Preparation and Properties of Piperazine Silicate (EU-19) and a Silica Polymorph (EU-20)

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The hydrothermal crystallisation of a piperazine (pipz) silicate (EU-19) from the reaction mixture $(p - 2y)\text{pipz}\text{–}y\text{M}_2\text{CO}_3\text{–}20\text{SiO}_2\text{–}w\text{H}_2\text{O}$ (p = 15, 20, or 25; y = 0—2.5; w = 250 or 1 000; M = Na, K, or Cs) at 120 and 150 °C is described. Dependent on w, plate-like or lath-like morphologies are observed. The chemical and physical properties of EU-19 are those of a layer structured material. On calcination the EU-19 crystals are pseudomorphically converted into a thermally stable silica polymorph (EU-20).

The static hydrothermal crystallisation of the reaction mixture $p\text{pipz–}20\text{SiO}_2\text{–}w\text{H}_2\text{O}$ (pipz = piperazine) at 180 °C was recently found to give the clathrasil pipz-ZSM-39 (dodecasil 3C).[1] There have been few attempts to crystallise similar reaction mixtures at lower temperatures; the only product recorded[2] is the silica molecular sieve ZSM-48.[3] We now report a more extensive investigation of hydrothermal crystallisation in the pipz–SiO_2–H_2O system at 120 and 150 °C. At these temperatures we find the major product is a piperazine silicate (EU-19)[4] which on calcination gives a silica polymorph (EU-20). The structure of EU-19 has been determined by single-crystal *X*-ray diffraction measurements using the high-intensity synchrotron source at the Daresbury Laboratory. It consists of silica double layers, separated by and hydrogen bonded to piperazinium ions.[4]

Experimental

The reaction mixtures had the composition $p\text{pipz–}20\text{SiO}_2\text{–}w\text{H}_2\text{O}$ (p = 15, 20, or 25; w = 250 or 1 000), and were prepared by adding an aqueous solution of piperazine hexahydrate (98%, Aldrich) to the fumed silica gel (CAB-O-SIL M5, BDH). Care was taken always to prepare the mixtures in the same way and to stir the components into a smooth paste. For some reactions alkali-metal carbonates were used to give the reaction composition $(15 - 2y)\text{pipz}-y\text{M}_2\text{CO}_3\text{–}20\text{SiO}_2\text{–}250\text{H}_2\text{O}$ ($0.25 < y < 2.50$). For these a solution of the carbonate (BDH Ltd., AnalaR) was added to the dry silica. The crystallisations were carried out at 120 or 150 °C. Most of the mixtures were crystallised under static conditions in polytetrafluoroethylene (ptfe)-lined stainless-steel bombs (30 cm^3). These were periodically cooled to room temperature and a small sample taken for examination by optical microscopy. The reactions were terminated when the products appeared to be fully crystalline. Stirred reactions were carried out in stainless-steel autoclaves (500 cm^3) (Baskerville and Lindsay Ltd.) These could be sampled during the crystallisation without perturbing the reaction conditions.

X-Ray powder diffraction patterns were obtained with a Philips diffractometer using Cu-K_α radiation. All of the samples were thoroughly ground to a fine powder and equilibrated with atmospheric moisture before examination by powder diffraction. Percentage crystallinities of EU-19 were estimated from the height of the peak at $2\theta = 7.73°$ ($d = 11.43$ Å).[5] Electron micrographs were obtained with a Cambridge Instruments type 604 scanning electron microscope. Differential thermal analysis (d.t.a.) and thermal gravimetric analysis (t.g.a.) were carried out with a Stanton Redcroft STA780 simultaneous thermal analyser using flowing air (30 cm^3 min^{-1}) and a heating rate of 10 °C min^{-1}. The equipment was interfaced to a BBC microcomputer (Model B+) which was used to collect the experimental data and to correct for baseline drift in both the d.t.a. and t.g.a. traces.

Table 1. Reactions and products[a]

Code	$p - 2y$	y	w	T/°C	t/d	Description	Other products
S1	10	0	250	120	70	Plates	
S2	15	0	250	120	102	Plates	*ca.* 95% amorphous
S3	10	0	250	150	35	Plates	ZSM-39
S4	15	0	250	150	35	Plates	ZSM-39
S5	15	0	1 000	150	102	Laths, >300 μm	ZSM-39
S6	20	0	1 000	150	49	Laths, 80—100 μm	
S7[b]	20	0	1 000	150	10	Laths, *ca.* 5 μm	
S8	25	0	1 000	150	56	Laths, 80—100 μm	
S9[b]	25	0	1 000	150	10	Laths, *ca.* 5 μm	
S10	13	1.00Na	250	120	42	Plates	Amorphous
S11	10	2.50Na	250	120	35	Plates	Magadiite
S12	10	2.50K	250	120	42	Plates	
S13	10	2.50Cs	250	120	51	Plates	Amorphous
S14	14.5	0.25Na	250	150	25	Plates	
S15	14	0.50Na	250	150	16	Plates	
S16	13	1.00Na	250	150	14	Plates	ZSM-39 magadiite

[a] Reaction composition: $(p - 2y)\text{pipz–}y\text{M}_2\text{CO}_3\text{–}20\text{SiO}_2\text{–}w\text{H}_2\text{O}$. Reactions were stopped after the given times t. In all cases the major crystalline product was EU-19. Examination by scanning electron microscopy showed the products to be free from amorphous material except as indicated.
[b] Reaction carried out in stirred (300 revolutions min^{-1}) autoclaves.

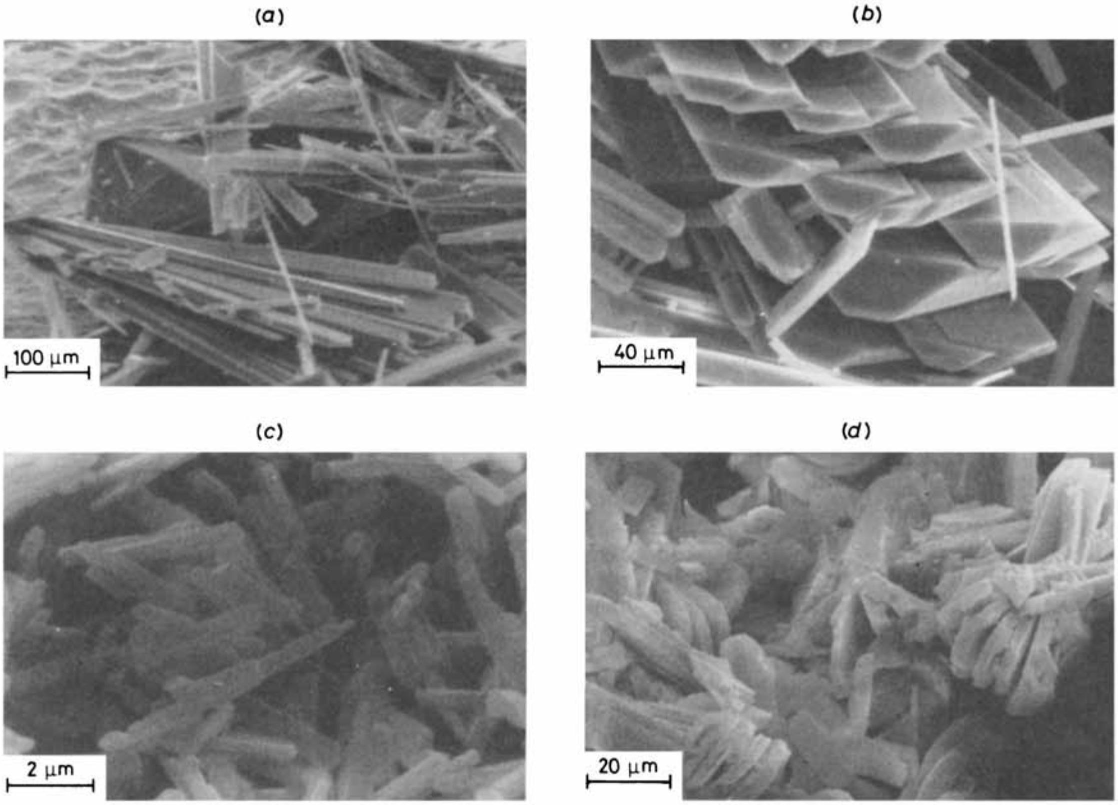

Figure 1. Electron micrographs of the products from reactions S5 (*a*) and (*b*), S9 (*c*), and S14 (*d*)

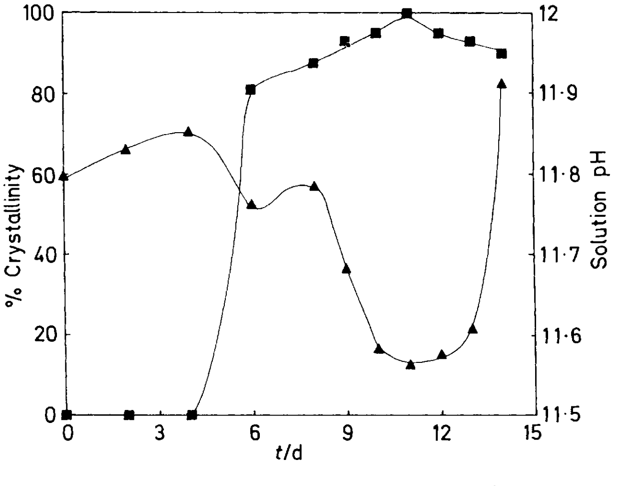

Figure 2. Crystallinity (■) and pH (▲) measurements for reaction S9

A Vickers Photoplan M41 microscope was used for optical examination of the products. Measurements of pH were made with a Philips type 9422 digital pH meter fitted with an E.I.L. type 1180/200/BNC electrode using the procedure described.[6,7]

Results and Discussion

Full details of the reaction mixtures and the products obtained at 120 and 150 °C are given in Table 1. In all cases EU-19 was the major product. Two morphologies were observed: the reaction mixtures with high water contents gave lath-like crystals whilst those with low water contents gave plate-like ones (Figure 1). At 150 °C with the dilute reaction mixtures (w = 1 000) EU-19 formation is favoured by high piperazine levels (*cf.* S5, S6, and S8); with low levels ZSM-39 was produced as a minor impurity (Figure 1), but longer EU-19 crystals were obtained (Table 1). With concentrated reaction mixtures (w = 250) and low piperazine levels (S4), ZSM-39 is again an impurity, but crystallisation of EU-19 is faster than with the corresponding dilute mix (S5). At 120 °C with concentrated reaction mixtures (w = 250) the crystallisation is most rapid with the lower piperazine level (*cf.* S1 and S2). The rate of crystallisation is increased substantially by agitation and much smaller crystals are obtained (*cf.* S6 with S7, and S8 with S9). Partial replacement of piperazine by sodium carbonate increases the rate of crystallisation of EU-19, but larger quantities give magadiite[8] as an impurity (*cf.* S4, S14, S15, and S16; and S2, S10, and S11). In contrast potassium carbonate and caesium carbonate increase the rate of crystallisation without the formation of magadiite (*cf.* S12 and S13 with S11).

Figure 2 shows the changes in percentage crystallinity and pH that occurred during the crystallisation of EU-19 from the reaction mixture 25pipz–20SiO$_2$–1000H$_2$O (S9, stirred, 150 °C). After an induction period of 4 d the crystallisation is rapid and 80% complete within 2 d. The variations in the crystallinity observed after 10 d may not be significant as other factors besides the presence of amorphous silica can reduce the *X*-ray peak height;[5] all of these samples were free from amorphous material. During the induction period the pH rises; this could be explained by a rearrangement of the solid gel phase to a more stable (less soluble) form (*cf.* the crystallisation of ZSM-48[9]). The crystallisation is accompanied by a fall in pH caused by the incorporation of the base into the crystalline product, and reaches a minimum after 11 d. The rise in pH that occurs thereafter is probably due to a reduction in the silica content of the solution phase during the final stages of the crystallisation; alternatively it may herald the formation of a

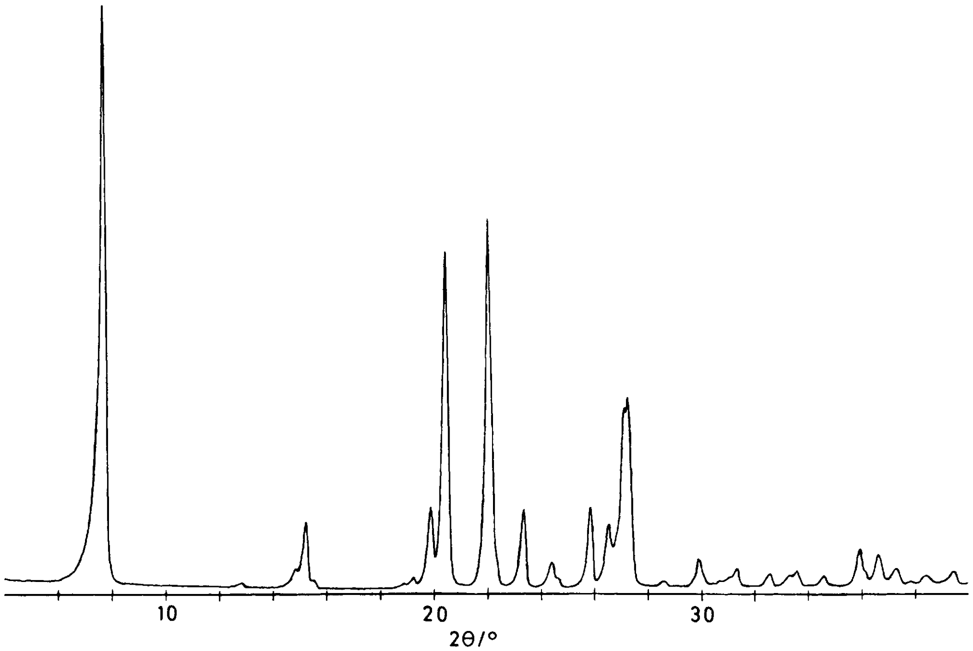

Figure 3. *X*-Ray powder diffraction pattern for EU-19 (S9)

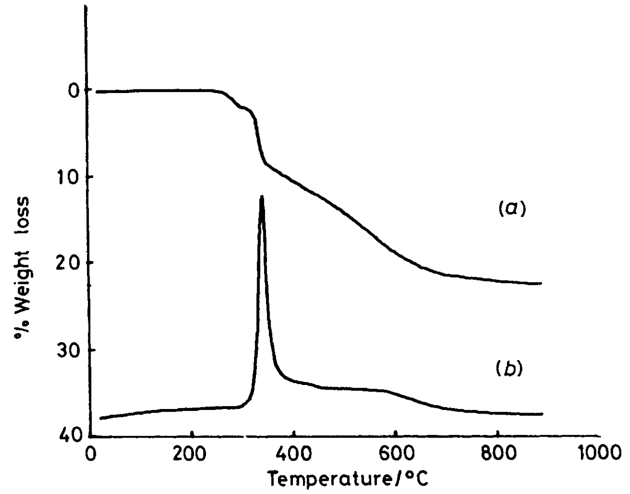

Figure 4. T.g.a. (*a*) and d.t.a. (*b*) curves for EU-19 (S9) obtained with a 10.34-mg sample. D.t.a. peaks are exothermic

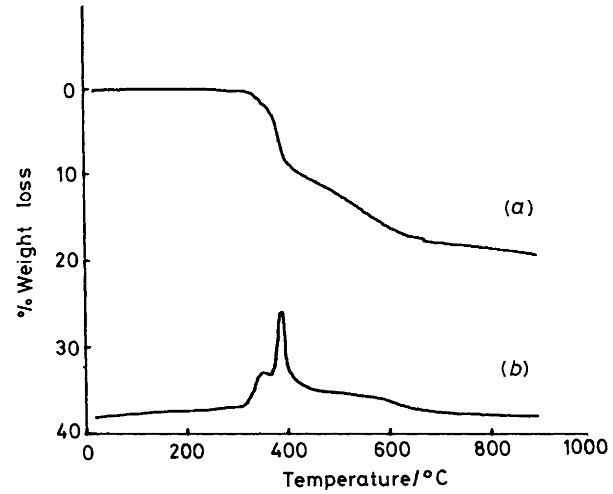

Figure 5. T.g.a. (*a*) and d.t.a. (*b*) curves for EU-19 (S14) obtained with a 9.67-mg sample. D.t.a. peaks are exothermic

dense crystalline phase such as quartz, although this was not detected in the *X*-ray diffraction pattern of the final sample (14 d). The dip in the pH curve that occurs at 6 d is probably a consequence of perturbations in the equilibrium between the amorphous solid and the solution phase consequent on the rapid crystallisation. Similar effects are observed in zeolite crystallisation.[10]

The *X*-ray powder diffraction pattern for EU-19 is shown in Figure 3 and the *d* spacings and relative intensities are given in Table 2.

Chemical analysis of sample S9 gave 9.50 C, 2.55 H, and 5.90% N and a repeat analysis gave 9.75 C, 2.55 H, and 6.00% N. The corresponding atomic ratios C:H:N are 3.74:11.99:2.00 and 3.81:11.85:2.00. The poor agreement between the % C figures suggests that there was incomplete combustion of the organic component, and that the true composition is $C_4H_{12}N_2$ which corresponds to a fully protonated piperazine molecule H_2pipz^{2+}.

Typical thermal analysis results for lath-like and plate-like morphologies are shown in Figures 4 and 5 respectively. The complete absence of any weight loss below 250 °C indicates that EU-19 does not contain any loosely bound or occluded water. Hence the entire weight loss is due to piperazine and structural water. Both the t.g.a. and d.t.a. curves show that this takes place in several stages; rapidly from 250 to 400 °C, but less so from 400 to 750 °C for S9 and from 400 to > 900 °C for S14. With the lath-shaped crystals (S9) the piperazine is completely removed during the analysis, but with the plate-shaped ones (S14) the final material is black and the overall total weight loss is smaller. On prolonged heating at 900 °C the material becomes white and the two weight losses agree (22.6%). The difficulty encountered in removing the organic moiety from EU-19 at the higher

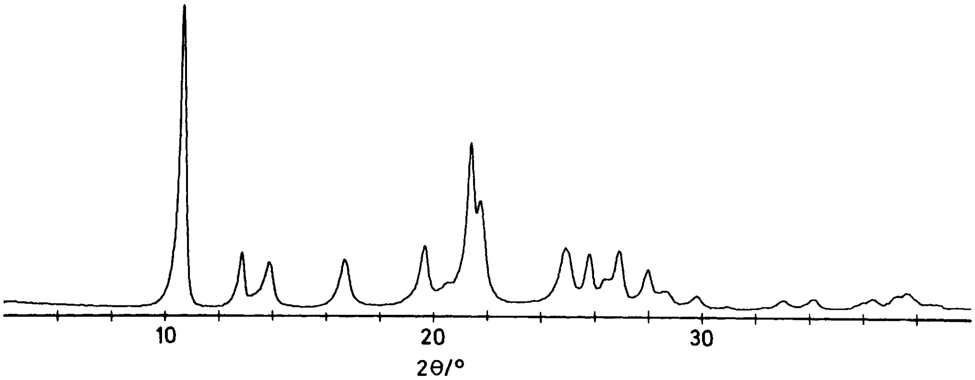

Figure 6. *X*-Ray powder diffraction pattern for EU-20 (prepared from product S9)

Table 2. *X*-Ray diffraction data for EU-19 (S9)

h	k	l	$d_{obs.}$/Å	$d_{calc.}$*/Å	$(I/I_0)_{obs.}$
0	0	2	11.43	11.42	100.0
2	0	0	6.900	6.885	0.7
−2	0	2	5.977	6.022	3.2
2	0	2	5.821	5.777	11.1
0	0	4	5.712	5.708	1.4
1	1	0	4.617	4.621	1.6
−2	0	4	4.465	4.499	14.3
−1	1	2	4.333	4.308	58.1
−1	1	3	4.019	3.978	64.3
0	0	6	3.802	3.805	13.4
			3.650		4.1
−1	1	4	3.616	3.620	1.4
4	0	0	3.435	3.442	13.4
3	1	0	3.352	3.352	10.6
3	1	1		3.300	
			3.282		30.4
−1	1	5		3.274	
2	0	6	3.270	3.266	32.5
−3	1	3	3.118	3.107	0.9
−4	0	4		3.011	
			2.986		4.6
−1	1	6		2.961	
1	1	6	2.912	2.915	0.7
4	0	4	2.882	2.888	1.6
0	0	8	2.856	2.854	3.0
3	1	4		2.848	
−3	1	5	2.746	2.747	1.8
−1	1	7	2.690	2.685	1.4
3	1	5	2.666	2.659	2.1
2	0	8	2.592	2.594	1.7
4	0	6	2.499	2.495	5.8
0	2	0	2.453	2.453	5.3
1	1	8	2.410	2.411	2.8
−3	1	7		2.379	
5	1	1	2.378	2.378	0.7
5	1	2		2.370	
0	2	3	2.342	2.335	1.4
−2	2	1	2.302	2.303	0.7
0	0	10	2.285	2.283.	2.1

* Calculated for the unit cell $a = 13.785(18)$, $b = 4.906(5)$, $c = 22.856(23)$ Å, $\beta = 92.70(11)°$, $U = 1\,544$ Å^3, which was refined against measured d spacings using the program for least-squares unit-cell refinement LSQC (R. A. Howie, University of Aberdeen, 1970).

Table 3. *X*-Ray diffraction data for EU-20 (from S9)

d/Å	I/I_0	d/Å	I/I_0
8.26	100.00	3.31	16.70
6.88	18.50	3.18	11.50
6.37	14.10	3.12	6.20
5.32	15.90	3.00	4.40
4.50	18.90	2.89	0.90
4.33	7.10	2.77	0.90
4.15	53.70	2.70	2.60
4.08	34.40	2.60	2.60
3.57	17.60	2.47	2.60
3.45	15.90	2.41	4.00
3.38	7.10	2.39	4.80

temperatures is probably related to the concurrent formation of a silica polymorph (EU-20); this could cause the piperazine to become trapped and it could prevent the access of air for the oxidative degradation. Combination of the thermal analysis and C,H,N results gives the chemical composition pipz·H_2O·5.94SiO_2. The idealised composition pipz·H_2O·6SiO_2 = $H_2pipz^{2+}Si_6O_{13}{}^{2-}$ corresponds to 10.35% C (*cf.* observed 9.50, 9.75%), 6.00% N (observed 5.90, 6.00%), and 2.60% H (observed 2.55, 2.55%). Neither EU-19 nor EU-20 possesses any sorptive properties, nor can EU-19 be converted into a sorbent by carefully controlled calcination at 250 °C.

The piperazine was not removed by Soxhlet extraction for 72 h with water nor by ion exchange with sodium ions (1 mol dm^{-3} NaCl, 100 cm^3 g^{-1} at room temperature) or tetramethylammonium ions (1 mol dm^{-3} NMe_4Br, 100 cm^3 g^{-1} at room temperature). However treatment with hydrochloric acid (0.1 mol dm^{-3}, 24 h, 7 × 100 cm^3 g^{-1} at room temperature) or aluminium sulphate (0.1 mol dm^{-3}, 24 h, 4 × 100 cm^3 g^{-1} at room temperature) removes some of the piperazine and causes the structure to collapse to a product with a few broad peaks in its *X*-ray diffraction pattern. On calcination at 900 °C this hydrogen-exchanged material becomes completely amorphous. The ion exchange with H^+ (from the acid or from the hydrolysis of aluminium sulphate) could perhaps be represented by equation (1). Hydrolysis of the silicate layers is improbable and although they become disordered the morphology remains unchanged. The composition and chemical properties of EU-19 are entirely consistent with its crystallographic structure.[4]

$$(\equiv\text{Si–O}^- \ H_2\text{pipz}^{2+} \ {}^-\text{O–Si}\equiv) + 2H^+ \longrightarrow (\equiv\text{Si–OH HOSi}\equiv) + H_2\text{pipz}^{2+} \quad (1)$$

When EU-19 is heated in air at temperatures above 300 °C it is converted into a new silica polymorph EU-20. The crystallinity of the new phase increases with temperature. It is stable at 900 °C and probably at much higher temperatures. The transformation occurs both with the lath (S9) and the plate (S4) forms of EU-19. In both cases the crystal morphology remained unchanged during the transformation. The *X*-ray diffraction pattern of EU-20 is shown in Figure 6 and its *d* spacings are given in Table 3. EU-20 is very stable and its d.t.a. and t.g.a. traces from room temperature to 900 °C are entirely featureless. The structure of EU-20 is unknown, but its high thermal stability and its complete lack of sorptive properties suggest that it is a narrow-pore tectosilicate. It is probably formed by cross-linking of the silicate layers of EU-19 [equation (2)], and if so its

$$(\equiv\text{Si–O}^- \ \text{H}_2\text{pipz}^{2+} \ {}^-\text{O–Si}\equiv) \longrightarrow (\equiv\text{Si–O–Si}\equiv) + \text{volatile products} \qquad (2)$$

structure will consist predominantly of eight- and five-silicon atom rings.

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