

Studies on Clathrasils VIII. Nonasils-[4¹⁵⁸], 88SiO₂ · 8M⁸ · 8M⁹ · 4M²⁰: Synthesis, Thermal Properties, and Crystal Structure*

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Abstract. Nonasils-[4¹⁵⁸], 88SiO₂ · 8M⁸ · 8M⁹ · 4M²⁰, have been synthesized with 2-methylpyrrolidine, hexamethyleneimine, 2-(aminomethyl)-tetrahydrofuran, 1,2-diaminocyclohexane, 2-methylpiperidine, 2-methylpiperazine, 1-aminobutane, 2-aminobutane, and 2-aminopentane as guest molecules, M²⁰. The samples have been prepared from aqueous silicate solutions which were sealed in silica tubes and heated at about 200°C for several weeks. These clathrasils crystallize in space group *Fmm*. For the nonasil with 2-aminopentane as the guest molecule and the unit cell dimensions $a_0 = 22.232(6)$ Å, $b_0 = 15.058(4)$ Å, and $c_0 = 13.627(4)$ Å, the structure has been refined using 550 non-equivalent single crystal reflexions to a reliability factor $R_w = 0.125$. The 3-dimensional 4-connected silica host framework has three types of cage-like voids, [5⁴6⁴], [4¹5⁸], and [5⁸6¹²], the latter housing the structure-controlling guest molecules, M²⁰. The non-spherical shape of the guest molecules is the most important factor for the formation of nonasils-[4¹⁵⁸]. On heating nonasils-[4¹⁵⁸] up to 950°C the organic guest species are driven out and the pure silica form of nonasil is obtained.

Key words: Clathrasil, nonasil, synthesis, crystal structure, porous silica.

1. Introduction

Clathrasils, i.e., clathrate compounds with 3-dimensional 4-connected host frameworks of silica, represent a class of porous tectosilicates with no exchange properties for the guest species. They are, therefore, distinct from zeolites [2]. Using a variety of organic and inorganic guest molecules, four topologically different frameworks have been synthesized [3,4]. The clathrasils all contain, as a common feature, cage-like voids occupied by guest species. Three of the silica frameworks of clathrasils reported so far are isotopological to clathrate hydrates: melanophlogites to clathrate hydrates of type I, dodecasils 3C to clathrate hydrates of type II, and dodecasil 1H to its recently synthesized clathrate hydrate analogue [5]. We report here on a new clathrasil family, the nonasils-[4¹⁵⁸], which have no structural analogues in clathrate hydrate chemistry.

2. Nomenclature

A clathrasil is systematically designated by its fundamental cage or cages from which its tetrahedral framework can be constructed. For example, the phase described in this paper is named nonasil-[4¹⁵⁸] since its silica framework can be completely constructed by linking

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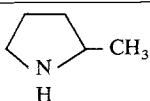
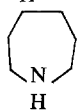

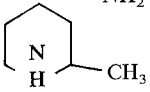
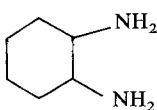
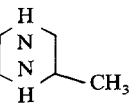
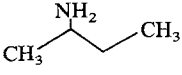
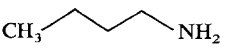
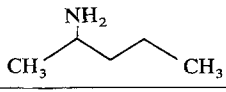
9-hedra which are bounded by one tetragon and eight pentagons. Its ideal chemical formula can be given by the unit cell content $88\text{SiO}_2 \cdot 8\text{M}^8 \cdot 8\text{M}^9 \cdot 4\text{M}^{20}$ where M^8 , M^9 , and M^{20} are potential guest molecules in cage-like 8-hedra, 9-hedra (fundamental cage), and 20-hedra of the host framework. Not all cages have to be occupied by guest molecules. Since the nonasils-[4¹5⁸] are the only nonasils known so far, the short term nonasils will be used throughout this paper. (For a more detailed proposal for the nomenclature of clathrasils, zeolites and other porous framework compounds see [6]).

3. Experimental

3.1. SYNTHESIS

Nonasils have been synthesized from aqueous silicate solutions using 2-methylpyrrolidine, hexamethyleneimine, 2-methylpiperidine, 2-(aminomethyl)-tetrahydrofuran, 1,2-diaminocyclohexane, 2-methylpiperazine, 1-aminobutane, 2-aminobutane, and 2-aminopentane as guest molecules (Table I).

Table I. Clathrasils synthesized with different guest substances at various temperatures. When two phases were obtained under the same conditions the main product is given in the upper line

Guest substance	Reaction temperature (°C)					
	150	160	170	180	190	200
2-Methylpyrrolidine 	Ns	Ns	Ns	Ns	Ns D1H	Ns D1H
Hexamethyleneimine 	-	-	Ns	Ns	D1H Ns	D1H
2-(Aminomethyl)-tetrahydrofuran 	Ns	Ns	Ns	Ns	-	D1H
2-Methylpiperidine 	Ns	Ns	Ns	Ns	Ns D1H	Ns D1H
1,2-Diaminocyclohexane 	Ns	Ns	Ns D1H	Ns D1H	Ns D1H	D1H Ns
2-Methylpiperazine 	Ns D1H	D1H	D1H	D1H	D1H	D1H
2-Aminobutane 	Ns	Ns D3C	Ns D3C	Ns D3C	D3C Ns	D3C Ns
1-Aminobutane 	-	-	-	Ns ^a D3C	-	-
2-Aminopentane 	Ns	Ns	Ns	Ns	Ns	Ns

Ns: nonasils; D1H: dodecasils 1H; D3C: dodecasils 3C; -: no experimental data.

^a 150 bar Ar pressure.

Tetramethoxysilane was hydrolyzed in aqueous 1M ethylenediamine to obtain a homogeneous 0.5 M silicate solution. After adding the guest (*ca.* 10 vol%) mixtures were sealed in silica tubes and heated in an oven at 150–200°C for several weeks. For 1-aminobutane as guest molecule a steel autoclave with a Teflon reaction vessel was used. The reaction mixture was kept at 160°C and 150 bar Ar pressure. The different phases obtained are listed in Table I. In the most favourable cases, e.g. with hexamethyleneimine as guest species, almost 100% yield of the product has been obtained.

3.2. THERMAL ANALYSIS

Non-simultaneous thermal analyses (TGA, DSC) have been performed on a Dupont 1090 Thermal Analyzer. Simultaneous DTA, TGA, and mass spectroscopic measurements were made using a Mettler system.

3.3 X-RAY CRYSTALLOGRAPHIC STUDIES

X-ray powder data were recorded on a Philips diffractometer. The powder pattern has been indexed with $a_o = 22.232(6)$ Å, $b_o = 15.058(4)$ Å, $c_o = 13.627(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$ (Table II).

Table II. Indexed X-ray powder data of nonasil-[4¹⁵8] with 2-aminopentane as guest molecule (CuK α , $\lambda = 1.5418$ Å)

<i>hkl</i>	<i>I</i> / <i>I</i> _o	<i>d</i> (Å)	<i>hkl</i>	<i>I</i> / <i>I</i> _o	<i>d</i> (Å)
200	23	11.1	133/620	24	3.329
111	35	9.2	204	31	3.256
020	3	7.56	531	16	3.231
002	3	6.83	513/024	4	3.107
220	3	6.25	333	3	3.068
311	5	5.98	711	3	3.028
202	4	5.82	224/622	7	2.989
131/222	66	4.61	442	4	2.834
420	28	4.47	800	2	2.778
402	100	4.30	351	5	2.732
113	32	4.26	533	10	2.684
331	50	3.97	640/731	2	2.635
040/313	14	3.752	802/713	3	2.565
600	28	3.704	044	4	2.526
240	27	3.567	060/604	15	2.509
004	5	3.406			

For single crystal structure determination intensity data were collected on a Philips PW 1100 four circle diffractometer. With MoK α radiation ($\lambda = 0.7107$ Å) 2795 non-equivalent reflexions were recorded in θ - 2θ scan mode ($\theta_{\max} = 30^\circ$). Since the crystal used was very small ($0.035 \times 0.050 \times 0.120$ mm; $\mu = 6.43$ cm⁻¹) no absorption correction has been applied. Structure refinement was performed with the SHELX system [7].

The structure was solved by direct methods and model building and refined using 550 intensities with $|F_o| > 2\sigma(|F_o|)$ in space group *Fm $\bar{3}$ mm* to a weighted reliability factor

$$R_w = 0.125 (R_w = [\Sigma(|F_o| - |F_c|)\sqrt{w}]/[\Sigma|F_o|\sqrt{w}]) .$$

Difference Fourier syntheses indicated that the guest molecules (2-aminopentane) are positionally disordered in agreement with the observation that the symmetry of the guest molecules is lower than the symmetry of the cages in which they are enclathrated (see Section 4.2). Therefore, for the refinement procedure the guest molecules were simulated by spherical scatterers located in three crystallographically non-equivalent positions. The coordinates of these positions (Table III) were obtained from the highest maxima of the difference synthesis

$$\rho_{\text{exp}} - \rho_{\text{calc}}(\text{Si, O})$$

Table III. Fractional coordinates and thermal parameters $U(\text{\AA}^2)$ for the nonasil-[4¹⁵⁸] 88SiO₂ · 4M²⁰, M²⁰ = CH₃CH(NH₂)C₃H₇, refined in space group *Fmmm*. The guest species is represented by the positions C(1) to C(3)

Atom	Wyckoff notation	x	y	z	U
Si(1)	32p	0.3745(4)	0.1635(7)	0.3103(8)	0.021(2)
Si(2)	8g	0.2798(10)	0.5	0.5	0.026(7)
Si(3)	16o	0.2950(7)	0.3270(13)	0	0.036(5)
Si(4)	16m	0.5	0.1051(9)	0.6156(12)	0.004(3)
Si(5)	16n	0.3173(7)	0.5	0.2831(13)	0.029(4)
O(1)	32p	0.3356(13)	0.3282(19)	0.9056(20)	0.065(9)
O(2)	32p	0.4427(8)	0.1462(15)	0.3374(16)	0.025(7)
O(3)	32p	0.3520(15)	0.4050(50)	0.2525(39)	0.128(15)
O(4)	16o	0.2702(28)	0.4329(39)	0	0.162(28)
O(5)	16n	0.3197(17)	0.5	0.5937(29)	0.043(13)
O(6)	16l	0.3667(37)	0.25	0.25	0.217(36)
O(7)	8i	0	0	0.1392(38)	0.026(14)
O(8)	8h	0.5	0.1155(28)	0.5	0.005(11)
O(9)	8c	0.25	0	0.25	0.023(13)
O(10)	8e	0.25	0.25	0	0.126(33)
C(1)	16m	0.5	0.4489	0.5700	0.242
C(2)	16o	0.4659	0.3547	0.5	0.128
C(3)	4b	0	0	0.5	0.410

Fmmm is the highest possible space group symmetry (aristotype in the sense of Megaw [8]) of the nonasil framework. Possibly because of the very small specimen used, no violations of the systematic extinction rules for *Fmmm* have been observed in the data set. Weissenberg photographs, however, revealed weak intensities leading to space group *Pbca*, a subgroup of *Fmmm*. Attempts to refine the structure with X-ray intensities in *Pbca* gave unrealistic bond lengths and angles for the silica framework. Further attempts to refine the framework using space groups *Fmmm* or *Pmm2* also failed. Therefore, it is possible that the structure described here in space group *Fmmm* is an average structure. For this structure, fractional coordinates and isotropic thermal parameters of Si and O are given in Table III.

4. Results and Discussion

4.1. CRYSTAL PROPERTIES

The nonasils were formed as colourless crystals of orthorhombic morphology irrespective of the guest molecule used for synthesis. Sometimes lath-shaped crystals of up to 0.3 mm length have been found; in general, spherulitic bundels and sphere-like aggregates of crystals of characteristic shape were observed (Figure 1).

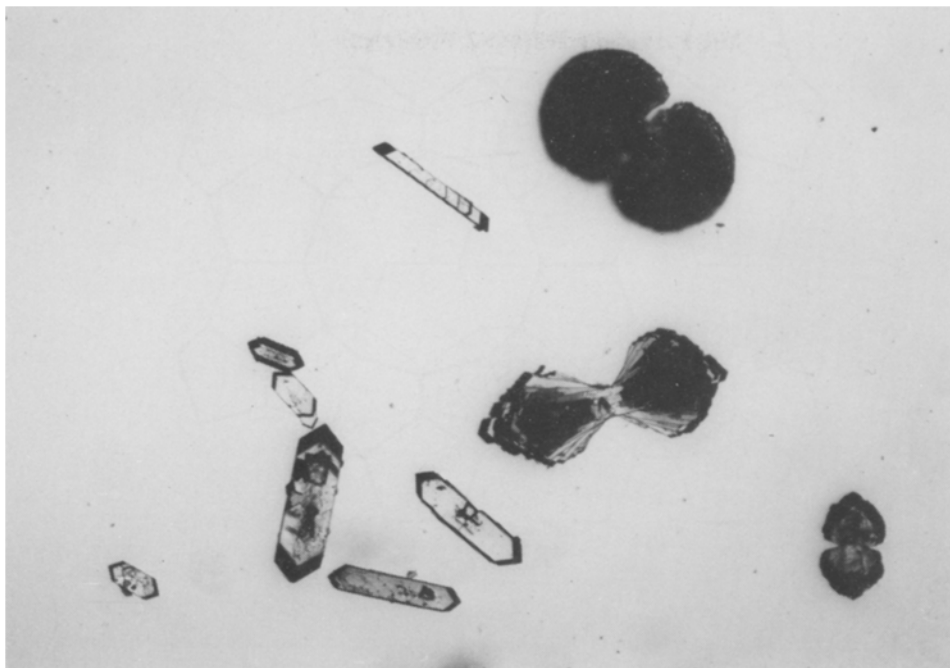


Fig. 1. Micrograph showing the morphology of nonasils-[4¹⁵8]: lath-shaped single crystals and characteristic spherulitic aggregates.

The density of the nonasil synthesized with hexamethyleneimine as guest molecule is 2.07 g/cm³. The density of the heated sample is 1.95 g/cm³ compared with 1.94 g/cm³ calculated from X-ray data for the silica framework. The tetrahedrol density of the nonasils is 19.40 tetrahedra per 1000 Å³.

In agreement with the low density of the open silica framework, the refractive indices for the nonasil with 2-aminopentane as guest molecule are low: $\bar{n}_{\text{Na-D}} = 1.475$ with $n_x = 1.473$, $n_y = 1.475$, and $n_z = 1.477$. For the guest-free sample $\bar{n}_{\text{Na-D}}$ was found to be 1.407.

4.2. DESCRIPTION OF THE STRUCTURE

[SiO₄] tetrahedra are corner-linked via common oxygen atoms and form a 3-dimensional 4-connected net. 15 [SiO₄] tetrahedra build a [4¹⁵8] cage, which is the fundamental cage of the nonasils host framework. Two fundamental cages share their four-membered rings to give a double-cage unit. Each such unit is connected by four common edges to four others to give a B-centered 2-dimensional layer parallel to (010) (Figures 2). Linking such layers via Si—O—Si bridges in a stacking sequence which is in accordance with an F-centered 3-dimensional 4-connected framework produces two other types of cage: a small [5⁴6⁴] cage and a larger [5⁸6¹²] cage (Figure 3), the latter housing the guest molecule. The unit cell content is 88 SiO₂ · 8M⁸ · 8M⁹ · 4M²⁰.

The two smaller cages [5⁴6⁴] and [4¹⁵8] have free volumes of approximately 25 and 30 Å³, respectively, and are therefore, too small to house guest molecules. The [5⁸6¹²] cage ($V = ca. 290 \text{ \AA}^3$) contains the guest species, M²⁰, which controls the formation of this specific framework. The ideal point symmetry of this cage is *mmm*. This symmetry is lower than the

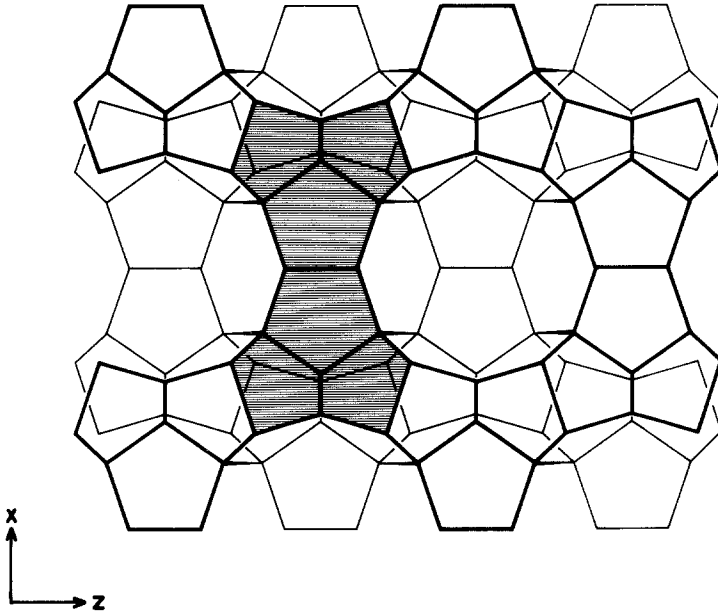


Fig. 2(a). a, c projection of nonasil-[4^15^8]. One unit consisting of two face-sharing fundamental cages is emphasized by hatching. These units are linked via common edges to form layers parallel to (010). The two layers per unit cell are distinguished by heavy and thin lines respectively.

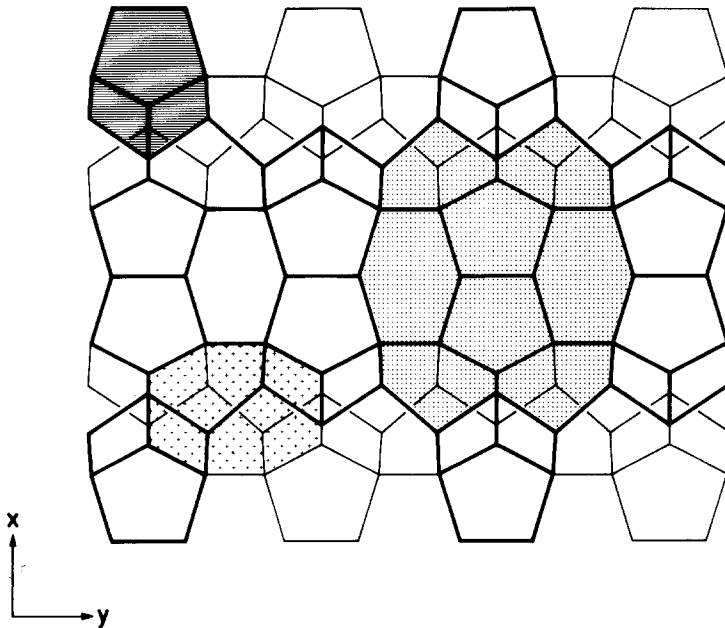


Fig. 2(b). a, b projection of nonasil-[4^15^8]. The three different types of cage are emphasized: [5^46^4]: $\ddagger\ddagger\ddagger$, [4^15^8]: \equiv , [5^86^{12}]: \dots

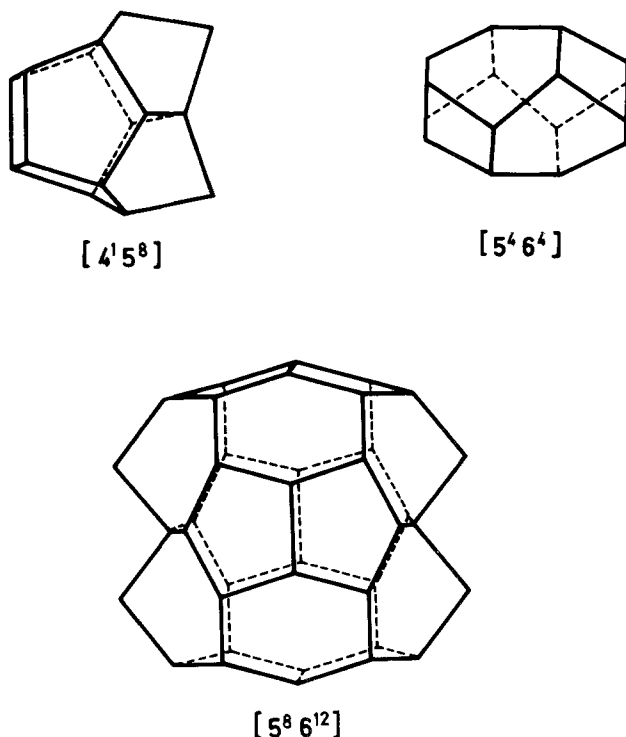


Fig. 3. The tree types of cage in nonasils-[$4^1 5^8$].

aristotype symmetries $m\bar{3}$ and $6/mmm$ of the two cages [$5^{12} 6^4$] and [$5^{12} 6^8$] in dodecasil 3C and dodecasil 1H respectively. As a consequence symmetry requirements for the guest species of nonasil-type clathrasils are reduced in comparison with symmetry requirements for the guest molecules of the dodecasils-[5^{12}].

The influence of the guest molecules on the lattice constants of nonasils was found to be very small, indicating that the silica framework is very rigid. The cell dimensions of degassed nonasils are within the limits of error identical to those of nonasils of the smallest guest molecules (Table IV). Larger guest molecules cause increases of a_o and b_o by approximately 0.2%.

Table IV. Comparison of lattice parameters in nonasils-[$4^{15} 8$] with different guest molecules and degassed nonasil. Standard deviations are less than 0.01 Å

Lattice parameters	Guest molecule			
	1,2-Diamino-cyclohexane	2-Amino-pentane	2-Amino-butane	No guest
a_o (Å)	22.21	22.23	22.17	22.17
b_o (Å)	15.04	15.06	14.99	15.01
c_o (Å)	13.64	13.63	13.63	13.63

4.3. FACTORS WHICH INFLUENCE NONASIL FORMATION

With the exception of hexamethyleneimine, all compounds successfully enclathrated into the nonasil framework, are either aliphatic amines with a chain length of four or five C and N atoms or monocyclic compounds with one or two side chains (Table I). These compounds are non-spherical and have no symmetry.

The data listed in Table I show that some guest molecules which form dodecasils at higher temperatures, form nonasils at lower temperatures. This ability of guest species to form more than one clathrasil type has already been reported for other clathrasils [3]. Table V lists guest molecules which stabilize different clathrasils at different temperatures together with type, free volume, and point symmetry of the cages which house the structure-controlling guest molecules.

Table V. Guest molecules which stabilize the nonasil framework at lower temperature and another clathrasil framework at higher synthesis temperature. Types of cage containing the guest molecules, free cage volumes and site symmetry of the cages are indicated

Guest species	Low temperature phase		High temperature phase	
	Host framework	Cage type free cage volume cage symmetry	Host framework	Cage type free cage volume cage symmetry
1-Amino-butane			Dodecasil 3C	[5 ¹² 6 ⁴] ca. 250 Å ³ m3
2-Amino-butane				
2-Methyl-pyrrolidine				
Hexamethyleneimine	Nonasil	[5 ⁸ 6 ¹²] ca. 290 Å ³ mmm		
2-Methyl-piperidine			Dodecasil 1H	[5 ¹² 6 ⁸] ca. 430 Å ³ 6/mmm
1,2-Diamino-cyclohexane				
2-Methyl-piperazine				

From the data in Table V it is evident that a particular molecule which is entrapped in the low-symmetry [5⁸6¹²] cage of nonasil at lower synthesis temperature, becomes entrapped in cages of higher symmetry of the dodecasils at higher synthesis temperature. The smaller of these guest molecules require at higher synthesis temperature the smaller [5¹²6⁴] cages of dodecasil 3C, whereas the larger ones require the larger [5¹²6⁸] cages of dodecasil 1H.

4.4. THERMAL BEHAVIOUR

4.4.1. DTA

Differential thermal analysis with a heating rate of $10^{\circ}\text{C}/\text{min}$ shows three exothermic peaks: A very weak one in the range $250\text{--}350^{\circ}\text{C}$, a stronger one in the range $530\text{--}610^{\circ}\text{C}$ with a maximum at 590°C , and finally one in the range $520\text{--}750^{\circ}\text{C}$ with lower heat of reaction.

4.4.2. TGA

Two kinds of thermogravimetric analysis experiments have been made: a dynamic one with $10^{\circ}\text{C}/\text{min}$ heating rate and an isothermal one at 25 or 50°C intervals from room temperature up to 900°C . In the dynamic experiment the weight loss began slowly at about 150°C and became faster in the temperature intervals $520\text{--}610^{\circ}\text{C}$ and $800\text{--}1000^{\circ}\text{C}$. In the isothermal experiment (Figure 4) about 0.9% weight loss occurred between 125 and 275°C . A total of 5.75% weight loss was observed up to 700°C . Hardly any weight loss occurred between 700 and 900°C , and at 1000°C a constant weight was obtained with a total weight loss of 7.2% .

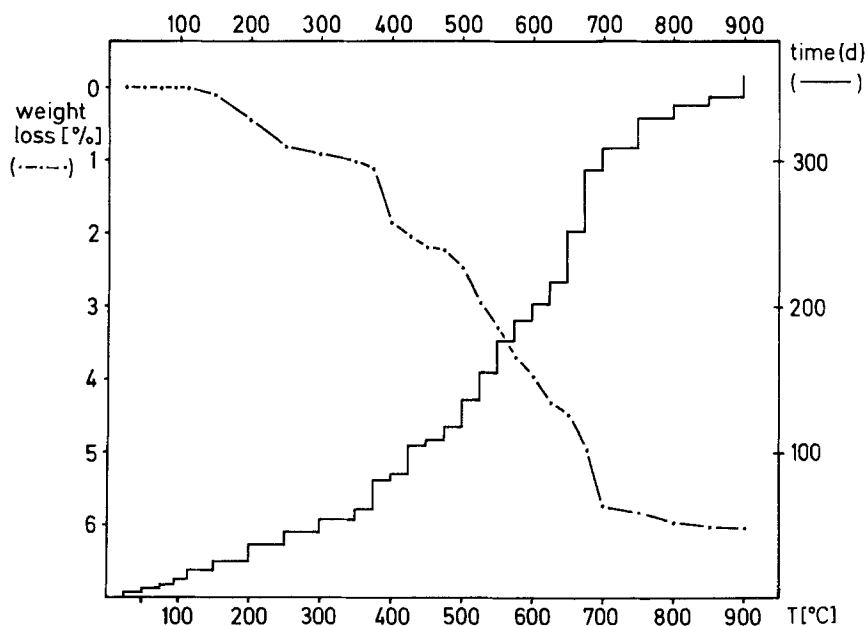


Fig. 4. Isothermal gravimetric analysis (TGA): weight loss curve and tempering time of the sample are shown.

4.4.3. Mass Spectrometry

In one of the experiments, DTA, TGA, and mass spectrometric measurements of masses 2 (H_2), 17 (OH), 18 (H_2O), 22 ($\frac{1}{2}\text{CO}_2$), and 44 (CO_2) have been recorded simultaneously at a heating rate of $10^{\circ}\text{C}/\text{min}$. These measurements show that water is expelled between 150 and 390°C and above 500°C . Expulsion of H_2 is recorded between 400°C and 700°C with a prominent maximum at 540°C (Figure 5). No loss of CO_2 has been observed under these conditions.

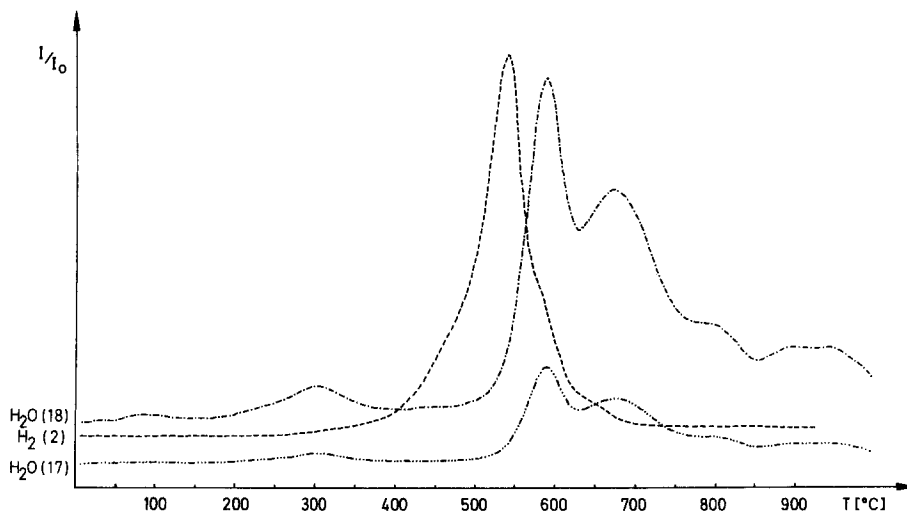


Fig. 5. Diagram of the mass spectroscopic analysis.

4.4.4. Conclusions from Thermal Studies

Like other clathrasils but unlike zeolites, nonasils show no exchange properties for the organic guest species incorporated during synthesis. The maximum free diameter of the cage windows (2.8 Å for six-membered rings [9]) is too small to let organic guest molecules pass. The heating experiments, however, show that the guest molecules are thermally decomposed and the fragments have escaped. These have been measured as H_2 and its oxidation product H_2O . On the other hand, carbon seems to be retained up to at least medium temperatures. However, the nonasil framework is thermally stable up to about 950°C and, even after four months of heat treatment at this temperature, the framework is retained.

The overall weight loss of 7.2% of nonasil with hexamethyleneimine as guest species indicates that each of the $[5^86^{12}]$ cages in nonasils had been occupied by one guest molecule (theoretical weight loss 6.98%) and that the smaller cages $[5^46^4]$ and $[4^{15}8]$ were essentially empty.

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