

KAOLINITE CRYSTALLIZATION FROM H-EXCHANGED ZEOLITES

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ABSTRACT

Kaolinite has been synthesized starting from various zeolites, erionite, mordenites and analcite, respectively. In a first stage, hydrogen-exchange was carried out as far as possible. Subsequent hydrothermal treatment under acid conditions during 10 days at 175° or 230°C gave rise to kaolinite formation. Transformation scale corresponds to erionite > natural and a synthetic mordenite > analcite and zeolon, a commercial synthetic mordenite. The mode of formation is discussed in relation with the internal accessibility of the zeolites.

INTRODUCTION

A condition for the successful synthesis of kaolin minerals at low temperature is to use an aluminous starting material in which aluminum already exists in six-fold coordination. Thus appreciable yields of crystalline material were observed by De Kimpe, Gastuche and Brindley (1964) when gibbsite, pregibbsitic gels or bayerite were reacted with ethyl silicate or high surface area silica gels, for a few days in N/10 HCl solution at 175°C.

The fixation of silica by the alumina network seems to be governed by the tendency for aluminum trihydrate lattices to transform into boehmite in this temperature range, although boehmite itself is an unsuitable source of aluminum. This serves to show the importance of the degree of organization of the starting material.

At high temperature and pressure where the temperature coefficient of the reaction is very favorable, almost any appropriate mixture of hydrated aluminas and silicas would produce kaolin minerals, provided that the ratio of the number of hydrogen to metal cations in the system is not too low. On the other hand, when temperature and pressure are progressively lowered, the prerequisite conditions for obtaining kaolinite become increasingly more severe. Fripiat and Gastuche (1963), Gastuche (1963) and De Kimpe (1964) have discussed these requirements in terms of the organization of the tetrahedral and octahedral layers. They suggest that the degree of order of the starting material primarily affects the entropy of activation of the reaction. This view is further supported by the subsequent observations made almost simultaneously by Poncellet and Brindley (1967) and by Van Moort, De Kimpe, Herbillon and Fripiat (1966). The latter reported that at 230°C and 28 bars, montmoril-

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lonite was extensively transformed into kaolinite after 2 weeks in N HCl solution. Because of the high activation energy of the reaction, no trace of kaolinite was found when the reaction was carried out at 175°C.

Using montmorillonite interstratified with polynucleic aluminum complexes, Poncelet and Brindley (1967) obtained an appreciable yield of kaolinite after 10 days at 170°C indicating that the interstratification of 2:1 minerals and octahedral Al-layers gives rise to a faster rate process.

A common characteristic of these reactions is the aluminization process of a more or less complex and ordered silica layer, in contrast to the desilication or resilication process often invoked. Moreover these aluminization processes may belong to the class of "solid state reactions" in which the complete dissolution of the starting material is unnecessary.

If the aluminization concept is correct, it would be expected that three-dimensional minerals such as zeolites could be transformed into kaolinite, provided that adequate pH and temperature conditions are realized. Since tetrahedral aluminum is unstable under acid conditions (De Kimpe *et al.*, 1964), it is expected that exchanging Na-zeolites by H_3O^+ prior to the treatment and adding aluminum cations during the treatment in acid solutions to match the right Si/Al ratio would give rise to the transformation into kaolinite.

It was felt that an interesting step in the understanding of kaolin genesis should be achieved in the case of such reactions being observed.

EXPERIMENTAL

Materials. In order to investigate the possible transformations of various zeolite lattices, two main conditions have to be fulfilled: (1) the zeolitic cages must be accessible to H_3O^+ and to $Al(H_2O)_6^{3+}$ cations, and (2) the structure must be stable in acid solutions.

The latter condition precludes the use of the Linde Y and X (near-Faujasite) molecular sieves for they are unstable in acid medium. For instance, the Na-Y zeolite exchanged at 30 percent by H_3O^+ loses its structural characteristics, as revealed by the disappearance of the X-ray diffraction pattern.

On the other hand, analcite, mordenite and erionite are quite stable in acid solutions and were used in this study.

The starting materials originated from the following sources. The synthetic zeolites, analcite and mordenite were prepared from amorphous silico-aluminas as described by De Kimpe, Herbillon and Fripiat (1966).

Zeolon is a synthetic mordenite commercially produced by the Norton Company. Natural erionite comes from Jersey Valley, Nevada, and natural mordenite originates in Maine. The structure of natural erionite has been described by Defeyes (1959) and Staples and Gard (1959).

PROCEDURES

Decationation was carried out at 25°C by shaking a 500 mg sample with 80 ml N/10 HCl for one hour using an end-over-end shaker. The solid was separated by centrifugation

TABLE 1. CHEMICAL COMPOSITION, STRUCTURAL CHARACTERISTICS FROM FISCHER AND MEIER (1965) AND DESATURATION DEGREE

Mineral	Chemical composition	Smallest diameter of widest channel (Å)	Intracrystalline volume (cm ³ H ₂ O/cm ³ zeolite)	% desaturation and (Al ₂ O ₃) content on a dry basis (%)			
				starting material	Pretreated by		
					HCl N/10 (b)	M ₂ AlCl ₃ (a) (b)	
<i>Analcite</i>	0.85 Na ₂ O; 0.10 K ₂ O; Al ₂ O ₃ ; 5 SiO ₂ ; 2.1 H ₂ O	2.6	0.18	0 (22.11)	—	0 (23.92)	0 (23.12)
<i>Erionite</i>	0.45 Na ₂ O; 0.25 K ₂ O; 0.60 CaO; 0.20 MgO; Al ₂ O ₃ ; 7.5 SiO ₂ ; 3.5 H ₂ O	3.6–3.7	(0.46 in chabazite)	0 (15.61)	48.5 (15.69)	—	40 (16.06)
<i>Mordenite</i>							
Natural	0.50 Na ₂ O; 0.18 K ₂ O; Al ₂ O ₃ ; 9 SiO ₂ ; 3.1 H ₂ O	4.0	0.33	0 (13.90)	—	44.0 (14.20)	50 (14.10)
Synthetic	0.95 Na ₂ O; 0.05 K ₂ O; Al ₂ O ₃ ; 10.2 SiO ₂ ; 3.5 H ₂ O			0 (13.00)	44.5 (14.00)	34.0 (14.18)	38.8 (14.20)
<i>Zeolon</i>	0.88 Na ₂ O; 0.06 K ₂ O; Al ₂ O ₃ ; 11.6 SiO ₂ ; 3.3 H ₂ O	6.0	0.33	0 (11.00)	94 (10.1)	65 (11.75)	77 (10.80)

(a) samples shaken during five days

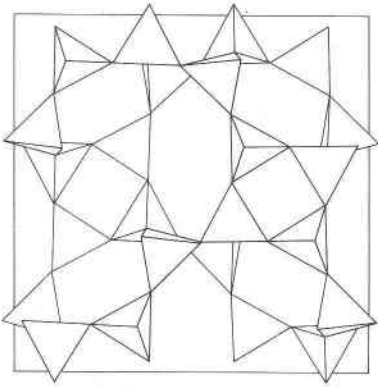
(b) samples treated six times during one hour.

and the Na content in solution was determined. This procedure was repeated five times to ensure that pseudo-equilibrium is achieved. It was also interesting to verify whether Al-exchanged zeolites would follow the same transformation scheme as that shown by H₃O⁺ zeolites. The exchange by Al³⁺ was carried out using a molar AlCl₃·6H₂O solution and shaking for 5 days. Removal of cations was not as pronounced as with the acid solution as it appears in Table I, which also gives some structural characteristics of the materials used. Diagrams of the structure of the zeolites used in this work are presented in Figure 1.

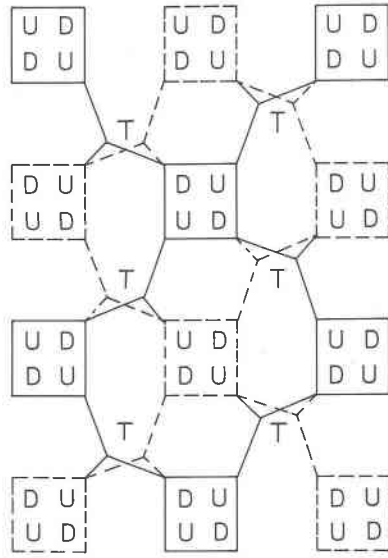
The exchange mechanism is obviously dependent on the accessibility of the bulk material. No exchange was observed for analcite which has a channel diameter of 2.6 Å. This



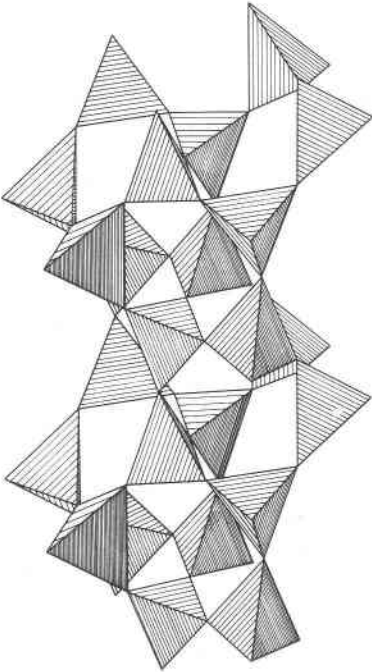
FIG. 1. Schematical structure of the zeolites used in the present study. (a) and (b): projection on (001) of the lower half aluminosilicate framework of analcite, showing six- and four-membered rings of tetrahedra (after Deer, Howie and Zussman (1963) and Smith (1963)). (c): The cage-like unit of erionite. The corners represent the centers of the tetrahedra, the oxygen atoms not being represented. Shaded quadrilaterals represent the points of attachment of hexagonal prisms of tetrahedra, two of them being shown (after Barrer and Kerr, 1959). (d): The characteristic chain of mordenite (after Meier, 1961) representing one-fourth of the unit cell. (e): Projection along (001) of the mordenite framework, showing the main central channel (after Gottardi and Meier, 1963).



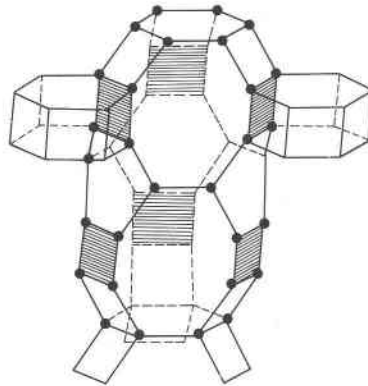
(a)



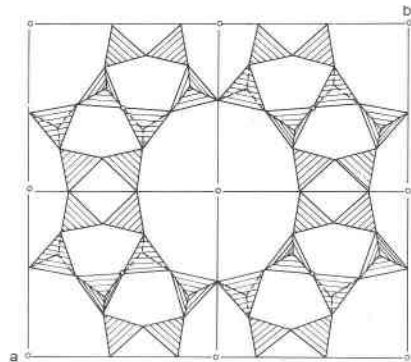
(b)



(d)



(c)



(e)

may also explain why K^+ ions are not exchanged in erionite and only partially in mordenite. More remarkable is the fact that even in $M.AlCl_3$ solution, Al^{3+} cations do not replace Na^+ ions. Though at least 30 percent of the exchangeable cations were replaced, there was *no noticeable increase in the alumina content*. It is therefore assumed that H_3O^+ ions essentially contribute to the exchange process.

The X-ray diffraction patterns of samples at maximum exchange were almost identical with those given by the starting materials. These observations confirm the exceptional stability of the chosen materials. It may thus be expected that structural transformations will be initiated at increasing temperature and pressure since Al tetrahedra have been shown to be unstable in an acid environment.

The transformations were performed for 10 days in N/10 HCl solution at 175°C in sealed pyrex tubes or at 230°C in gold cells contained in a stainless steel bomb. The water vapour pressures were 8.8 and 27.6 kg/cm² respectively.

In each case and according to the composition of the starting material, varying amounts of $AlCl_3$ were added in order to make the final Al/Si ratio equal to unity.

It follows that an additional alumina phase should or should not be formed according to whether the transformation of the starting material into kaolinite is partial or complete.

In addition to X-ray diffraction, infrared spectroscopy has been extensively used to detect the presence of the first traces of the secondary lattice. There are two sensitive spectral regions where the transformation of a three-dimensional zeolite lattice into that of kaolinite may be observed, the region of the OH stretching vibration (3700–3500 cm^{-1}) and that of the Si-O stretching and Si-O-Al combination bands (1200–400 cm^{-1}). The Al^{VI} -O-H deformation band in the region of 900 cm^{-1} is also very useful. For IR studies, usual KBr pellets with sample concentration of 0.5 percent were scanned between 4000 and 400 cm^{-1} . Morphology changes during the transformation were followed by electron microscopy.

RESULTS

Among the three zeolites species used here, only erionite has undergone a noticeable transformation at 175°C. However at 230°C all the samples have been transformed to some extent since a mixture of kaolinite and boehmite is obtained in almost all cases, besides the starting material. As the most complete set of results is observed for erionite, they will be discussed in more detail.

X-ray diffraction and infrared spectroscopy. Figures 2 and 4 represent, respectively, the X-ray diagrams and infrared spectra of erionite after various treatments. Similarly Figures 3 and 5 show the X-ray patterns and infrared spectra for the mordenite and analcite series. In all cases the time of reaction was 10 days.

a) Erionite series: The first X-ray diffraction trace (Fig. 2) shows the pattern of the starting material. At 230°C, without any pretreatment or addition of alumina, the transformation into kaolinite is obviously negligible (trace 1a). Pretreatment with $M.AlCl_3$ or N/10 HCl solutions and matching the contents in silica and alumina (with $AlCl_3$) to give a Si/Al ratio equal to 1 considerably increases the yield in kaolinite. At 230° and starting from H-pretreated zeolite, the degree of transforma-

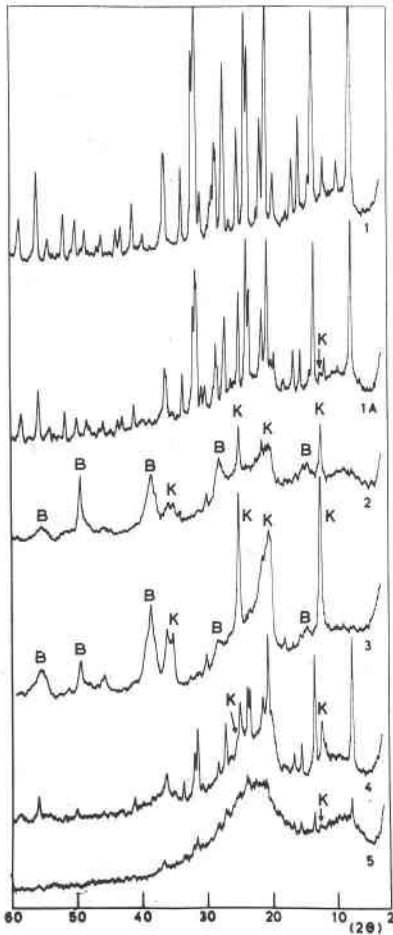


FIG. 2. (left above). X-ray patterns of the erionite series after various treatments. 1: natural erionite; after heating at 230°C for 10 days in acid solution: 1a: natural erionite; 2: Al-pretreated; 3: H-pretreated; after heating 10 days at 175° in acid solution: 4: Al-pretreated; 5: H-pretreated. The X-ray peaks are those of erionite, except when otherwise indicated by the letters K for kaolinite and B for boehmite.

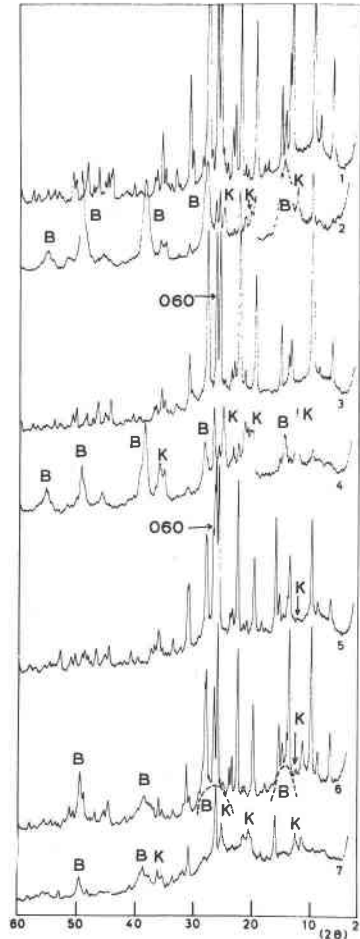


FIG. 3. (right above). X-ray patterns of the mordenite and analcite series after the hydrothermal treatment (10 days in N/10 HCl solution at the given temperature). Commercial Na-zeolon: 1; Al-pretreated natural mordenite at 230°: 2; Al-pretreated natural mordenite at 175°: 3; Al-pretreated synthetic mordenite at 230°: 4 and at 175°: 5; Al-pretreated zeolon at 230°: 6; Al-pretreated analcite at 230°: 7. The X-ray peaks are those of the zeolite, with a special indication of the 060 line, except when otherwise specified by the letters K for kaolinite and B for boehmite.

tion is higher. A few lines of erionite were still observable in the Al-pretreated sample. At 230° diffraction lines of boehmite are also present. It can be accounted for by the formation of an additional aluminous phase when the transformation into kaolinite is not complete. Surprisingly enough, at 175° , boehmite is not observed. This may be attributed to an increase in the temperature of crystallization due to the presence of silica (De Kimpe *et al.*, 1964).

The reaction of H- and Al-pretreated material at 175° shows the earlier stages of transformation. While the Al-pretreated sample (trace 4) still contains the erionite lines (noticeably weakened) in addition to those of kaolinite, the H-pretreated sample (trace 5) is at the transient and disorganized state where the lines due to erionite have almost completely disappeared and the kaolinite crystallization process is initiated.

The infrared spectra (Fig. 4) of these materials illustrate more clearly this sequence. The starting material (spectrum 1) is characterized by the presence of very broad absorption bands in the OH band and SiO stretching vibration regions. As the Si/Al ratio in erionite is equal to 3, the Si-O-Al combination bands may be quite intense. The disorganized transient state (spectrum 5) already shows a slight reinforcement of the

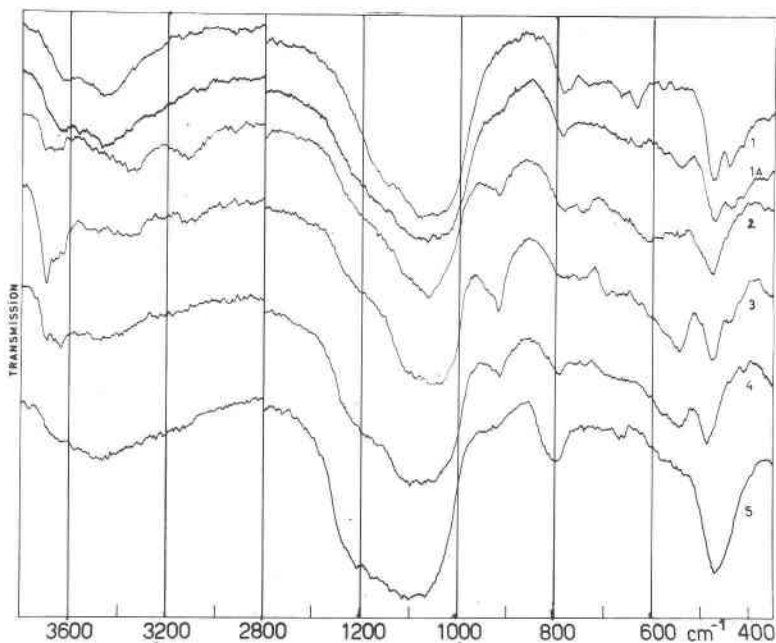


FIG. 4. Infrared spectra obtained for the erionite series. Legend similar to that of Fig. 2.

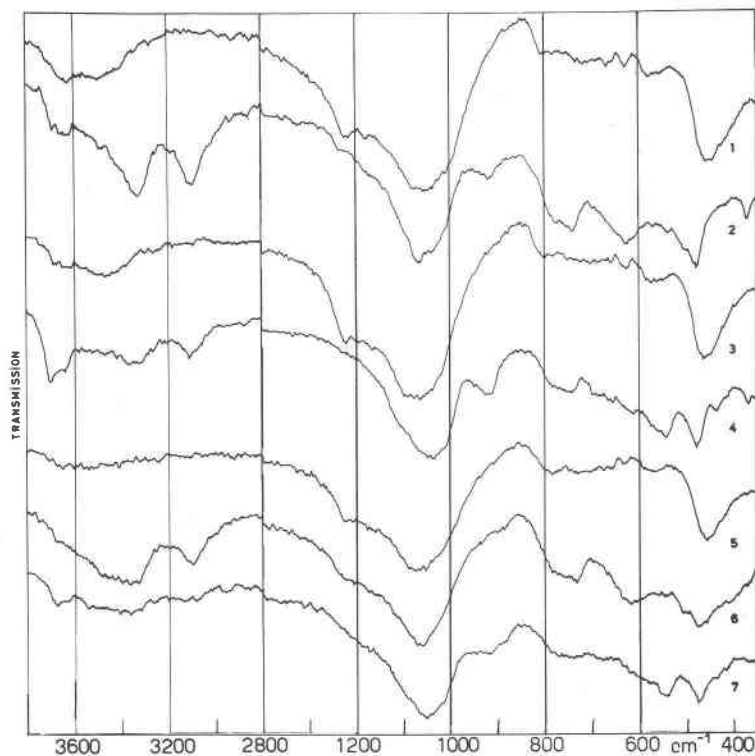


Fig. 5. Infrared spectra obtained for the mordenite and analcite series.

Same legend as in Fig. 3.

band in the $3700\text{--}3650\text{ cm}^{-1}$ region and the presence of two shoulders centered around 920 and 545 cm^{-1} which correspond to the $\text{Al}^{\text{VI}}\text{-O-H}$ deformation and the $\text{Si-O-Al}^{\text{VI}}$ combination bands, respectively. Moreover, the shift of the Si-O band towards higher frequency indicates that a fraction of the aluminum cations are octahedrally coordinated (De Kimppe *et al.* 1964, Léonard *et al.*, 1964).

With increasing crystallinity, as in the Al-pretreated material at 175° (spectrum 4), the complex OH stretching band of kaolinite already appears. The Si-O stretching is centered around $1050\text{--}1100\text{ cm}^{-1}$ and thus fits better the corresponding band of kaolinite. The $\text{Al}^{\text{VI}}\text{-O-H}$ deformation band is also well defined.

After aging at 230° , in the more advanced state, bands due to kaolinite and boehmite are clearly seen (spectra 2 and 3). They are characterized (1) by the OH stretching band, above 3600 cm^{-1} and by the $\text{Al}^{\text{VI}}\text{-OH}$ deformation at 920 cm^{-1} and the $\text{Si-O-Al}^{\text{VI}}$ lattice vibration bands at 545

cm^{-1} of kaolinite; and (2) by the OH stretching bands at 3300 and 3100 cm^{-1} of boehmite respectively.

b) Mordenite and analcite series: Figure 3 shows by X-ray diffraction the evolution of mordenite samples. The X-ray pattern of Na-zeolon may be taken as a reference spectrum all through Figure 3, for it represents adequately the diffraction features of natural and synthetic mordenites.

In pattern 3, corresponding to the Al-pretreated natural mordenite heated at 175°C, the 00 l reflections of kaolinite are not detectable. However, changes in the relative intensity of the various diffraction lines suggest that some lattice reorganization has already occurred. At the next step (trace 5), the clay mineral makes its first appearance. The 060 line of mordenite, much more intense, is then split into three components. However, when the transformation is more advanced, as indicated by the increase in kaolinite contents (trace 2), the remaining diffraction lines of mordenite have amplitudes similar to those of the untransformed sample. This sequence might indicate that the nucleation of kaolinite occurs in a structurally reorganized material.

Zeolon does not transform to the same extent as the other mordenite although the exchange of Na^+ by H_3O^+ was highly effective (Table 1). At 175°, the transformation is not yet initiated, the X-ray pattern remaining unchanged. At 230°, the crystallization into kaolinite has just begun as shown by the appearance of a weak 001 line of kaolinite (trace 6). Apparently, there is no transient amorphous stage in this process although extensive morphology changes were observed, as shown in figure 6C and D.

Under the experimental conditions used here, analcite does not undergo any Na exchange by protons. The overall intensity of the X-ray diffraction pattern of the Al-pretreated sample, heated at 175°C, is strongly reduced but reflections due to kaolinite are not yet visible. At 230°, starting from the same species, the amount of clay mineral formed increases but some diffraction lines of analcite are still present, as shown in pattern 7.

The infrared spectrum (Fig. 5) of Na-zeolon (trace 1) is quite comparable to that of other mordenites. The complex Si-O stretching band has one component centered at 1225 cm^{-1} , which is rather well defined. As the relative content of alumina is low, the Si-O-Al combination bands are poorly developed. The first evidence of mordenite transformation at 175°C (traces 3 and 5) is found in the OH stretching region where a reinforcement may be observed in the band between 3600 and 3700 cm^{-1} corresponding to the OH band of kaolinite.

After heating at 230°, stronger modifications in the infrared spectrum

are observed, in agreement with the higher transformation degree. The OH stretching bands of kaolinite become well defined whilst the high frequency component of the narrower SiO stretching band at 1225 cm^{-1} has disappeared. The $\text{Al}^{\text{VI}}\text{-OH}$ deformation at 920 cm^{-1} and the Si-O- Al^{VI} lattice vibration at 545 cm^{-1} are clearly observed. Finally, the Si-O deformation band has shifted to 475 cm^{-1} , the corresponding frequency in kaolinite.

The low transformation rate obtained with Na-zeolon, even at 230° , is evidenced by the infrared pattern (trace 6).

Trace 7 in Figure 5 corresponds to Al-pretreated analcite, heated at 230° . According to the above description, some evidence of transformation into kaolinite is noticeable.

Morphology transformations.

Erionite. The original sample of erionite is composed of bundles of fibers, which are often cemented to form large aggregates but may sometimes exist as single strands (Fig. 6 A). Preliminary hydrogen exchanges with N/10 HCl or M. AlCl_3 solutions (subsequently referred to as H or Al pretreated samples) do not modify greatly the general appearance but tiny sheets are observed at some points probably by the unrolling of parts of the fibers (Fig. 6 B).

Samples pretreated by H^+ or Al^{3+} solutions and heated at 175° under acid conditions show a very different morphology. In H-pretreated zeolite, the fibers seem to be cut into small irregular and thin pieces, still more or less ordered in a fibrous matrix (Fig. 6 C). In Al-pretreated samples, these small elements appear as being reordered in a new manner, forming larger aggregates (Fig. 6 D). As, at this temperature (Fig. 2), the destruction of erionite and the degree of transformation into kaolinite are more pronounced for the Al- than for the H-pretreated samples, the morphology in Figure 6 D might be representative of a more advanced stage than the one shown in Figure 6 C. After hydrothermal treatment at 230°C under acid conditions a new transformation is noticeable. The Al-pretreated sample (Fig. 7A), only partially transformed into kaolinite at this temperature, is composed of thin fibers. These fibers appear to be made up of small elements reorganized after the aggregation stage observed at 175°C . The H-pretreated sample in which the transformation into kaolinite (Fig. 7B) is almost complete still contains these fibers but they are more and more "fused" into thin two-dimensional plates.

From the point of view of morphology alone the transformation of erionite into kaolinite appears as a result of a very intricate process. Assuming that the Al- and H-pretreated samples undergo a similar trans-

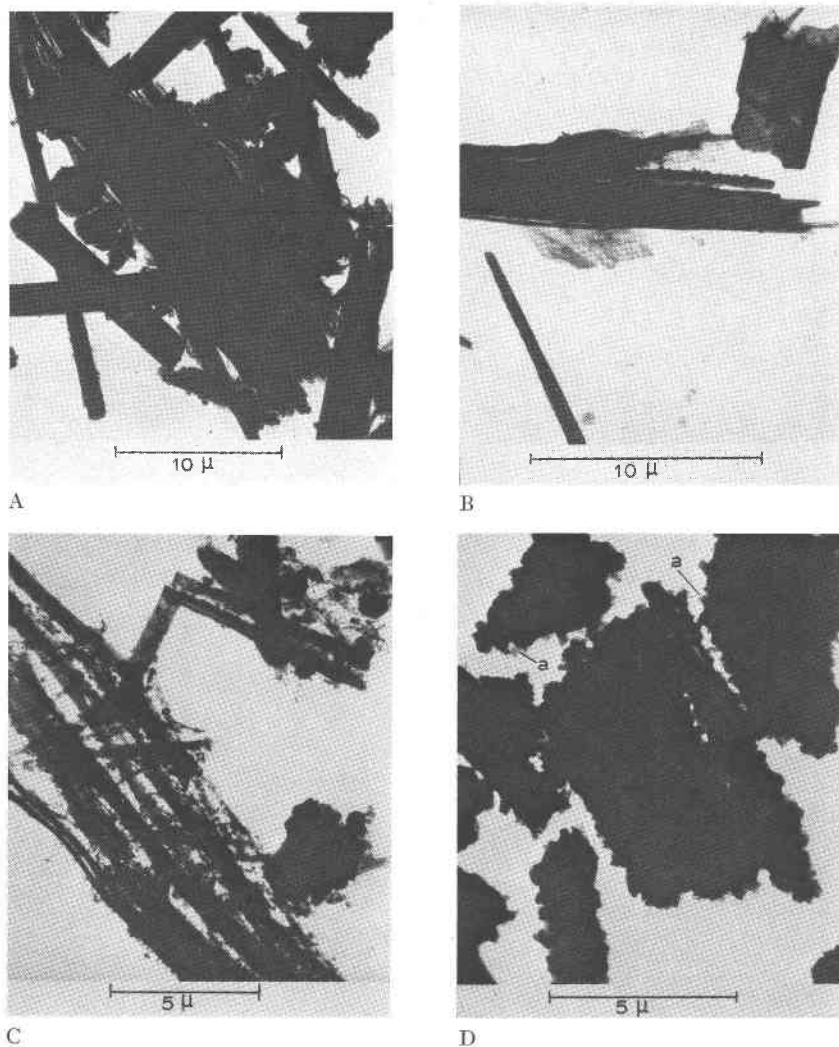


FIG. 6. Electron micrographs of the transformation of erionite. A: starting material; B: Al-pretreated; C: H-pretreated and heated at 175°; D: Al-pretreated and heated at 175°. The small letters refer to the different stages: a: fragmentation in small elements; b: reaggregation; c: formation of small rolled sheets; d: formation of small bidimensional sheets.

formation (in both cases approximately half the Na cations has been replaced by H_3O^+), the different stages may be described as follows: fragmentation of the fibers into small and thin elements, aggregation of these elements and organization into tiny fibers, finally, reorganization

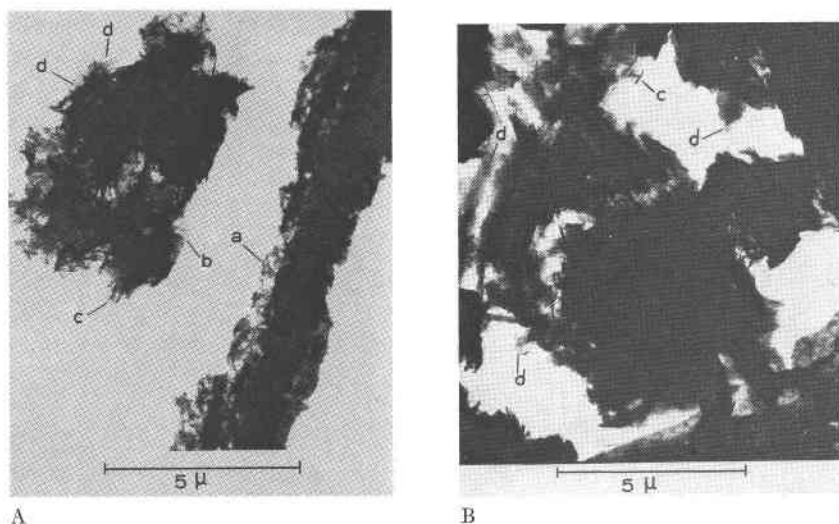


FIG. 7. Electron micrographs of the transformation of erionite. A: Al-pretreated and heated at 230°; B: H-pretreated and heated at 230°. For the small letters, see Figure 6.

into two-dimensional plates. The kaolinite pattern first appears at the aggregation stage and complete transformation seems to be achieved at the last stage even when the fibers are far from being completely reorganized into two-dimensional plates. According to the X-ray diffraction diagrams, Figure 6 C may be considered as representing the most amorphous stage obtained in the series. The fibrous habit maintained at this stage seems to indicate that the amorphous character is due to a transient structural disorganization in the solid but not to a dissolution and reprecipitation process. The amorphous elements reorganize slowly at the agglomeration phase of Figure 6 D. Afterwards, a continuous increase in the crystalline character of the samples is observed. According to this hypothetical mechanism the transformation of erionite into kaolinite should be a solid state process.

Mordenites. It is interesting to compare the mechanism suggested for erionite with those observed for zeolites showing less extensive transformation. Both natural and synthetic mordenite are representative of this intermediate class for which the degree of transformation into kaolinite and Na removal are not complete. The hydrothermal treatment at 175° does not affect the ribbons characteristic of the initial stage. Deeply weathered materials may be found occasionally for the H-pretreated synthetic mordenite at 175°C. According to the X-ray diffraction pattern, the transformation into kaolinite has started under these conditions. At 230°C the transformation is more pronounced and

may be related to the order of magnitude of that obtained for erionite at 175°. At this stage, thin sheets, partially rolled, are mixed with some platy materials. The morphology is then quite comparable with that observed for erionite but large and thick sheets are also present. General appearance of the residual mordenite has been greatly modified and it is probable that the initial rods have been cleaved along the fiber axis, producing new fibers distinguishable by their smaller diameter.

Analcite and Na-zeolon. The two last cases are represented by analcite and Na-zeolon, respectively. In analcite, prolonged contact with N/10 HCl solution does not succeed to remove the exchangeable Na⁺ ions. Therefore the degree of transformation into kaolinite is very low, even at 230°. In Na-zeolon, Na removal is easily obtained but the transformation into kaolinite is still lower.

After the hydrothermal treatment at 230°, analcite has almost disappeared as shown by the X-ray diffraction pattern and very thin sheets partially rolled are then formed. It is unlikely that the small amounts of pseudo-boehmite, observed on the X-ray diagram, could account for this morphology, which is representative of almost the entire sample. The thin and flat sheets could represent the small amount of kaolinite produced under these conditions.

DISCUSSION

In summary, the morphological observations reported here suggest that the transformation of hydrogen-exchanged zeolites into kaolinite follows a general pattern whatever the nature of the starting materials but that the rate of change is appreciably different from one structure to another. The transformation would occur in four stages tentatively shown in the micrographs by letters: fragmentation of the initial material in small particles (a), aggregation of these small elements (b), formation of thin partially rolled sheets (c), unrolling and formation of thicker two-dimensional sheets (d).

It may be appropriate to suggest that the coordination change of aluminum is at the origin of the dislocation mechanism responsible for the initial fragmentation process. This would produce Si-O-Al^{VI} units having a strong polymerization tendency and thus forming the thin sheets observed further.

From the comparison of electron micrographs with X-ray diffraction patterns and infrared spectra, it may be concluded that extensive morphological changes precede the transformation of a zeolitic into a kaolinitic lattice under acid conditions. An X-ray amorphous stage, characterized by steps a and b in the electron micrographs of Figure 6 and

7, appears before any noticeable transformation of H-exchanged erionite and mordenite into kaolinite takes place. Besides the X-ray 001 reflection of kaolinite, the infrared OH stretching and Al-O-H deformation bands are the first spectral features to appear, together with the shift toward higher frequencies of the Si-O stretching band, due to the progressive coordination change of aluminum cations. These observations strongly suggest that the very first step of the transformation is the "hydration" of aluminum tetrahedra and their subsequent transformation into Al octahedra. This process breaks an important percentage of the Al-O-Si bonds and probably accounts for the amorphous character observed at the stage of extensive fragmentation (step a in electron micrographs).

The further polymerization of Al^{VI}-O-Si chains into a more ordered framework (step b) would lead to the formation of kaolinite "needles" (step c) and finally of kaolinite flakes (stages d).

The possibility of exchanging an appreciable part of the Na content by H₃O⁺ ions seems to facilitate the transformation of zeolite minerals into kaolinite since this occurs at appreciably lower temperature from H-exchanged materials obtained after H- or Al-pretreatments. The close approach of H₃O⁺ cations to Al tetrahedra may explain this more advanced transformation degree.

Zeolon, although almost completely H-exchanged, does not behave in a similar manner to synthetic or natural mordenite. The initial fragmentation (step a) is not observed and this seems to indicate, according to the above, that the coordination shift does not occur. The reason for this anomalous behavior is not clearly understood.

Keough and Sand (1961) have already reported the high thermal stability of H-exchanged zeolon without further explanation. Yet more surprising is the discrepancy observed between the synthetic mordenite obtained in this laboratory, which behaves as the natural mineral, and the commercial synthetic mordenite zeolon. It is known, however that the cages in zeolon are entered through larger windows than those in natural mordenites, indicating that the distribution of Al tetrahedra in both materials is dissimilar. Further, the intensity of the diffraction lines in zeolon is different from that in natural mordenite. For these reasons, it seems probable that the transformation of Al from four- to six-fold coordination occurs with greater difficulty in zeolon than in the natural mineral.

In conclusion, the transformation of H-exchanged zeolite such as erionite into kaolinite at temperature as low as 175°C suggests that the formation of short Si-O-Al^{VI} chains might be the determining step in the synthesis of kaolin minerals rather than the grafting of Al octahedra

on preorganized silica sheets or the reverse process. The crystal growth of kaolinite from "aluminized montmorillonite" as shown by Poncellet and Brindley (1967) and by Van Moort *et al.*, (1966) would therefore occur parallel to the *c* axis of the expanding lattice.

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