Hydrothermal Synthesis of Sodium Zirconium Silicates and Characterization of Their Properties

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By studying reactions in the system $Zr(OC_3H_7)_4$−silicic acid (Na_2SiO_3, $Na_2Si_3O_7$)−NaOH−H_2O under mild hydrothermal conditions (180−190 °C) the formation of three novel layered sodium zirconium silicates, $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$, $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$, and $Na_2ZrSi_3O_9\cdot 3H_2O$, and five other compounds: $Na_4Zr_2Si_3O_{12}$, $Na_3HZrSi_2O_8$, $Na_4Zr_2Si_5O_{16}\cdot H_2O$, $Na_4ZrSi_3O_{10}$, and $Na_2ZrSi_3O_9\cdot 2H_2O$, have been found. All the synthesized materials were characterized by elemental analysis, TGA, X-ray, IR, and ^{29}Si MAS NMR spectroscopy. The ion-exchange behavior of sodium zirconium silicates toward alkali, alkaline-earth, and some di- and trivalent metal cations was studied.

Introduction

Among the inorganic adsorbents, zeolites are the most widely used in industry and agriculture and for environmental protection.[1,2] This is a result of certain properties exhibited by zeolites: high thermal and radiation stability, high adsorption capacity, marked selectivity, as well as their preparation in a granular form. Unfortunately, aluminosilicate-based zeolites have one essential drawback, a low chemical stability in acid and alkaline media, which imposes certain restrictions on their application. For this reason an active search for new types of inorganic exchangers, lacking these drawbacks and meeting stringent requirements of technology, was undertaken in the past decades.[3,4] Our interest lies in producing acid or alkaline stable highly selective exchangers. Some of the titanium silicates, such as $Na_2Ti_2SiO_7\cdot 2H_2O$[5,6] and $Na_2TiSi_2O_7\cdot 2H_2O$,[7] among a large family of known titanium-containing minerals and synthetic compounds, exhibit promise as selective ion exchangers suitable for highly alkaline nuclear waste remediation. By studying the details of their structures and ion exchange behavior, Clearfield and co-workers[6,8] have found that the reason for the unique behavior of crystalline titanium silicates is connected with the correspondence of the geometrical parameters of their adsorption sites (channels, cavities) to the size of the selectively adsorbed Cs^+ or Sr^{2+} ions. By analogy it could be expected that the study of other polyvalent metal silicates, for example, zirconium silicates, might be as fruitful in yielding the desired exchangers as was the case for titanium silicates. Moreover, zirconium silicates occur widely in nature, and their formation under hydrothermal conditions (in a wide range of temperatures from 300 to 550 °C) has been given considerable attention, though mainly for the solution of general geophysical and mineralogical problems.[9−13] More than 20 natural and synthetic sodium zirconium silicates (SZS) are known and for about one-third of them the crystal structures have been solved.[13] On the basis of the literature data, it is reasonable to expect that some of these compounds, due to the presence of ion-exchange functional groups, as well as the existence in their structure of well-defined channels and cavities, could exhibit interesting ion-exchange properties, namely, high selectivity to certain ions and molecules. But unfortunately the ion-exchange behavior of such zirconium silicates has not been studied in sufficient detail yet.

In this paper we present some preliminary data on sodium zirconium silicates formation under relatively mild hydrothermal conditions (180−190 °C), including the influence of the type of silicon-containing reagent, the molar ratio, and concentrations of reagents in the reaction mixture on the yield of products. The ion-exchange behavior of the synthesized compounds is also discussed.

Experimental Section

Reagents. All reagents were of analytical grade (Aldrich).

Synthesis of Sodium Zirconium Silicates. In all cases a 70% solution of $Zr(OC_3H_7)_4$ in propanol was used as the initial source of zirconium and a 10 M solution of NaOH was used as the source of alkali. A synthesis procedure included first the preparation of a silicon-containing solution by dissolving a calculated amount of silicic acid, Na_2SiO_3, or $Na_2Si_3O_7$ in NaOH−H_2O solution, and then mixing it with the

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zirconium-containing solutions in a desired molar ratio (Si:Zr = 0.5−5). The reactions were carried out in 100 mL stainless steel Teflon-lined vessels, and in all cases the total volume of the reaction mixture was 50 mL. The reaction mixture was sealed and heated at 180−190 °C for 5−6 days. The cooled mixture was filtered to recover a solid that was then thoroughly washed with an excess of deionized water and dried in air at 60 °C.

Conversion of sodium zirconium silicates into the "hydrogen" form (SZS−H) was achieved by successive treatment of the exchangers with an excess of 0.1−2 M HNO_3.

Analytical Procedures. The diffractometer used was a Seifert-Scintag PAD-V with Cu Kα radiation. Thermal analysis was performed by a TA 4000 thermogravimetric unit (under nitrogen, the heating rate 10 °C/min). The zirconium, silicon and sodium content in the solids was determined by using a SpectraSpec spectrometer DCP-AEC after dissolving a weighed amount of the sample in HF. IR spectra were obtained on a Perkin-Elmer 1720-X FT spectrophotometer by a KBr pellet technique using air-dried samples. ^{29}Si NMR spectra at magic angle were obtained on a Bruker MSL-300 spectrometer. Micrographs were recorded with a JEOL JSM- 6100 electron microscope operating at 20 kV.

Amine Intercalation. *n*-Propylamine intercalation compounds were obtained by a direct contact of zirconium silicates converted into the hydrogen form with a 2 M *n*-propylamine solution (V:m ratio 20:1) for 3 days at room temperature.

Ion-Exchange Study. Exchange of alkali- and alkaline-earth metal cations by sodium zirconium silicates converted into the hydrogen form was studied using 0.001 M $MeCl_n$ (M = Li, Na, K, Cs, Ca, Sr, Ba; n = 1,2) solutions at V:m = 200:1 (mL:g) and room temperature. In all cases the contact time was 5 days with constant shaking. The affinity of the exchangers (in hydrogen and salt forms) to some heavy-metal cations was studied from solutions, containing 1×10^{-3} M^{n+} ($M^{n+} = Cr^{3+}$, Cd^{2+}, Hg^{2+}, Pb^{2+}, $Cu^{2+}$and Co^{2+}) or 1×10^{-3} M^{n+} + 1 M NaCl ($NaNO_3$) at V:m ratio 200:1 (mL/g). The influence of the acidity of the solution upon the alkali and alkaline-earth metals uptake was studied by the potentiometric titration method from 0.05 N MCl_2−$M(OH)_2$ solutions. The pH of model solutions after equilibration with adsorbent were measured using a Corning 340 pH meter. Final concentrations of alkali metal ions in solutions were measured using a Varian SpectrAA-300 atomic absorption spectrometer.

The affinity of the exchangers for alkali, alkaline earth, and some transition elements was expressed through the distribution coefficient (K_d, mL/g) values, that were found according to the formula $K_d = ((C_o - C_i)/C_i)V/m$, where C_o and C_i are the ion concentrations in the initial solution and in the solution after equilibration with adsorbent, respectively; V/m is the volume to mass ratio.

Results and Discussion

Preparation of Sodium Zirconium Silicates. By studying the reactions in the system $Zr(OC_3H_7)_4$−silicic acid−NaOH−H_2O, the formation of several different sodium zirconium silicate (SZS) phases was obtained depending on the molar ratio of silicon- and zirconium-containing reagents used and the alkalinity of the reaction system. Analysis of the data given in Figure 1, where the SZS phases found are presented versus Si:Zr molar ratios and alkalinity of the reaction mixture, shows that eight different sodium zirconium silicates are formed in the system studied. Three of these compounds are new and they have not been described in the literature previously. Two trends could be followed from the data. They are the enrichment of SZS compounds in silicon upon increase of the Si:Zr molar ratio in the system, and second, the decrease of Si:Zr ratio in the solids with increase of the alkalinity at a constant Si:Zr ratio in solution. The latter is undoubtedly the result of the depolymerization of polymeric silicate species, existing in solution, in the presence of concentrated sodium hydroxide. This process favors the formation of the most thermodynamically stable compounds, containing predominantly meta- or orthosilicate units.

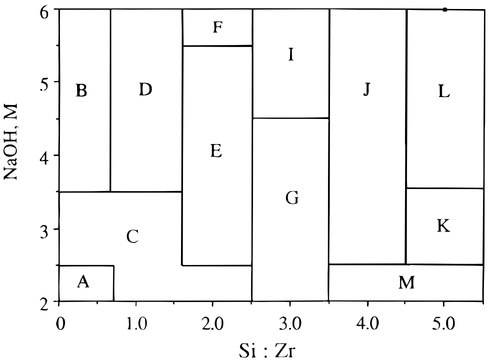

Figure 1. Phase diagram for sodium zirconium silicates formation in the system $Zr(OC_3H_7)_4$−silicic acid−NaOH−H_2O under mild hydrothermal conditions (180−190 °C). (A) $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$; (B) $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$; (C) $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ + $Na_4Zr_2Si_5O_{16}\cdot H_2O$; (D) $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$ +$Na_4Zr_2Si_5O_{16}\cdot H_2O$; (E) $Na_4Zr_2Si_5O_{16}\cdot H_2O$ + $Na_3HZrSi_2O_8$; (F) $Na_3HZrSi_2O_8$ + $Na_4Zr_2Si_3O_{12}$; (G) $Na_4Zr_2Si_5O_{16}\cdot H_2O$ + $Na_2ZrSi_3O_9\cdot 2H_2O$; (I) $Na_4Zr_2Si_5O_{16}\cdot H_2O$; (J) $Na_2ZrSi_3O_9\cdot 2H_2O$; (K) $Na_2ZrSi_3O_9\cdot 3H_2O$; (L) $Na_2ZrSi_3O_9\cdot 3H_2O$ + $Na_2ZrSi_3O_9\cdot 2H_2O$; (M) amorphous.

Detailed analysis of the experimental data presented in Figure 1 shows that two novel SZS of formula $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ or $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$ are formed when the Si:Zr ratio is 0.5:1 and the NaOH concentration is less than 3 M (area A) or higher than 3M (area B), respectively. An increase of the Si:Zr ratio to 1:1 results in the formation of mechanical mixtures of $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ and $Na_4Zr_2Si_5O_{16}\cdot H_2O$ (area C) or $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$ and $Na_4Zr_2Si_5O_{16}\cdot H_2O$ (area D). In area F (Si:Zr = 2, NaOH = 6 M) a predominant formation of $Na_3HZrSi_2O_8$ together with a small admixture of a Nasicon-type compound $Na_4Zr_2Si_3O_{12}$ was found. Mixtures of $Na_4Zr_2Si_5O_{16}\cdot H_2O$ with $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ and $Na_4ZrSi_3O_{10}$ were formed at the Si:Zr ratio 2:1 and NaOH concentration from 3 to 5 M (area E), whereas the formation of $Na_4Zr_2Si_5O_{15}\cdot H_2O$ mixtures with $Na_2ZrSi_3O_9\cdot 2H_2O$ (gaidannaite) was observed at the Si:Zr ratio 3:1 and NaOH < 5M (area G). $Na_4Zr_2Si_5O_{16}\cdot H_2O$ as a single phase is formed at the Si:Zr ratio 3:1 and relatively high NaOH concentration (area I). The formation of gaidannaite as a single phase (area J) was observed at the Si:Zr ratio 4:1 in a wide range of alkalinity (NaOH = 3−6 M). A novel layered sodium zirconium silicate of a tentative formula $Na_2ZrSi_3O_9\cdot 3H_2O$ (designated further as the 12.8 Å phase) was formed at the Si:Zr = 5:1 and 3 M NaOH (area K), whereas mechanical mixtures of the 12.8 Å phase, gaidannaite, and $Na_4Zr_2Si_5O_{16}\cdot H_2O$ were produced at higher alkalinity of solution (area L). At high Si:Zr ratios (4−5) and low alkalinity of the reaction mixture (2 M NaOH) only amorphous products were formed (area M).

Summarizing these data, we note the predominant formation of hydrated sodium zirconium silicates in this system in contrast to mainly anhydrous SZS (Na_2ZrSiO_5, $Na_2ZrSi_2O_7$, $Na_4Zr_2Si_3O_{12}$, etc.) when carrying out the reactions at much higher temperatures (300−550 °C).[13] This suggests that a relatively low temper-

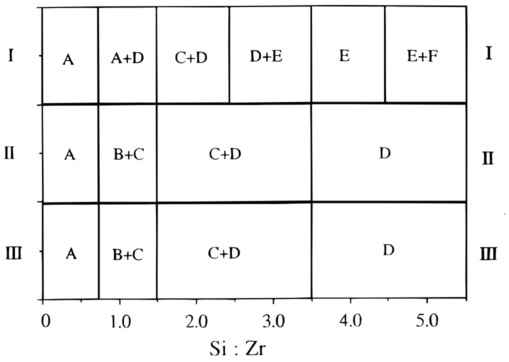

Figure 2. Phase diagram for sodium zirconium silicates formation in the system $Zr(OC_3H_7)_4$−silicon-containing reagent−NaOH (4 M)−H_2O under hydrothermal conditions (180−190 °C). Silicon-containing reagent: (I) silicic acid; (II) $Na_2Si_3O_7$; (III) Na_2SiO_3. Sodium zirconium silicates formed: (A) $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$; (B) $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$; (C) $Na_4Zr_2Si_5O_{16}\cdot H_2O$; (D) $Na_3HZrSi_2O_8$; (E) $Na_2ZrSi_3O_9\cdot 2H_2O$; (F) $Na_2ZrSi_3O_9\cdot 3H_2O$.

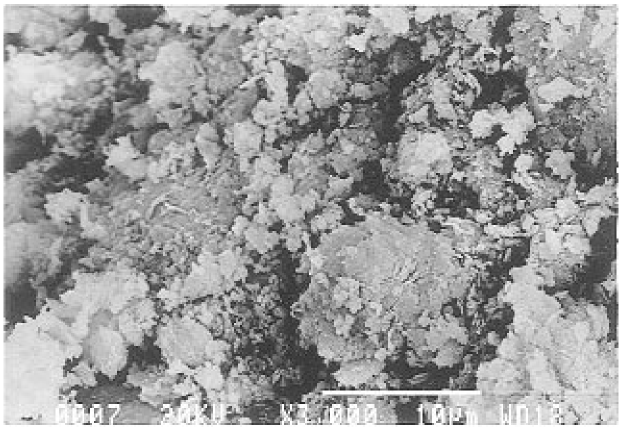

Figure 3. Electron micrograph at 3000× magnification showing the morphology of the hydrothermally grown crystals of $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$.

ature of hydrothermal synthesis could be one of the factors favorable for the preparation of hydrated zirconium silicates, possessing the ability for ion exchange. Then, the second controlling factor, giving a certain diversity of compounds, is the type of the initial silicon-containing reagent. As an illustration is the experimental results for SZS syntheses where Na_2SiO_3 or $Na_2Si_3O_7$ were used instead of silicic acid, while NaOH concentration in the reaction system was maintained constant at a level of 4 M (Figure 2). The comparison shows that in a wide range of Si:Zr ratios (2−5:1) used in the systems $Zr(OC_3H_7)_4$−$Na_2Si_3O_7$−NaOH−H_2O and $Zr(OC_3H_7)_4$−Na_2SiO_3−NaOH−H_2O the main product is $Na_4Zr_2Si_5O_{16}\cdot H_2O$. No formation of $Na_2ZrSi_3O_9\cdot 2H_2O$ or the novel 12.8 Å phase was found. The second feature is the formation of $Na_4ZrSi_3O_{10}$ (as admixture or main phase) even at a Si:Zr ratio of 1:1, which was not observed when Silicic acid as the silicon containing reagent was used.

Characterization of the Novel Sodium Zirconium Silicates. $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$. Under the given experimental conditions: Silicic acid:$Zr(OC_3H_7)_4$ = 0.5:1, [NaOH] < 3 M, $T = 180$ °C, only SZS samples with a relatively low crystallinity are formed. The electron micrograph at 3000× magnification, presented in Figure 3, shows the morphology of the hydrothermally grown crystals of the sodium zirconium silicate. Its particles have a broad size range (from 0.2 to 25 μm) and an irregular form. The lack of a clearly defined morphology correlates with a low crystallinity of the compound. The XRD powder pattern of SZS, having a first X-ray reflection at 11.7 Å, is presented in Figure 4A. According to the elemental analysis the 11.7 Å SZS phase contains 55.2% Zr, 6.6% Si, and 5.7% Na, which corresponds well with the theoretically calculated values for the formula $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ (FW = 851): Zr, 53.47%; Si, 6.58%; Na 5.40%.

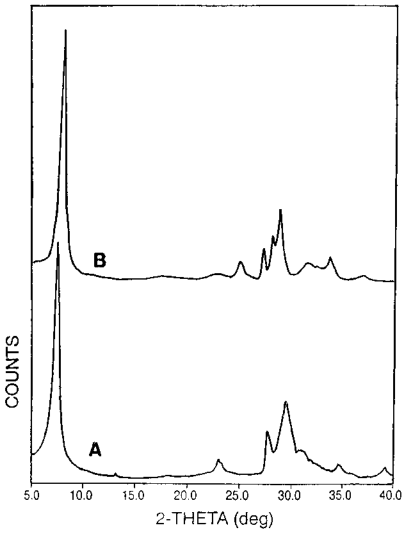

Figure 4. XRD powder patterns for $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ (A) and $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ (B).

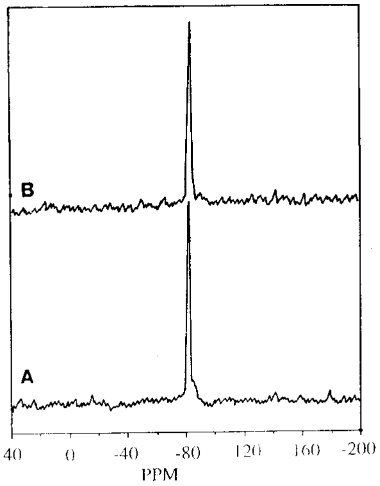

Figure 5. ^{29}Si MAS NMR spectra of $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ (A) and $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ (B).

The novel zirconium silicate is stable in both acid and alkaline solutions. In acid media the sodium phase could be easily converted to the proton phase by exhaustive treatment with 0.5−2 M HCl or HNO_3. Found: Zr, 56.5%; Si, 7.1%. Calcd for $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ (FW = 808.3): Zr, 56.38%; Si, 6.94%. The XRD powder pattern of $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ is shown in Figure 4B. This phase has a first strong reflection in the XRD powder pattern at 10.8 Å.

^{29}Si MAS NMR spectra are shown in Figure 5. According to the ^{29}Si NMR both sodium and protonic phases contain only one type of silicon atom with the same coordination. The ^{29}Si NMR peak for these compounds is located at −83.0 ± 0.5 ppm. This is strongly indicative that in the SZS the hydroxyl groups, possessing the ability for ion exchange, are not con-

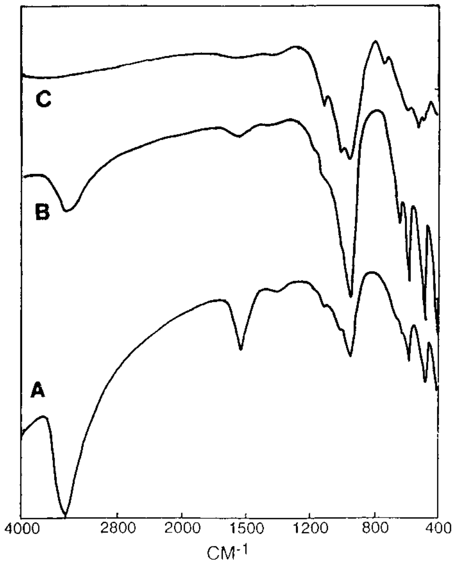

Figure 6. IR spectra of $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ (A) and of $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ thermally treated at 300 °C (B) and 800 °C (C) .

nected with silicon atoms, as was found in the case of both framework and layered sodium titanium silicates,[7,8b] but rather to zirconium atoms. Not knowing the crystal structure of $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ (and $H_2Zr_5Si_2O_{15}\cdot 3H_2O$), it is difficult to make a correct assignment for the recorded peaks. By analogy with zeolites[14] and titanium silicates,[7,8a,15,16] it could be assigned to silicon coordinated with silicon and at least two zirconium atoms (2Si, 2Zr).

The infrared spectra of the novel sodium zirconium silicate, $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$, and its proton form, both air-dried, are presented in Figures 6A and 7A, respectively. The spectrum of the air-dried phase $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ contains a complex hydroxyl stretching band. At least three components of the band are recognizable and indicate the presence of free water (3480, 3411, and 1633 cm^{-1}) and H_3O^+ (3245 cm^{-1}). In addition the presence of ZrO–H hydroxyl stretching bands may also be present. The sodium phase spectrum also shows the presence of the coordinated and free water and perhaps some ZrO–H bands not associated to sodium ion. The bands at 1120, 1025, and 991 cm^{-1} are most likely the SiO_4 asymmetric and symmetric stretching vibrations. The bands appearing at 617, 563, and 443 cm^{-1} may be due to the vibrations of the Zr–O bending mode.

The bands with low intensity at 869, 781, and 701 cm^{-1} may be due to vibrations of the Zr–O and Si–O bonds.

Figure 8 contains the thermogravimetric weight loss curves for the zirconium silicate in the sodium ion form (curve A) and in the hydrogen form (curve B). The total weight loss for the sodium phase is 5.80% and the final product should have the formula $Na_2Zr_5Si_2O_{15}$ (FW = 798.2). Thus, the formula weight initially was 847.4. On the assumption that this increase in weight is totally due to water, the original solid contained 2.73 mol of H_2O (slightly less than 3 mol in the proposed formula). The weight loss occurs in three steps. In the first step (50–120 °C) 1.53% or 0.72 mol of water is released. We attribute this weight loss to a weakly bound interlayer crystal water. In the next two steps (120–320 and 320–460 °C) the weight losses amount to 3.24% (1.52 mol) and 1.03 (0.48 mol), respectively. These two losses are attributed to the water localized in the inner cavities of the compound and coordinated with the sodium ions.

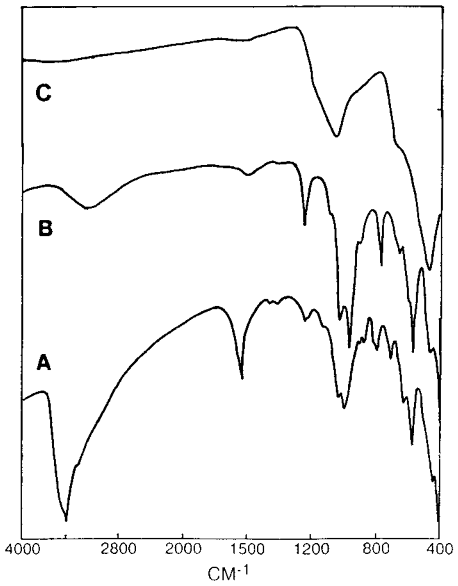

Figure 7. The IR spectra of $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ (A) and of $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ thermally treated at 300 °C (B) and 800 °C (C).

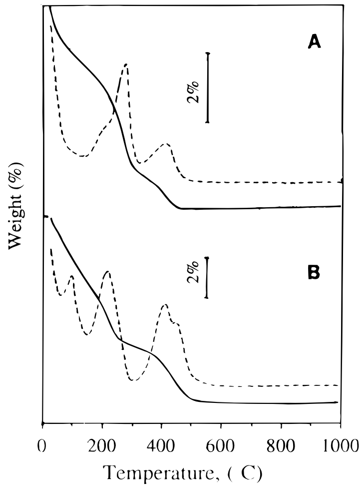

Figure 8. TG (—) and DTG (- - -) curves for $Na_2Zr_5Si_2O_{15}\cdot 3H_2O$ (A) and $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ (B).

The protonic phase (Figure 8B) yielded a total weight loss of 8.96% which corresponds to the weight loss expected for the formula $H_2Zr_5Si_2O_{15}\cdot 3.12H_2O$. The water release occurs in three main steps: 50–150 °C it amounts to 2.46% or 1.12 mol; 150–270 °C 2.97% or 1.36 mol, and in the range 270–740 °C 3.55% or 1.64 mol. The first two weight losses total 2.48 mol of H_2O and are attributed to the interlayer crystal water, whereas in the third step 1.0 mol of structurally bound water is lost, due to condensation of free hydroxyl groups, and the residual 0.64 mol of tightly bound interlayer water.

According to the TGA data the following routes of the thermal decomposition may be proposed for Na_2Zr_5-

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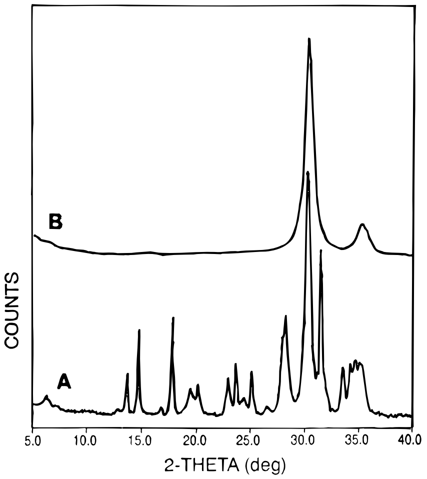

Figure 9. XRD powder patterns for $Na_2Zr_5Si_2O_{15}·3H_2O$ (A) and $H_2Zr_5Si_2O_{15}·3H_2O$ (B) thermally treated at 800 °C.

$Si_2O_{15}·3H_2O$ and $H_2Zr_5Si_2O_{15}·3H_2O$, which are shown in eqs I and II:

$$Na_2Zr_5Si_2O_{15}·2.72H_2O \xrightarrow[-0.72H_2O]{50-120\ °C} Na_2Zr_5Si_2O_{15}·2.00H_2O \xrightarrow[-1.52H_2O]{120-320\ °C}$$

$$Na_2Zr_5Si_2O_{15}·0.48H_2O \xrightarrow[-0.48H_2O]{320-460\ °C} Na_2Zr_5Si_2O_{15} \quad (I)$$

$$H_2Zr_5Si_2O_{15}·3.12H_2O \xrightarrow[-1.12H_2O]{50-150\ °C} H_2Zr_5Si_2O_{15}·2.00H_2O \xrightarrow[-1.36H_2O]{150-270\ °C}$$

$$H_2Zr_5Si_2O_{15}·0.64H_2O \xrightarrow[-1.64H_2O]{270-460\ °C} 5ZrO_2 + 2SiO_2 \quad (II)$$

Additional points in support of thermal decompositions schemes (I, II) were obtained from IR, ^{29}Si MAS NMR, and XRD studies of the intermediate products of thermal treatment of the novel zirconium silicate at 300 and 800 °C. It was found that the heating of SZS and SZS−H at 300 °C practically does not result in any significant changes in the position of reflections in the XRD patterns in comparison with the air-dried samples. At the same time the thermal treatment of both compounds at 800 °C is accompanied by a complete change of their XRD powder patterns (Figure 9). In the case of SZS the formation of an unknown zirconium silicate (or mixture of several phases) was observed. This compound has the following XRD reflections (*d*, Å; I/I_0): 6.54 (16%); 6.08 (37%); 4.99 (38%); 4.59 (11%); 4.24 (13%); 3.90 (18%); 3.78 (22%); 3.56 (18%); 3.17 (40%); 2.96 (100%); 2.85 (67%); 2.68 (19%). The position of the reflections in the XRD powder pattern of SZS−H sample treated at 800 °C suggests the formation of ZrO_2 (analogous to cubic ZrO_2[17]) and amorphous SiO_2 as the main products.

Practically no changes were observed in the IR spectra of SZS in Na (Figure 6B) and H forms (Figure 7B) thermally treated at 300 °C, with the exception of the decrease of the band intensities characteristic for water molecule vibrations. This suggests that no essential changes in the structure of compounds takes place in this temperature range. The IR spectrum of SZS treated at 800 °C (Figure 6C) differs from that of the material treated at 300 °C. The main changes take place in the region 400−600 cm^{-1} (Zr−O vibrations) and may be connected with phase transformations as shown by the X-ray patterns. The appearance of a new weak band at 1400 cm^{-1} could be connected with CO_2 uptake from air due to increased adsorptive ability of SZS after its complete dehydration. At the same time the IR spectrum of the protonic phase heated at 800 °C (Figure 7C) differs drastically from all other IR spectra. Only two broad bands (with two shoulders) were observed in the 850−1250 and 400−700 cm^{-1} regions, which may be connected with the decomposition of the compound and formation of amorphous SiO_2 and cubic ZrO_2, respectively.

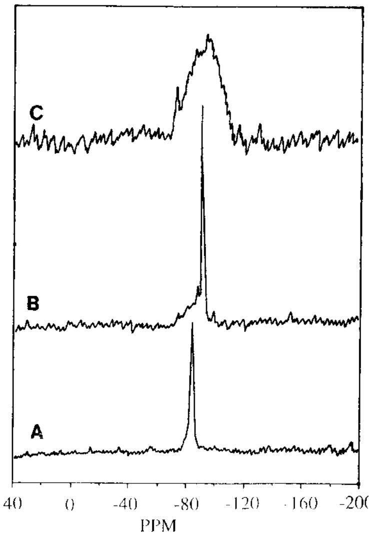

Figure 10. ^{29}Si MAS NMR spectra of $Na_2Zr_5Si_2O_{15}·3H_2O$ thermally treated at 300 °C (A) and at 800 °C (B) and of $H_2Zr_5Si_2O_{15}·3H_2O$ thermally treated at 800 °C (C).

According to the ^{29}Si MAS NMR data (Figure 10A,B) the thermal treatment of sodium zirconium silicate results in the gradual shift of the silicon peak to stronger field: to −85.2 ppm at 300 °C and then to −94 ppm at 800 °C. In the case of $H_2Zr_5Si_2O_{15}·3H_2O$ thermally treated at 300 °C the position of the NMR peak is close to that for SZS-300 (−85.5 ppm), whereas heating at 800 °C gives one broad band with maximum near −100 ppm (Figure 10C). The observed shifts of NMR signals indicate almost no change in the silicon coordination in compounds thermally treated at 300 °C but stronger coordination of silicon in SZS-800 (3Si, 1Zr) and, especially, in its protonic form treated at 800 °C. These facts could be explained from the position of near-complete dehydration of SZS, resulting in a decrease of the interlayer distance in this layered compound (which will be shown later) enabling closer interaction of atoms in adjacent layers. At higher temperature formation of a silicon-rich zirconium silicate glass of unknown composition and ZrO_2 takes place. This is shown by the appearance of X-ray peaks for ZrO_2 only in Figure 9B.

The estimation of the affinity of the novel layered zirconium silicate for alkali and alkaline earth metal ions has been carried out by the potentiometric titration method. The experimental curves, which show the dependencies of alkali-metal ions uptake by $H_2Zr_5Si_2O_{15}·3H_2O$ in 0.05 M MCl−MOH (M = Li, Na, K, Cs)

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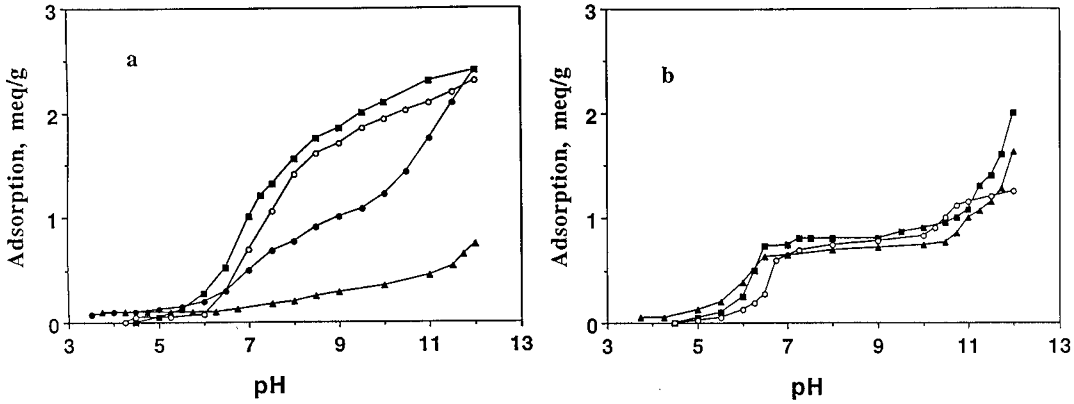

Figure 11. Potentiometric titration of $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ with (a) LiOH (■), NaOH (○), KOH (●), and CsOH (▲). (b) $Ca(OH)_2$ (■), $Sr(OH)_2$ (○), and $Ba(OH)_2$ (▲).

solutions are presented in Figure 11a. Analysis of the ion-exchange data shows that SZS−H is a weakly acidic exchanger. It starts take up alkali metals at pH > 4, but the absolute values of the ion exchange are extremely low (0.05−0.2 mequiv/g, pH = 4−6). A considerable increase in exchange of Li^+, Na^+, and K^+ ions is observed in the pH range 6−8, reaching the maximum of 2.3−2.4 mequiv/g only in alkaline media (pH = 12). These IEC values are close to the theoretically calculated IEC value of 2.48 mequiv/g for the compound with formula $H_2Zr_5Si_2O_{15}\cdot 3H_2O$.

The ion-exchange capacity of the layered zirconium silicate in neutral and alkaline media depends on the type of cation. The following selectivity series was found in the pH range 7−11: $Li^+ > Na^+ > K^+ \gg Cs^+$. This suggests the alkali-metal cations are taken up without their hydration shell and that a high rigidity of the $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ layered structure prevents insertion of large cations such as K^+ in neutral media and Cs^+ over the entire pH range due to steric reasons.

In the absence of a knowledge of the structure of this novel layered zirconium silicate only a working hypothesis of its behavior may be proposed. The basal spacing of the exchanger in protonic form, 10.8 Å, cannot provide sufficient free space to allow Cs^+ to be taken up in its unhydrated condition, but it does accommodate about 0.8 mequiv/g K^+ without layer expansion. Since the ionic diameter of Cs^+ is about 3.6 Å and for K^+ is about 2.7 Å, the thickness of the zirconosilicate layer must be more than 7.2 Å but less than 8.1 Å (about three oxygens thick). At the level of ~1/3 exchange, the K^+ ions must be well shielded from each other and fit into a pocket of oxygens that is correctly oriented to create favorable coordination. Further uptake of potassium ion (pH > 8) is accompanied by the interlayer distance increase (d = 12.3 Å at pH = 12).

Potentiometric titration curves of $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ with alkaline-earth metal hydroxides are presented in Figure 11b. There is no substantial differences in their ion-exchange behavior. Uptake of alkaline-earth metal cations starts at a pH higher than 3−4. The first increase in their uptake was observed at pH 6.0−6.5, where only 1/3 of the theoretical IEC was realized (IEC 0.7−0.85 mequiv/g), and then no changes occur until pH 10.5−11.0. The second increase of ion exchange takes place at pH 10.5−11.0 and continues at pH higher than 12. In this case the IEC values in the range 1.2−2.0 mequiv/g (or 50−80% of the theoretical IEC) were found. Considering a step increase of the potentiometric titration curves for Ca^{2+} and Ba^{2+} ions, it is possible to expect complete substitution of all exchange sites of $H_2Zr_5Si_2O_{15}\cdot 3H_2O$ by alkaline-earth metals at pH higher than 12.

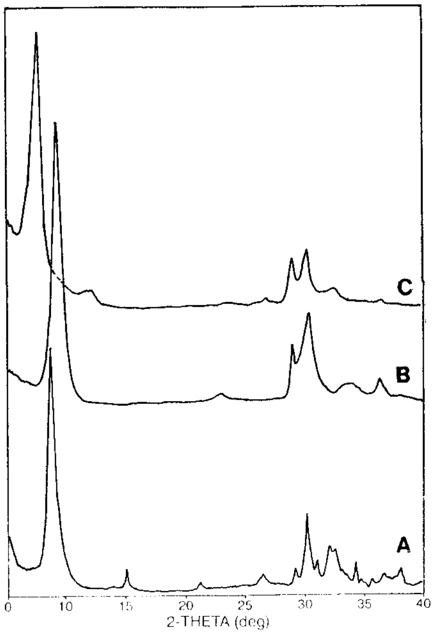

Figure 12. XRD powder patterns for $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$ (A), $H_2Zr_5Si_2O_{15}\cdot 5H_2O$ (B) and $(C_3H_7NH_3)_{1.81}H_{0.19}Zr_5Si_2O_{15}\cdot 1.53H_2O$ (C).

$Na_2Zr_5Si_2O_{15}\cdot 4H_2O$. $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$ is formed as a single phase when the ratio silicic acid: $Zr(OC_3H_7)_4$ = 0.5:1, [NaOH] > 3 M, and T = 180 °C. As in the previous case only SZS samples with a relatively low crystallinity are formed under the given experimental conditions. The XRD powder pattern of this novel highly hydrated sodium zirconium silicate, which has a first reflection at 15.0 Å, is presented in Figure 12A. According to elemental analysis the SZS 15.0 Å phase contains 53.2% Zr, 6.6% Si, and 5.5% Na, which fits the theoretically calculated values for the formula $Na_2Zr_5Si_2O_{15}\cdot 4H_2O$ (FW = 870.3): Zr, 52.39%; Si, 6.43%; Na, 5.29%. The 15.0 Å phase was converted into the proton form by exhaustive treatment with 1 M HNO_3. Found: Zr, 54.5%; Si, 6.9%. Calcd for $H_2Zr_5Si_2O_{15}\cdot 5H_2O$ (FW = 844.3): Zr, 54.01%; Si, 6.63%. The XRD powder pattern of $H_2Zr_5Si_2O_{15}\cdot 5H_2O$ is shown in Figure 12B. This phase has a first strong reflection in the range 12.3−13.0 Å, depending on the interlayer water content. Its thermal treatment even at low temperatures (60−

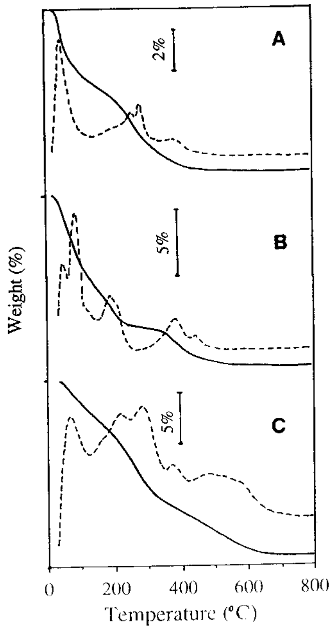

Figure 13. TG (—) and DTG (- - -) curves for $Na_2Zr_5Si_2O_{15}\cdot4H_2O$ (A), $H_2Zr_5Si_2O_{15}\cdot5H_2O$ (B), and $(C_3H_7NH_3)_{1.81}H_{0.19}Zr_5Si_2O_{15}\cdot1.53H_2O$ (C).

80 °C) results in water release, which is accompanied by an irreversible interlayer distance collapse to 10.8 Å.

The same chemical composition and the lack of differences between SZS 15.0 and 11.7 Å phases in their ^{29}Si MAS NMR (single peak at −83.0 ppm) and IR spectra suggests that we are dealing with the same layered sodium zirconium silicate but with different extents of hydration.

Figure 13 contains the thermogravimetric weight loss curves for the zirconium silicate in the sodium ion form (curve A) and in the hydrogen form (curve B). The total weight loss for the sodium phase is 7.94% and the final product should have the formula $Na_2Zr_5Si_2O_{15}$ (FW = 798.2).

Reasoning as in the previous case, the formula weight initially was 867.1. On the assumption that this increase in weight is totally due to water, the original solid contained 3.83 mol of H_2O. The weight loss occurs in three overlapped steps. In the first step (50−150 °C) 3.80% or 1.83 mol of a weakly bound interlayer crystal water is released. In the next two steps (150−330 and 330−460 °C) the weight losses amount to 3.20% (1.54 mol) and 0.94% (0.46 mol), respectively. These two loses could be attributed to the water localized in the inner cavities of the compound and coordinated with the sodium ions.

The protonic phase (Figure 13B) yielded a total weight loss of 13.09%, which corresponds to the weight loss expected for the formula $H_2Zr_5Si_2O_{15}\cdot5.15H_2O$. The water release occurs in four main steps: 40−70 °C it amounts to 2.00% or 0.94 mol; 70−150 °C 4.97% or 2.33 mol; 150−285 °C 2.97% or 1.40 mol; and in the range 285−870 °C 3.15% or 1.48 mol. The first three weight losses total of 4.67 mol are attributed to the interlayer crystal water, whereas in the fourth step is attributed to the release of 1.0 mol of structurally bound water, due to condensation of free hydroxyl groups, and the residual 0.48 mol of tightly bound interlayer water.

It was found that $H_2Zr_5Si_2O_{15}\cdot5H_2O$ (d = 12.6 Å) reacts easily with a 2 M solution of *n*-propylamine giving the corresponding amine intercalate with expansion of the interlayer distance to 18.4 Å (Figure 12C). This is a strong indication of the layered structure of this novel SZS. The lack of amine intercalation observed in the case of $H_2Zr_5Si_2O_{15}\cdot3H_2O$ (d =10.8 Å) could be due to its smaller interlayer distance that could lead to strong hydrogen bonding between layers. According to the TGA data (Figure 13C) thermal decomposition of the *n*-propylamine intercalate occurs in four main steps with a total weight loss of 17.14%. Since uptake of propylamine occurred from the mixed water−amine solution, we assume that the final product could contain a certain amount of interlayer water. Thus the weight loss of about 3.10% (up to 125 °C) is due to 1.53 mol of this water release. An additional 1 mol of water (or 2.03%) splits out from condensation of the two hydroxyl groups. This leaves 12.01% propylamine and amounts to 1.81 mol. Thus, the amine intercalate has the tentative composition $(C_3H_7NH_3)_{1.81}H_{0.19}Zr_5Si_2O_{15}\cdot1.53H_2O$, indicating practically complete substitution of protons in SZS−H for amine. The *n*-alkylamine insertion results in a drastic decrease of the water content in the interlayer space.

The potentiometric titration curves showing the alkali-metal ion uptake by $H_2Zr_5Si_2O_{15}\cdot5H_2O$ from 0.05 M MCl−MOH (M = Li, Na, K, Cs) solutions are presented in Figure 14a. Analysis of these data shows that the 12.6 Å phase (5 hydrate) is a weakly acidic exchanger and its ion-exchange behavior toward Li^+ and Na^+ ions is similar to that of $H_2Zr_5Si_2O_{15}\cdot3H_2O$. Lithium and sodium ion uptake starts at pH > 4, which is followed by a considerable increase in their uptake in the pH range 6−8, reaching the maximum value of 2.3−2.4 mequiv/g at pH = 12. The difference found is concerned with the heavy alkali metals uptake. Contrary to the 10.8 Å phase (3 hydrate) the zirconium silicate with a 12.6 Å d spacing does not exclude large cations such as K^+ and Cs^+, but, by contrast, it exhibits preference in their uptake in low acid and neutral media. The following selectivity series was found at pH 7: $K^+ > Cs^+ > Li^+ > Na^+$. This is a direct result of a much bigger interlayer distance in the 12.6 Å phase, which removes the steric restrictions for large cation uptake, existing in the case of the 10.8 Å phase.

Potentiometric titration curves of $H_2Zr_5Si_2O_{15}\cdot5H_2O$ with alkaline-earth metal hydroxides are presented in Figure 14b. In this particular case the influence of the bigger SZS−H interlayer distance upon the cations uptake shows itself most clearly. Exchange of alkaline-earth metal cations starts at pH > 3 and the IEC values stay extremely low (0.2−0.3 mequiv/g) until pH 6. The first and the last increase in alkaline-earth metal cations uptake from 0.2−0.3 mequiv/g to 2.3−2.4 mequiv/g (theoretical IEC 2.37 mequiv/g) was observed at pH 6−7. No other changes in cation uptake were found at pH > 8. As in the case of the 10.8 Å phase $H_2Zr_5Si_2O_{15}\cdot5H_2O$ does not show any differences in affinity to alkaline earth metal cations.

$Na_2ZrSi_3O_9\cdot3H_2O$. The formation of $Na_2ZrSi_3O_9\cdot3H_2O$ was observed when the Silicic acid: $Zr(OC_3H_7)_4$ ratio was 5:1 and NaOH concentration was 3 M. Unfortunately, as in all other cases this compound is characterized by low crystallinity, which does not allow

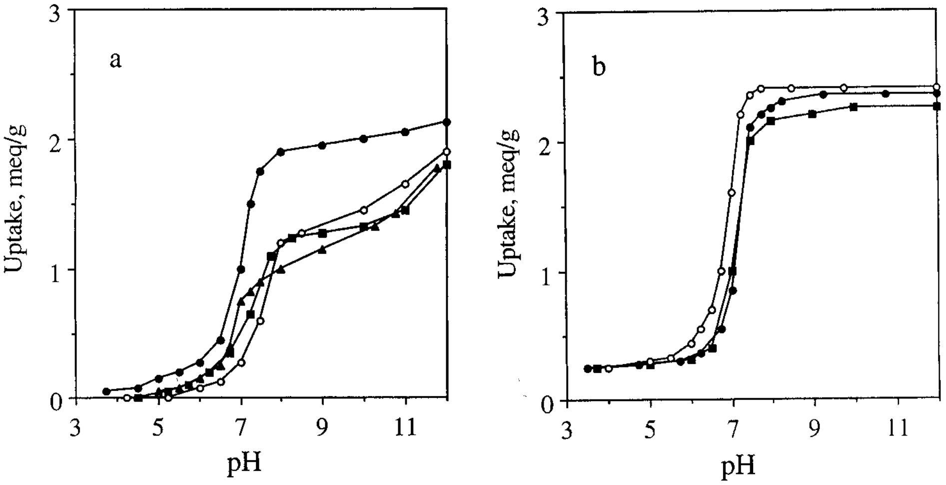

Figure 14. Potentiometric titration of $H_2Zr_5Si_2O_{15}\cdot 5H_2O$ with (a) LiOH (■), NaOH (○), KOH (●), and CsOH (▲). (b) $Ca(OH)_2$ (■), $Sr(OH)_2$ (○), and $Ba(OH)_2$ (●).

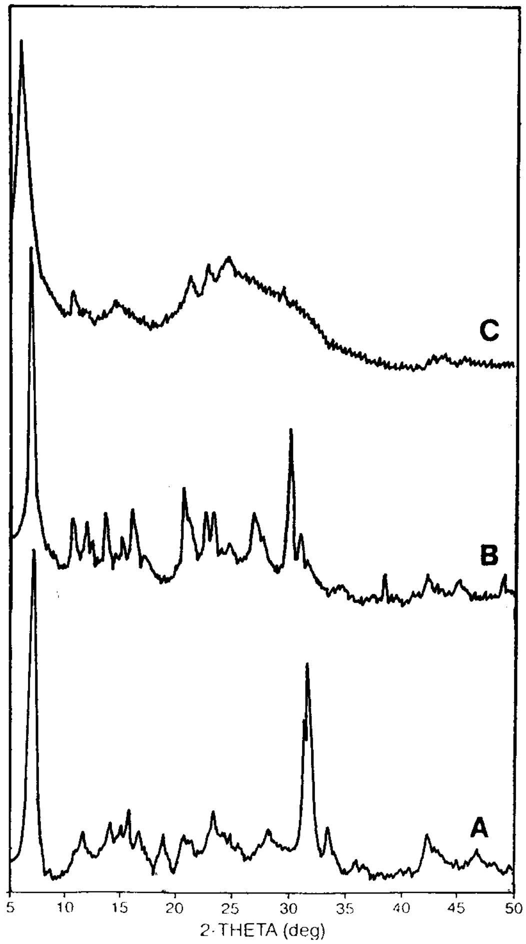

Figure 15. XRD powder patterns for $Na_2ZrSi_3O_9\cdot 3H_2O$ (A), $H_2ZrSi_3O_9\cdot 4H_2O$ (B), and $(C_3H_7NH_3)_{0.70}H_{1.30}ZrSi_3O_9\cdot 1.70H_2O$ (C).

us to solve its structure by the powder diffraction method. The XRD powder pattern of the novel sodium zirconium silicate having a first X-ray reflection at 12.8 Å is presented in Figure 15A. The SEM photographs of this compound, made at 500× magnification (Figure 16a), shows that its particles have a globular shape with a size of 15−30 μm. As seen at higher magnification (20 000×, Figure 16b) each particle is composed of a great amount of very thin (<0.1 μm) flakes. According to the elemental analysis the SZS 12.8 Å phase contains 21.1% Zr, 19.5% Si, and 12.1% Na, which corresponds fairly well to the theoretically calculated values for formula $Na_2ZrSi_3O_9\cdot 3H_2O$ (FW = 419): Zr, 21.72%; Si, 20.05%; Na, 10.98%.

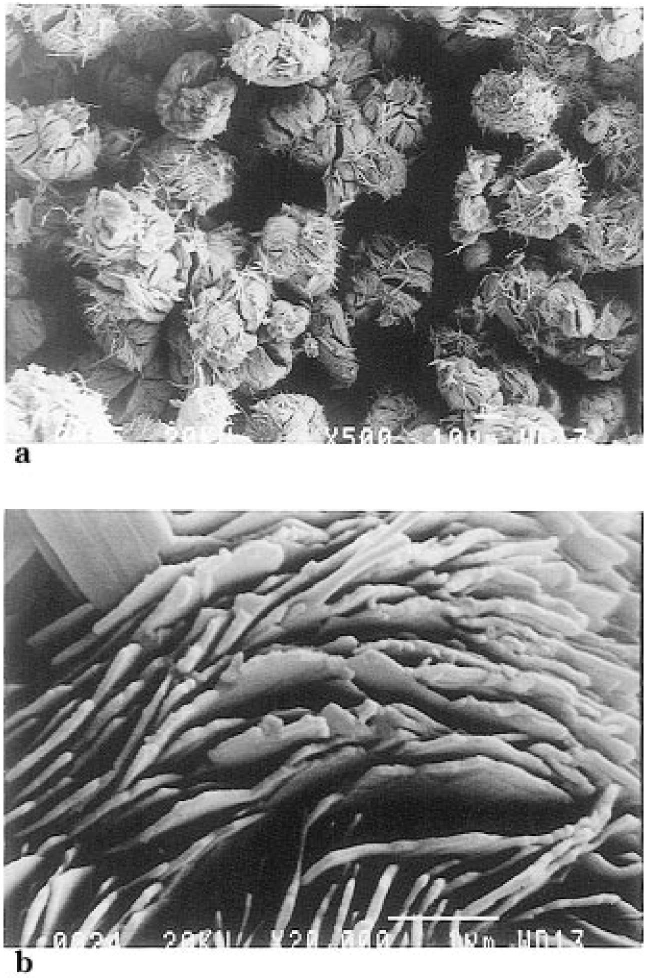

Figure 16. Electron micrograph at 500× (a) and 20 000× (b) magnification showing the morphology of the hydrothermally grown crystals of $Na_2ZrSi_3O_9\cdot 3H_2O$.

This novel sodium zirconium silicate is moderately stable in alkaline media but was easily decomposed by concentrated mineral acids. $Na_2ZrSi_3O_9\cdot 3H_2O$ was converted practically completely (>98%) into the proton form by exhaustive treatment with 0.05 M HNO_3. Some decomposition of the material was observed under these

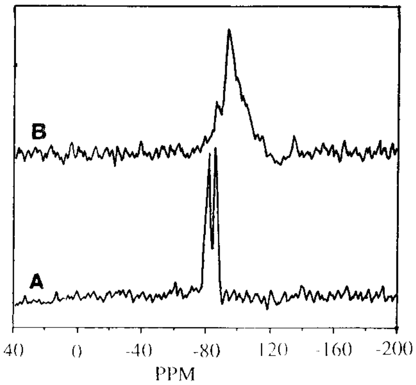

Figure 17. ^{29}Si MAS NMR spectra of $Na_2ZrSi_3O_9{\cdot}3H_2O$ (A) and $H_2ZrSi_3O_9{\cdot}4H_2O$ (B).

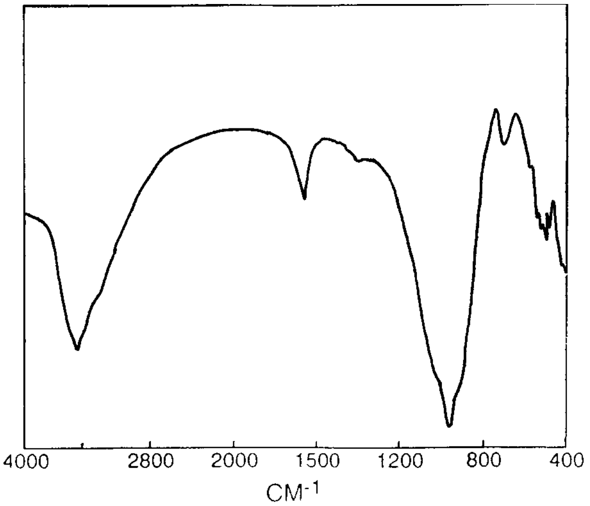

Figure 18. IR spectrum of $Na_2ZrSi_3O_9{\cdot}3H_2O$.

conditions. Found: Zr, 22.5%; Si, 20.4%. Calcd for $H_2ZrSi_3O_9{\cdot}4H_2O$ (FW = 393): Zr, 23.15%; Si, 21.37%. The XRD powder pattern of $H_2ZrSi_3O_9{\cdot}4H_2O$ is shown in Figure 15B. This phase has a first strong X-ray reflection at 13.4 Å.

In the ^{29}Si NMR spectrum of the sodium phase two peaks with practically equal intensity at −81.5 and −85.3 ppm were found, whereas in the protonic phase only one rather broad signal with a maximum at −97 ppm was observed (Figure 17). A significant shift of the NMR peak position ($\Delta H > 10$ ppm) accompanying the conversion of the compound from Na into H form is strongly indicative that in $H_2ZrSi_3O_9{\cdot}4H_2O$ the hydroxyl groups are connected with silicon atoms.

The infrared spectrum (400−4000 cm^{-1} range) of the air-dried $Na_2ZrSi_3O_9{\cdot}3H_2O$ sample is presented in Figure 18. It has a broad water O−H stretching band and two bands of middle intensity at 1630 and 1410 cm^{-1}. There is a very broad, intense composite band centered at 960 cm $^{-1}$ and a series of bands in the 400−600 cm^{-1} region.

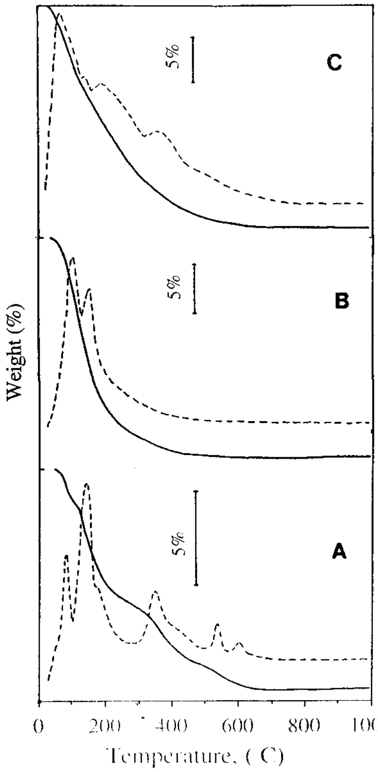

Figure 19. TG (—) and DTG (- - -) curves for $Na_2ZrSi_3O_9{\cdot}3H_2O$ (A), $H_2ZrSi_3O_9{\cdot}4H_2O$ (B), and $(C_3H_7NH_3)_{0.70}H_{1.30}ZrSi_3O_9{\cdot}1.70H_2O$ (C).

According to the TGA weight loss curve (Figure 19A) $Na_2ZrSi_3O_9{\cdot}3H_2O$ undergoes thermal decomposition in four main steps and two minor ones in the temperature range from 50 to 630 °C with a total weight loss of 11.58%. In the first two steps (50−95 and 95−250 °C) the weight losses amount to 1.54% (0.35 mol) and 5.47% (1.25 mol), respectively. These first two weight losses total to 1.60 mol of H_2O and are attributed to the interlayer crystal water. In the third region (250−450 °C, $\Delta M_3 = 3.39\%$) and fourth steps (450−630 °C, $\Delta M_4 = 1.18\%$) 0.78 and 0.27 mol of water coordinated with the sodium ions, respectively, are released. In the case of the protonic phase (Figure 19B) the total weight loss is higher, 22.12%, which corresponds to the weight loss expected for the formula $H_2ZrSi_3O_9{\cdot}3.78H_2O$. The water release for $H_2ZrSi_3O_9{\cdot}3.78H_2O$ occurs in two steps: in the temperature range 50−130 °C it amounts to 9.42% or 2.04 mol and in the range 130−570 °C 12.70% or 2.74 mol. The first weight loss is connected with the interlayer crystal water release, whereas in the second step the loss should be attributed to 1.0 mol of structurally bound water, due to condensation of hydroxyl groups, and the residual 1.74 mol of much more tightly bound interlayer water, possibly existing in the form of H_3O^+ cations occupying positions of the sodium atoms.

It was found that the protonic phase of this novel zirconium silicate reacts with liquid *n*-propylamine giving the corresponding intercalation product with an expansion of the interlayer distance. The XRD powder pattern of the *n*-propylamine intercalate is presented in Figure 15C. This compound has a first strong reflection at 16.0 Å. According to the TGA data (Figure 19C) thermal decomposition of the *n*-propylamine intercalate occurs in a three main steps with a total weight loss of 22.93%. Considering that the *n*-propylamine adsorption was studied from the mixed water−amine solution, we assume that the weight loss of about 7.8% (up to 120 °C) is due to the presence of about 1.70 mol of the interlayer water. An additional mol of water (or 4.58%) splits out from condensation of the two hydroxyl groups. This leaves 10.55% for propylamine, which amounts to 0.70 mol. Thus, the amine intercalate has the tentative composition $(C_3H_7NH_3)_{0.70}H_{1.30}ZrSi_3O_9{\cdot}1.70H_2O$, indicating the lack of a complete substitution of protons in SZS−H for amine.

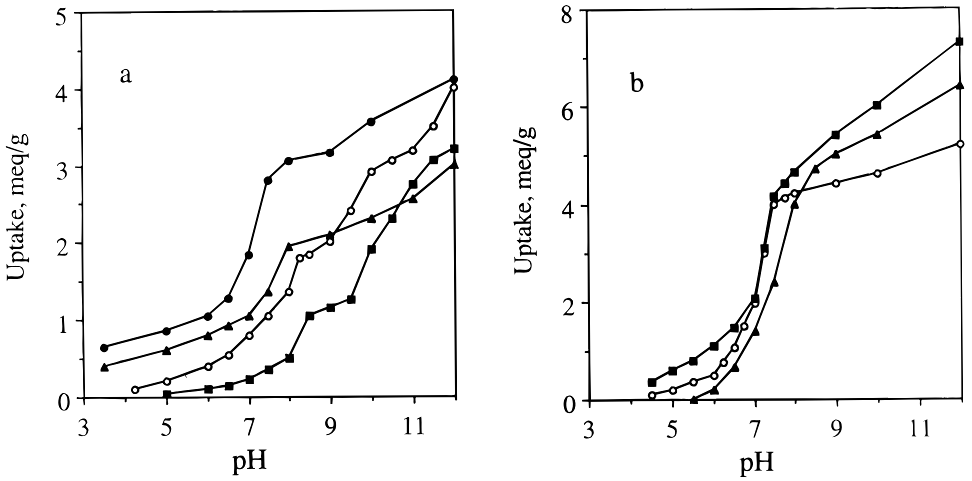

Figure 20. Potentiometric titration of $H_2ZrSi_3O_9{\cdot}4H_2O$ with (a) LiOH (■), NaOH (○), KOH (●), and CsOH (▲). (b) $Ca(OH)_2$ (■), $Sr(OH)_2$ (○), and $Ba(OH)_2$ (▲).

The presence in the structure of the hydrated zirconium silicate of the hydroxyl (Zr−OH and/ or Si−OH) functional groups and its layered nature indicates that this material should behave as a cation exchanger in neutral and alkaline media with a theoretical ion-exchange capacity (IEC) of about 5.09 mequiv/g. The experimental curves that show the dependencies of alkali-metal ions uptake on the pH by $H_2ZrSi_3O_9{\cdot}4H_2O$ from 0.05 M MCl−MOH (M = Li, Na, K, Cs) solutions are presented in Figure 20a. Analysis of these data shows that the novel layered zirconium silicate behaves as a moderately weak acid cation exchanger. Alkali-metal uptake starts at pH 3−5 (depending on the cation) and the ion-exchange capacity increases with increase of pH. The substantial cation uptake (0.5−0.8 mequiv/g) at such a relatively low pH values (3−4) suggests that Si−OH groups could be responsible for this behavior by analogy with known titanium silicates.[7,8b] In low acid and neutral solution this zirconium silicate prefers large cations—K^+ and Cs^+—and the selectivity series $K^+ > Cs^+ > Na^+ > Li^+$ is observed. A substantial increase in alkali-metals uptake starts in the pH range 6−7 for K^+ ion and at pH 7−9 for the other alkali cations. In the pH range 9−10 a change of selectivity takes place, and at pH > 10 we have another selectivity series: $K^+ > Na^+ > Li^+ > Cs^+$. The maximum value of alkali-metal ions uptake, found at pH = 12, is 4.3 mequiv/g, which is about 85% of the theoretical IEC.

Exchange of alkaline-earth metal ions by $H_2ZrSi_3O_9{\cdot}4H_2O$ was studied from 0.025 M $MeCl_2$−$Me(OH)_2$ solutions. As seen in Figure 20b zirconium silicate practically does not adsorb alkaline earth metal cations in acid solutions (pH < 5−6). The selectivity series $Ca^{2+} > Sr^{2+} > Ba^{2+}$ is observed at pH < 7. A drastic increase in all cations uptake (up to 4.0−4.5 mequiv/g), corresponding to 80−90% exchange, is observed in the pH range 6.5−7.5. The alkaline-earth metal uptake continues gradually with pH increase, reaching maximum values of 7.5 mequiv/g at pH 11.5 (for Ca^{2+} and Ba^{2+} ions). Such a superequivalent adsorption is apparently the result of precipitation of alkaline-earth metals in alkaline media in the pores of the exchanger in the form of the corresponding hydroxides.

Characterization of Ion-Exchange Properties of Sodium Zirconium Silicates. The ion-exchange affinity of sodium zirconium silicates toward alkali, alkaline earth, and some transition metals was determined by the batch technique from 0.001 M solutions. The equilibrium pH values were in the range 7.0−9.5, and the distribution coefficient values are presented in Tables 1 and 2.

Analysis of these data shows that all tested sodium zirconium silicates, in contrast to some sodium titanium silicates,[6−8] exhibit extremely low affinity for alkali metals (K_d < 1000). The only exception found is $Na_2ZrSi_3O_9{\cdot}2H_2O$, showing a distinct affinity for potassium over all other cations. There could be several reasons explaining this observation, and the main one is the lack of geometrical correspondence between the parameters of the exchange sites in exchangers and the size of a specific alkali metal. Another important factor here could be much less acidity of zirconium silicate functional groups in comparison with those in titanium silicates.

The affinity of sodium zirconium silicates for alkaline earth metals is considerably higher than for alkali metals. In almost all cases there is a tendency toward increasing K_d values with increase of the cation size. Particularly high affinity for Sr^{2+} (K_d >100 000) was shown by the novel layered zirconium silicate $Na_2ZrSi_3O_9{\cdot}3H_2O$, which suggests its possible use for a selective radioactive strontium recovery from highly alkaline nuclear waste. Sufficiently high distribution coefficients (5000−10 000) were found also for Sr^{2+} and Ba^{2+} ions on other exchangers, with the exception of $Na_2ZrSi_3O_9{\cdot}2H_2O$.

Investigation of di- and trivalent metal exchange by sodium zirconium silicates both from individual solutions and in the presence of 1 M $NaNO_3$ as a background electrolyte (Table 2) shows extremely high affinity of some of them for selected ions. For example, the layered $Na_2Zr_5Si_2O_{15}{\cdot}4H_2O$ preferably exchanges Cr^{3+}, Pb^{2+}, and Co^{2+} ions from individual solutions (K_d 30 000−100 000). The distribution coefficients drop drastically when a 500 times excess of sodium ions is added, but nevertheless they are sufficiently high for Cr^{3+} and Pb^{2+} ions (25 000 and 4900, respectively). Practically the same situation is observed in the case of another novel layered zirconium silicate $Na_2ZrSi_3O_9{\cdot}3H_2O$. This exchanger exhibits extremely high affinity for Co^{2+} and Cu^{2+} ions in individual solution (K_d >10 000 and 24 500, respectively), which is retained on a sufficiently high

Table 1. K_d Values (in mL/g) for Alkali and Alkaline Earth Metal Cations Uptake by Sodium Zirconium Silicates

sorbent	Li^+	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$Na_2Zr_5Si_2O_{15}\cdot H_2O$	33		330	390	340	815	5160	4600
$Na_2ZrSi_3O_9\cdot 3H_2O$	67		840	4400	75000	9340	>100000	24100
$Na_2ZrSi_3O_9\cdot 2H_2O$	150		6400	1280	6	22	590	2070
$Na_3HZrSi_2O_8$	15		75	1	80	1100	10000	5000
$Na_4Zr_2Si_5O_{16}\cdot H_2O$	23		75	50	83	240	10500	1400

Table 2. K_d Values (in mL/g) for Di- and Trivalent Metal Cations Uptake by Sodium Zirconium Silicates

sorbent	Cr^{3+}	Cu^{2+}	Co^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
$Na_2Zr_5Si_2O_{15}\cdot 4H_2O$	>100000	3500	28900	8900	70000	500
$Na_2ZrSi_3O_9\cdot 3H_2O$	1000	24500	>100000	4200	330	80
$Na_2ZrSi_3O_9\cdot 2H_2O$	1290	500	800	1060	140000	16
$Na_3HZrSi_2O_8$	1050	10700	18600	7500	6100	2500
$Na_4Zr_2Si_5O_{16}\cdot H_2O$	>100000	20200	17600	6900	17400	240
In the Presence of 1 M $NaNO_3$						
$Na_2Zr_5Si_2O_{15}\cdot 4H_2O$	25100	1960	4	57	4900	170
$Na_2ZrSi_3O_9\cdot 3H_2O$	19200	6000	3360	2600	32100	170
$Na_2ZrSi_3O_9\cdot 2H_2O$	60	5100	11	18	1600	33
$Na_3HZrSi_2O_8$	25800	6000	260	2060	29700	530
$Na_4Zr_2Si_5O_{16}\cdot H_2O$	33500	5280	110	500	27500	115

level in the presence of 1 M $NaNO_3$ (K_d(Co) 3360 and K_d(Cu) 6000). It was found also that sodium nitrate does not detract from but, quite the reverse, enhances lead and chromium uptake (K_d(Pb) 32 100; K_d(Cr) 19 200) by $Na_2ZrSi_3O_9\cdot 3H_2O$. A high affinity for Cr^{3+} and Pb^{2+} is also shown by $Na_6Zr_2Si_4O_{15}$ and $Na_4Zr_2Si_5O_{15}\cdot H_2O$.

Conclusions

The results presented here demonstrate that hydrothermal synthesis is a powerful method for the preparation of novel hydrated polyvalent metal silicates. Three novel sodium zirconium silicates were synthesized under mild hydrothermal conditions. Their chemical composition and physicochemical properties were studied with the use of elemental analysis, TGA, X-ray, IR and ^{29}Si MAS NMR spectroscopy. It was found that all of them are layered compounds. Thermal and chemical stability, different Zr/Si molar ratio, and intercalation ability suggest that these compounds could be promising for pillaring with inorganic and organic species for synthesis of new functionally designed and tailored catalysts and supports for catalyst and adsorbents. High affinity for some transition and toxic heavy metals makes sodium zirconium silicates attractive for high-level purification of certain technological solutions and wastes containing these elements.

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