Synthesis of microporous zirconosilicates containing ZrO_6 octahedra and SiO_4 tetrahedra

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Three novel crystalline zirconosilicate molecular sieves, analogous to elpidite, umbite and gaidonnayite minerals, containing zirconium in octahedral coordination and silicon in tetrahedral coordination are synthesized.

The isomorphous substitution of various metal ions into crystalline inorganic frameworks has been a very active area of research over the last two decades. By substituting metal ions with different oxidation states and electronegativities, it is possible to modify the acid strength and the ion-exchange capacities of zeolites.[1] Most of the isomorphous substitutions in zeolite frameworks involve the incorporation of the metal ions into tetrahedral positions. It has been shown that Ti,[2] Zr[3] and Sn[4] can form crystalline silicate materials,[5] where Si is in tetrahedral coordination and Ti, Zr or Sn is in octahedral coordination. Since these metal ions are in 4+ oxidation state and in octahedral coordination, this results in two negative charges on the framework for each of the metal ions incorporated.

In 1990, Chapman[6] reported two titanosilicate minerals (vinogradovite and zorite) containing Ti in octahedral coordination. Subsequently, Engelhard Corporation developed microporous titanium silicate molecular sieves, described as ETS-4[7] and ETS-10,[8] which contain silicon in tetrahedral coordination and titanium in octahedral coordination. Until now, only titanosilicates have been synthesized with large pore openings. Similarly to titanium, zirconium also forms a variety of silicate minerals having zirconium in octahedral coordination. Until now, zirconosilicate minerals have been synthesized at temperatures between 300 and 700 °C and pressures of up to 700 bar.[9]

Here, for the first time, we report the synthesis of gaidonnayite and umbite zirconosilicate minerals. We have also been able to synthesize elpidite at 200 °C under autogeneous pressure. The synthesis of zirconosilicates has been carried out using sodium silicate, zirconyl chloride, potassium fluoride, sodium hydroxide, potassium hydroxide, hydrochloric acid and tetramethylammonium bromide using the gel compositions reported in Table 1. All these chemicals were obtained from Aldrich. The syntheses were carried out hydrothermally at 200 °C under static conditions. After the specified crystallization time, the product was filtered off, washed with deionized water and dried at room temperature.

The XRD patterns of all three zirconosilicates shown in Fig. 1 match well with mineral counterparts. Umbite and gaidonnayite belong to $P2_12_12_1$ and $P2_1nb$ space groups, respectively[11,12] and all three minerals have an orthorhombic unit cell. The
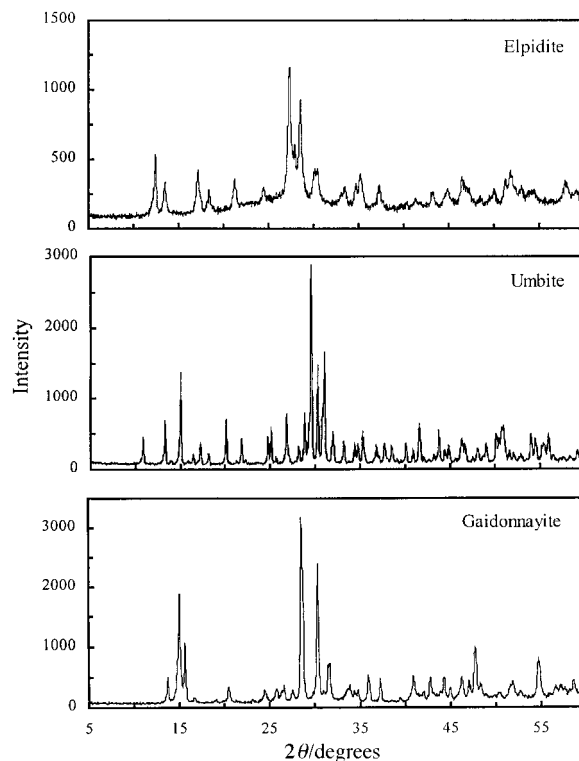

Fig. 1 The XRD patterns of zirconosilicates analogous to elpidite, gaidonnayite and umbite minerals.

samples calcined at 400 °C have XRD patterns identical to those of as-synthesized materials, indicating a good thermal stability. Thermogravimetric analysis of calcined and rehydrated elpidite and umbite samples showed 7 and 11 wt% loss, respectively between 35 and 300 °C. The BET surface area of zirconosilicates measured at liquid nitrogen temperature was negligible, showing that the pore size is less than the kinetic diameter of the nitrogen molecule. However, based on the structural data and the water adsorption measurements (type I isotherm), they can be classified as microporous materials. Recently, the titanium analogue of umbite also has been shown to adsorb water but not nitrogen.[10]

Chemical analysis data of well crystalline, pure forms of zirconosilicates are summarized in Table 2. The Si/Zr ratios of elpidite, umbite and gaidonnayite are 5.1, 4.3 and 3.0, respectively. The chemical formulas of umbite[11]

Table 1 Gel composition and crystallization times in the synthesis of zirconosilicates

Compound	SiO_2	ZrO_2	K_2O	Na_2O	R_2O^a	HCl	KF	H_2O	t/d
Elpidite	1.0	0.17	0.10	—	—	1.59	0.33	29.8	35
Gaidonnayite	1.0	0.20	0.25	1.17	0.20	0.40	0.50	35.0	19
Umbite	1.0	0.10	0.27	0.52	—	0.20	0.53	30.8	32
Umbite	1.0	0.10	1.19	0.23	0.3	0.20	0.50	36.8	2

^{a} R = Tetramethylammonium bromide.

Table 2 Chemical analysis of zirconosilicates

Compound	LOI^a (wt%)	Si/Zr	Si/Al	Si/ (Al + Zr)	(Na + K)/ (2Zr + Al)
Elpidite	10.7	5.07	59.78	4.67	0.78
Umbite	10.2	4.25	90.34	4.06	1.20
Gaidonnayite	10.3	3.06	60.52	3.06	1.02

^{a} LOI = loss of ignition.

$(K_2ZrSi_3O_9 \cdot H_2O)$, elpidite[9] $(Na_2ZrSi_6O_{15} \cdot 3H_2O)$ and gaidonnayite[12] $(K_2ZrSi_3O_9 \cdot 2H_2O)$ are reported in the literature. The calculated chemical formulas of umbite $(M_{2.4}ZrSi_4O_{11})$, elpidite $(M_{1.6}ZrSi_5O_{13})$ and gaidonnayite $(M_2ZrSi_3O_9)$ materials synthesized in this study are slightly different from those reported in the literature.

Owing to an aluminium impurity in the source materials, there is always some aluminium in these materials. If both Al and Zr are in the framework, this ratio should be 1.0. A deviation from this value indicates that either there is an excess of alkali metal ion (possibly due to the presence of defects) or a part of these metals are not substituted into the framework. The lower ratio for elpidite is most probably due to the presence of some amorphous material.

The ion-exchange capacity of umbite was tested by refluxing in 0.5 M NaCl solution. The original sample contains 29% Na and 71% K, while the Na-exchanged sample had 81% Na and 21% K cations adding up to a $(Na + K)/(2Zr + Al)$ ratio of 1.02. Since zirconium has two negative charges, two cations are required to balance the charge. The Si/Zr and Si/Al ratios of this sample were 3.6 and 76.6, respectively. These results confirm that at least 80% of the cations are exchangeable and most of the Zr and Al are present in the framework. Upon ignition, umbite lost about 13% of its weight as water, which is close to the value obtained by TGA.

The hydroxide concentration in the gel influences the rate of hydrolysis of the metal ions and also the rate at which the condensation of these species into the framework structures takes place. In general, an increase in the hydroxide concentration decreases the nucleation time and accelerates the crystal growth. As can be seen in Table 1, by increasing the hydroxide concentration and also by partially replacing sodium by potassium, the crystallization time of umbite was reduced from 38 to 2 days. We have been able to synthesize at least three more zirconosilicates by changing the OH^- ion concentration. However, the structures of these materials are not yet identified.

In conclusion, we have demonstrated the synthesis of microporous zirconosilicates analogous to minerals under hydrothermal conditions at temperatures significantly lower than those used previously in the literature. These zirconosilicates might be useful adsorbents for kinetic separation of smaller gaseous molecules such as water from a mixture with other components.

Notes and references

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