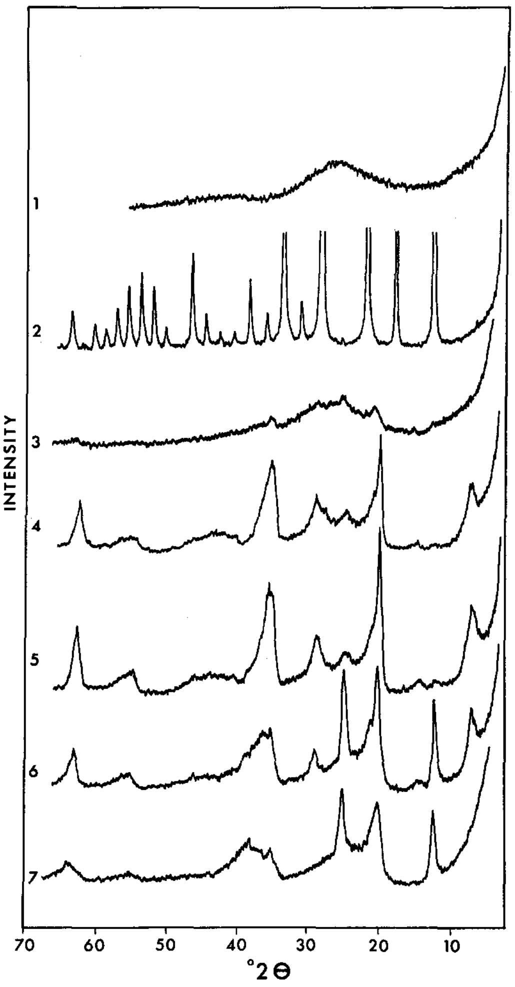

Fig. 5. X-ray diffraction patterns: 0.40 Al_2O_3 gel: 1; zeolite P: 2; "amorphous" product: 3; smectite: 4; smectite kaolinite: 5; kaolinite smectite: 6; kaolinite: 7.

Table 2. Aging at 130°C of 0.30 and 0.50 ratio Al_2O_3 gels in the presence of 10 ml 0.1 N NaOH†

Starting sample weight (mg)	Final product	Final pH	Final CEC (m-equiv./100 g)
0.30 $Al_2O_3/Al_2O_3 + SiO_2$ gel			
300	Am	11.2	365
600	P_1	10.6	440
900	P_3	10.5	352
1200	Am	9.9	330
1500	Am	9.6	279
1800	Am	9.0	248
0.50 $Al_2O_3/Al_2O_3 + SiO_2$ gel			
300	Am	10.9	396
600	P_1	8.8	440
900	P_1	8.3	374
1200	P_1	8.9	339
1500	P_3	9.7	246
1800	Ka_3	9.5	193

† For symbols, see Table 1.

Al_2O_3 gel, explaining the crystallization of zeolite *P* with 1500 mg of gel. Surprisingly, no zeolite *S* formed even from the silica-rich gel.

At 175°C and with the 0.40 Al_2O_3 gel an aluminous smectite was formed (Table 1). It was the only crystalline phase in the 900 mg sample (Fig. 5, curve 4). It was associated with zeolite in the 600 mg sample and with kaolinite in larger weight samples aged for 15 days. Swelling properties were verified by replacing the exchangeable cations by Ca^{2+} and K^+. In the 600, 900 and 1200 mg samples, the basal spacing that was around 12.4A with Na^+ increased only slightly to 12.9 with Ca^{2+} and shifted to 13.4 after glycerol-solvation. The basal spacing of the 1500 and 1800 mg samples was 14.7A with Ca^{2+} and shifted to 16.4A after glycerol-solvation. Upon K-saturation, basal spacings collapsed to values between 11.6 and 11.0A.

The behavior of this swelling mineral is thus more typical of a beidellite in the association beidellite–kaolinite obtained with 1500 or 1800 mg of gel than in the association beidellite–zeolite obtained at more alkaline pH values with a low amount of gel. These associations suggest that the smectite may correspond to an intermediate phase in the evolution towards the 1:1 minerals. The formation of beidellite is also in agreement with the results of Grubb (1969) who obtained montmorillonite at pH 10 in the temperature range of 120–145°C over a period of 20–90 days. As indicated in Table 1, the "amorphous" material in 900 and 1200 mg of gel at 150 and 130°C gave rise to some broad bands around 4.45 and 2.58A which could be perhaps related to the first stage of the development of *hk* reflections of a phyllosilicate.

There was no evidence that, at 130°C, a change in the relative composition of the starting gel would extend the range of crystallization of beidellite as was observed for zeolite P. After 30 days of aging, the products recovered from the 1200, 1500 and 1800 mg samples of the 0.30 ratio Al_2O_3 gel were amorphous.

Kaolinite was obtained in the whole range of temperatures with the 0.40 ratio Al_2O_3 gel (Fig. 5, curve 7). Transformation into a 1:1 mineral was controlled by pH and thus larger amounts of gels were necessary to reduce it to the adequate level at lower temperatures (Fig. 1). Increasing the reaction time also improved crystallinity. However, rather broad diffraction lines and high CEC values indicated only a moderate degree of crystallinity.

The transformation into a 1:1 phyllosilicate was strongly dependent on the relative composition of the starting material as one sample only, 1800 mg of the 0.50 ratio Al_2O_3 gel, gave a slight transformation with X-ray bands at 7.2, 4.45, 3.63, 2.35, 1.84 and 1.45A.

Thermal analysis. The total water content of the starting 0.40 Al_2O_3 gel was about 31%. Aging resulted in a decrease of the total water content and a redistribution between hydration and constitution water. Zeolite-rich samples lost H_2O below 300°C; phyllosilicate-rich samples lost H_2O mostly between 300 and 600°C (Fig. 6).

The DTA curve of zeolite *P* samples (Fig. 6, curve 1) indicated that water loss occurs in several steps in the low temperature range. This corresponds to the "type 1 dehydration" described by Van Reeuwÿk (1974) with apparently discrete reaction over a short temperature range and producing sharp DTA endothermic peaks. In addition, there was also an exothermic reaction at high temperature, around 900°C.

The "amorphous" product gave a double endothermic peak which indicated some organization that could correspond to a prezeolitic stage as deduced by comparison with the preceding curve. However, the presence of a strong exothermic reaction at 950°C and also the presence of *hk* bands in the X-ray powder diffraction pattern suggested an evolution towards a phyllosilicate rather than towards a zeolite.

The low temperature endothermic peak of the phyllosilicates (curves 3–6) was generally intense, and in some curves there was a second endothermic peak between 200 and 250°C that could be possibly related to a prezeolitic stage. These samples, which lost more than 25% water between 300 and 600°C had another endothermic reaction in this region. However, this endothermic peak occurred at lower temperatures than normally observed for phyllosilicates and this was particularly true for kaolinite samples, with the maximum of the peak being about 100°C lower than in true kaolinite. Wey and Siffert (1962) had also obtained a lower temperature for a "protokaolin". This confirmed the moderate degree of crystallinity. The high temperature reactions were an endo-exo doublet in smectite and an exothermic peak in kaolin.

I.r. spectroscopy. Samples were analyzed as KBr pellets (Fig. 7). The starting gel (curve 1) has broad and intense bands in the OH ($3450\,cm^{-1}$) and H_2O regions. The Si–O vibration band is centered on $1030\,cm^{-1}$ with a shoulder around $1160\,cm^{-1}$. The presence of six-fold coordinated Al is indicated by the Al–O–H deformation band at $900\,cm^{-1}$. The lattice deformation bands are weakly developed.

In the zeolite spectrum (curve 2), the OH band is displaced towards $3530\,cm^{-1}$. The Si–O band occurs at $1000\,cm^{-1}$ with another component at $1100\,cm^{-1}$ (Milkey, 1960). The Al–O–H deformation band is absent. Specific bands for zeolite in the lattice deformation region area occur at 745, 615 and $390\,cm^{-1}$.

The "amorphous" product (curve 3) is similar to that of the original gel. However, some transformation is suggested by a shoulder at $3570\,cm^{-1}$ in the OH vibration region, a somewhat displaced ($1000\,cm^{-1}$) and stronger Si–O vibration band (probably due to the addition of SiO_2 extracted from the Pyrex tube), and a stronger Si–O–Al deformation band at $700\,cm^{-1}$.

Smectite (curve 4) is characterized by a OH vibration band at $3640\,cm^{-1}$, a simple and strong SiO band centered on $1000\,cm^{-1}$, and lattice deformation bands at 720, 540 and $490\,cm^{-1}$.

In the association smectite–kaolinite (curves 5 and 6) with increasing kaolinite content (curve 6), the dif-

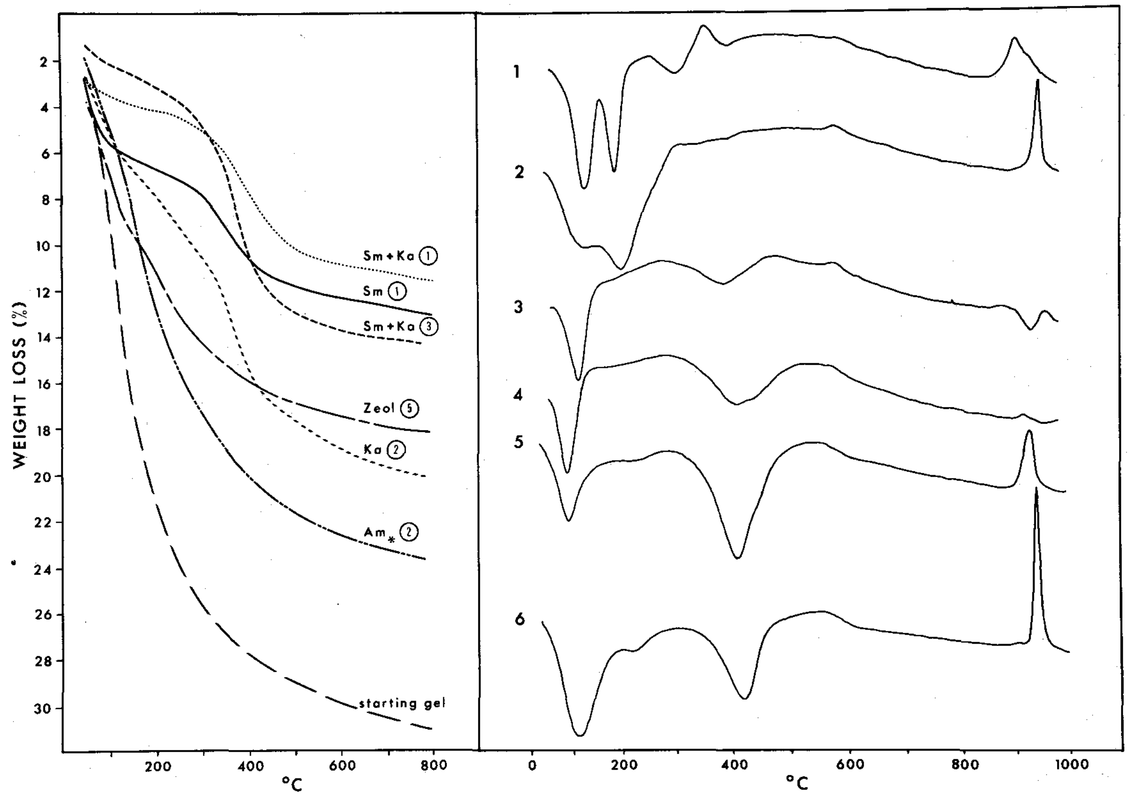

Fig. 6. Aging of 0.40 Al_2O_3 gel: TGA and DTA curves: 1: Zeol⑤; 2: Am*②; 3: Sm①; 4: Sm + Ka①; 5: Sm + Ka③; 6: Ka②. (Circled numbers refer to Table 1).

ferences from the smectite spectrum are a somewhat wider OH band with simultaneous decrease of the 3640 cm^{-1} band of smectite, a more complex vibration band and a stronger Al–O–H band at 915 cm^{-1}. The intensity of the 720 cm^{-1} lattice band is also weaker.

In the kaolinite spectrum (curve 7), the frequency of the OH band is larger; however the two or four components that characterize halloysite or kaolinite could not be differentiated. The Si–O vibration band has two components at 1010 and 1040 cm^{-1} but a band at 1100 cm^{-1} is not apparent. The Al–O–H band occurs at 910 cm^{-1} and the lattice bands are poorly developed.

Crystallization process

The hydrothermal aging of pure silica–alumina gels in presence of sodium hydroxide led to the crystallization of two classes of minerals due to a wide range in the final pH values. These were determined mainly by the gel/solution ratio in the reaction tube. Zeolites were produced at low gel/solution ratios (and hence very alkaline pH values) while kaolinite was obtained at less alkaline pH and with large gel/solution ratios. Smectite was obtained in a pH range of 7–9 by itself and in association with zeolite or kaolinite. Under the present experimental conditions, smectite was obtained at 175°C only, while Grubb (1969) produced it at 120°C and pH 10 but over a longer period of time. The presence of *hk* bands in some "amorphous" products and final pH values of 9.2–9.9 may indicate that smectite could have also formed at the temperatures of 150 and 130°C, if the reaction time had been extended beyond 30 days.

The increase of the CEC values and the presence of sharp endothermic peaks in the low temperature region of the DTA curve indicate that the synthesis of smectite and kaolinite proceeds through a "prezeolitic" stage that occurs very rapidly after the gel comes in contact with the sodium hydroxide solution. This stage would be characterized by an expansion of the gel, a reorganization of its structure and a greater accessibility of the total surface. At this stage, further transformation is controlled by pH. At very alkaline pH, there is a direct transformation into a crystalline zeolite. At less alkaline pH, the expanded gel provides rows of O–Si–O–Al–OH which recombine to yield a protokaolin. DTA curves and IR spectra indicate that the organization is in an early stage and X-ray powder diffraction patterns show that the *hk* bands are the first to develop.

The relative composition of the starting material is important for the crystallization of the phyllosilicates, as zeolite *P* was obtained from all gels between 0.30–0.50 ratio Al_2O_3, as long as the final pH was more alkaline than 8.0. The zeolite crystallized, with the 0.50 Al_2O_3 gel, with larger amounts of starting material (up to 1500 mg) despite seemingly more

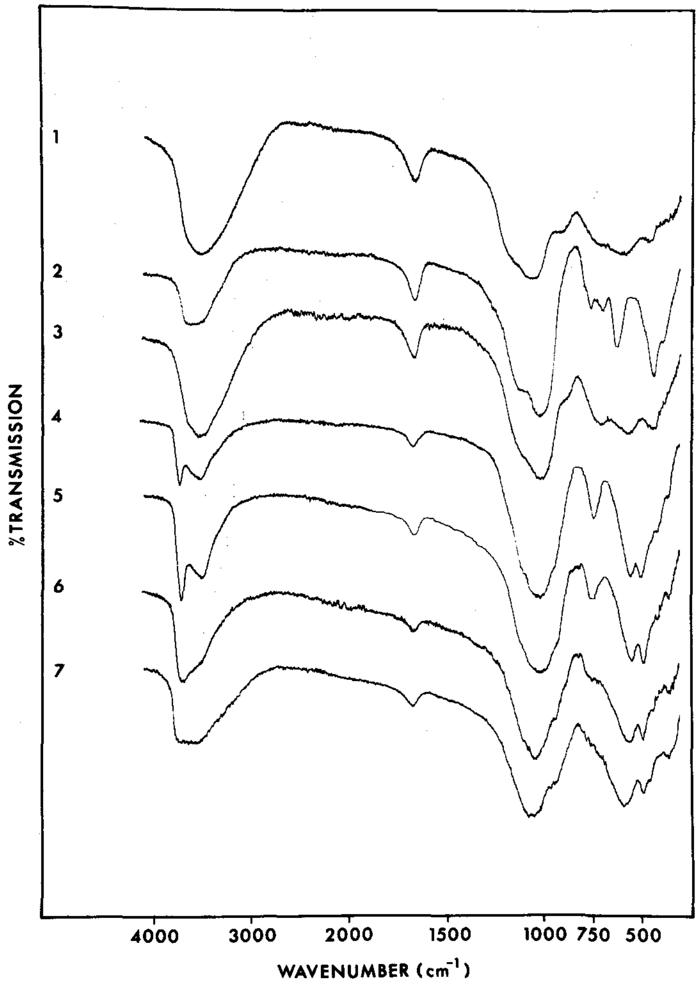

Fig. 7. Aging of 0.40 Al_2O_3 gel: i.r. spectra: 1: starting gel; 2: zeol⑤; 3: Am*②; 4: Sm①; 5: Sm + Ka①; 6: Sm + Ka③; 7: Ka② (see Table 1).

adverse Si/Al and OH^-/Al ratios. On the contrary, very poor results were obtained in the formation of a phyllosilicate. Only one sample showed evidence of some transformation under the experimental conditions.

It is also possible that because of the wider crystallization range of zeolite with the 0.50 ratio Al_2O_3 gel, larger amounts of gel than those used would have been required to obtain more neutral pH values and the formation of the phyllosilicate. The importance of this compositional factor was stressed by Rodrique *et al.* (1973) from their results and from the structures proposed by Cloos *et al.* (1969). The gels with a relative composition of $Al_2O_3/Al_2O_3 + SiO_2 \leqslant 0.40$ are characterized by a high Al^{IV}/Al^{VI} ratio and in addition, the Al atoms are not polymerized. Grubb (1969) observed that the gels which yielded more kaolinite had also more aluminum in tetrahedral coordination. The present results indicated that, when aging silica–alumina gels in presence of sodium hydroxide, the best results were achieved with the 0.40 ratio Al_2O_3 gel.

Formation of boehmite, pseudoboehmite or of a pseudoboehmitic phase was reported by several authors (Oberlin and Couty, 1970; Grubb, 1969) as a step in the evolution towards kaolinite or towards montmorillonite at more alkaline pH (Grubb, 1969). Rodrique *et al.* (1973) did not find any evidence of this stage but boehmite or pseudoboehmite was present in most products when the transformation in kaolinite did not occur. On the contrary, when the hydrothermal aging was conducted in the presence of sodium hydroxide, the alumina hydrate phase was not observed, even when the starting material had a relative composition of $Al_2O_3/Al_2O_3 + SiO_2 = 0.50$. The crystallization products were all alumino-silicates, either zeolites or phyllosilicates. The initial composition of the starting gel also suggested that substraction of silica was required to produce kaolinite, in line with the findings of Rodrique *et al.* (1973).

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