

SYNTHESIS, CRYSTALLOGRAPHIC, AND THERMAL PROPERTIES OF A NEW POROUS SILICA

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ABSTRACT. A new porous tectosilicate has been synthesized in the presence of boric acid and 1,2,2,6,6-pentamethylpiperidine as guest molecules. It crystallizes in the monoclinic system with $a_0 = 9.91(1)\text{\AA}$, $b_0 = 20.63(3)\text{\AA}$, $c_0 = 9.80(2)\text{\AA}$, and $\beta = 99.7(2)^\circ$. After heat treatment at 820°C for 1 hour the guest molecules are set free whereas the silica host framework is retained. From crystal morphology and thermal behaviour it is concluded that the new material possesses channel-like voids.

1. INTRODUCTION

A series of silica end-members of zeolites (zeosils) as well as clathrate compounds with framework composition SiO_2 (clathrasils) have been synthesized in the recent past [1, 2]. It has been concluded that the organic guest species alone act as templates for the formation of the open framework and that these guest molecules have a structure directing role. In a detailed study it has been shown that the size and dimensionality of the pore system in porous tectosilicates is dependent on the properties of the guest species used for synthesis [3].

In this paper we report on a new porous silica framework (porosil [1]) which has been crystallized in the presence of 1,2,2,6,6-pentamethylpiperidine and boric acid.

2. EXPERIMENTAL

The new porosil was synthesized from aqueous solutions of silicic acid and boric acid in the presence of 1,2,2,6,6-pentamethylpiperidine, , as guest molecule. Tetramethoxysilane was hydrolyzed in 1M aqueous ethylenediamine to give a homogeneous 0.5M silica solution.

h	k	l	$d_{\text{obs.}}$	I/I_0	h	k	l	$d_{\text{obs.}}$	I/I_0
0	2	0	10.18	10	-1	4	2	3.464	1
1	0	0	9.72	5	1	5	1		
0	1	1	8.715	1	3	0	0	3.255	1
0	3	1	5.574	1	-3	1	1	3.220	1
-1	3	1	5.102	1	3	2	0	3.102	1
-2	0	1	4.695	1	-2	1	3	2.892	2
-1	1	2	4.527	2	1	1	3		
2	2	0	4.407	3	-2	5	2	2.793	2
0	4	2	3.531	3	0	6	2		
-2	2	2			-1	7	1	2.746	2

Tab. 1: X-ray powder data of the new zeosil.

characteristic morphology in spherulitic bundles (fig. 1). Single crystal diffraction studies revealed that the crystals were twinned with high disorder parallel to (100). From electron diffraction experiments the unit cell parameters have been obtained. The X-ray powder pattern could be indexed in the monoclinic system with $a_0 = 9.91(1)\text{\AA}$, $b_0 = 20.63(3)\text{\AA}$, $c_0 = 9.80(2)\text{\AA}$, and $\beta = 99.7(2)^\circ$ (tab. 1).

Thermogravimetric analysis was performed in the temperature range 30 - 820°C with 10°C/min heating rate (fig. 2). Continuous weight loss was observed in the temperature range from 150 - 820°C. At 500°C the sample turned black due to the decomposition of the organic guest molecules. The host framework is retained even after the heat treatment of the product at 820°C for 1 hour.

Using an energy dispersive system only Si as framework constituent has been detected. Boron analysis yielded about 1% B in the as synthesized sample, whereas after calcination only traces were detected.

From conditions of synthesis, thermal properties, and chemical analysis it is concluded that the new material belongs to the class of porosils having host framework composition of essentially SiO_2 . The organic guest species 1,2,2,6,6-pentamethylpiperidine and the boric acid play an indispensable role as structure directing agents. From

To this boric acid (0.07M) was added. On mixing with boric acid a small amount of silica gel precipitated. After addition of the guest molecule (5-10vol%) the solution was sealed in silica tubes and kept in an oven in the temperature range 150 - 165°C. After about three months reaction time lath shaped crystals were obtained. The crystalline material was characterized by X-ray powder diffraction and electron diffraction. Silicon has been analyzed using an energy dispersive system. Boron analysis was performed with an Jobin Yvon JY38 plasma spectrometer (ICP) before and after calcining the sample. Thermogravimetric analysis was done using a DuPont 1090 Thermal Analyser.

3. RESULTS AND DISCUSSION

The new porosil framework typ could only be crystallized using 1,2,2,6,6-pentamethylpiperidine as guest molecule and in the temperature range 150 - 165°C and in the presence of boric acid. The variation of the concentration of the guest and of the ratio of guest/boric acid did not influence the formation of the product. However, at temperatures higher than 165°C and in the absence of boric acid at temperatures from 150' - 200°C only the clathrasil dodecasil 1H [4] was obtained.

The product appears as lath shaped transparent crystals of

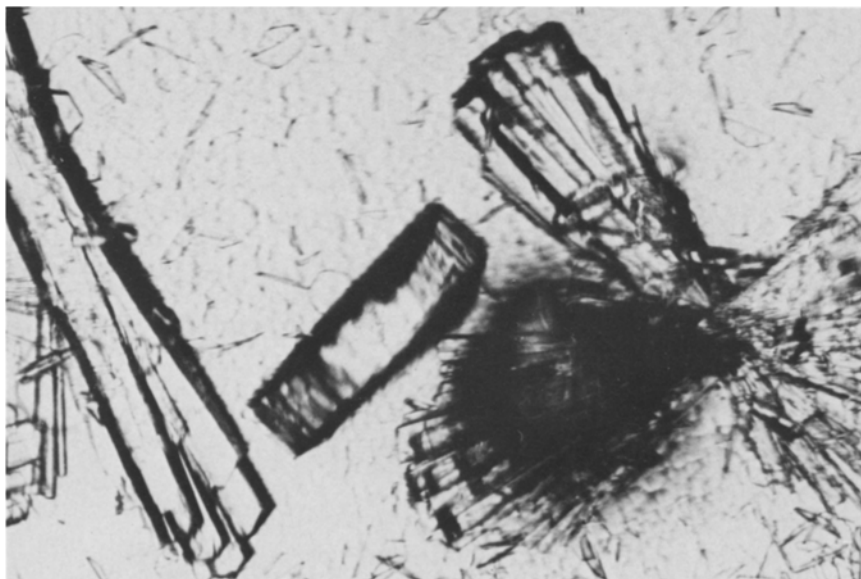


Figure 1: Micrograph of the new zeosil together with a dodecasil 1H crystal.

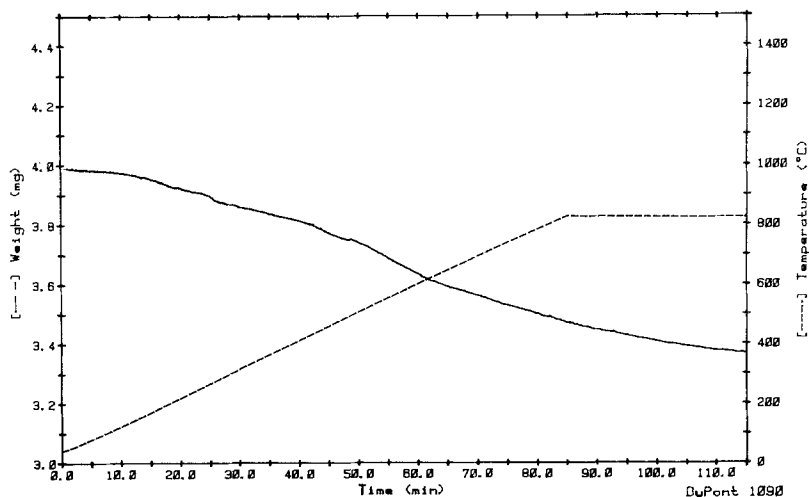


Figure 2: TGA curve of the new zeosil.

synthesis conditions it is evident that the organic guest species forms a Lewis acid-base complex with boric acid which probably acts as template. Therefore it is apparent that isomorphous replacement of Si by B in the host framework is unlikely to occur.

Moreover, continuous weight loss observed in TGA indicates that the new porosil possesses channel-like voids.

Structures of clathrasils and zeosils have regions of high tetrahedral density and regions of low tetrahedral density where the guest molecules are located. It has been observed that the crystal growth is fast in the regions of high tetrahedral density [5]. The rate determining step in crystal growth, however, is the formation of the framework around the guest species [6]. On this basis it may be suggested that the new porosil possesses channel-like voids parallel to the needle axis $[001]$.

Acknowledgement. The author thanks Dr. M. Czank for support in electron microscopy and Prof. R.P. Gunawardane for critically reading the manuscript.

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