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A comparative study of template removal from silicalite-1 crystals in pyrolytic and oxidizing regimes

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Abstract

The removal of tetrapropylammonium cations (TPA^+) from silicalite-1 crystals with a morphology of 90°-intergrowth and different crystal sizes was investigated. The effects of the nature of the gas (air or nitrogen) and of the hydrodynamics were examined using a stream flowing in parallel or across the crystal layer. The only process variable was the plateau temperature (T_{max}). Crystal domain boundaries became permeable to template degradation products when T_{max} exceeded 300 °C. The template removal was monitored by (i) light microscopy, (ii) degree of removal of the total organics α, of nitrogen species α_N and of carbon species α_C and (iii) accessibility of the channel system for N_2 molecules. The sorption isotherms for N_2 exhibited two steps. The upper step started to be perceptible for a degree of organic removal higher than 55%. Its height increased with α, and its position moved to lower pressure values. The plots of the gas accessibility versus the degree of removal were modelled. For template removal in air, all plots were linear. In a non-oxidizing atmosphere, the accessibility lagged behind α_N. Light microscopy showed that template degradation started along domain boundaries. Sorption kinetics of iodine into silicalite-1 crystals treated in a non-oxidizing atmosphere was considerably slower than that observed into crystals calcined in air. The tendency to crack formation increased with crystal size. The template removal efficiency was higher when using cross-flow than parallel flow calcination.

Keywords: Silicalite-1; TPA^+; N_2 sorption; I_2 sorption; Light microscopy; Template decomposition mechanism

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1. Introduction

There are many publications on template removal from as-synthesized zeolites, particularly on template degradation mechanisms under pyrolytic conditions [1]. Less attention has been paid to the effect of the nature of the gaseous agent in

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template removal procedures, first of all in relation to the presence of oxygen. Also there is a considerable knowledge gap between the effect of the hydrodynamic regime on the overall kinetics of template removal and the development of the accessible space in the zeolite channels. Finally, understanding the role of the hydrodynamics in the template removal process is of interest, e.g. for the manufacturing of zeolite-based composite membranes, where template removal proceeds using a gaseous agent, which flows in parallel to the membrane surface.

The most adequate method for monitoring the development of accessible space in microporous materials in the course of template removal appears to be the sorption of suitable probe molecules. This has been done for MFI and BEA type zeolites, e.g. by Ajot et al. [2] using equilibrium sorption of nitrogen at 77 K. Also the process of template removal from $AlPO_4$ and SAPO materials was studied in detail by sorption of water, as in the study by Malla and Komarneni [3].

The proper interpretation of the corresponding sorption data is, however, not straightforward, even not for template-free zeolite samples. In relation to MFI type materials, there has been a discussion in the literature about the occurrence of a step in adsorption isotherms for gases like nitrogen, argon, krypton and carbon monoxide. This step occurs at low relative pressures ($p/p_s < 0.2$). Two explanations for this step have been suggested in the literature. The first one is based on the assumption that the silicalite-1 framework distorts under the stress of the adsorbate [4]. A rearrangement of the adsorbed layer in the channel cross-sections seems to be a more plausible explanation for the occurrence of two steps in silicalite-1 adsorption isotherms [5–8]. Müller et al. [6] even distinguish three stages in the adsorption of N_2 in silicalite-1: (i) up to 20 molecules per unit cell, the adsorption is assumed to take place only in the straight and sinusoidal channels; (ii) a continuous adsorbed layer involving the space of the cross-sections is formed up to 24 molecules per unit cell (at this coverage the sorption isotherm of N_2 exhibits a distinct plateau); (iii) a further increase of the adsorbate partial pressure leads to a rearrangement of the adsorbate molecules in the cross-sections, and the adsorbed amount is enhanced in a rather sharp step up to 30.5 molecules per unit cell; this reordering occurs at the second distinct step in the isotherm. Thus, the two plateaus in the isotherms may be due to different packing densities of the adsorbate.

The aim of the present work was to examine the effects of the hydrodynamic conditions, of the gas composition and of the temperature program on the topochemical changes in non-consolidated silicalite-1 layers. The principal techniques used in this study were adsorption of nitrogen at 77 K, light microscopy in combination with the iodine indicator technique [9,10] and elemental analysis. The application of light microscopy provided maximum information on local crystal changes which are not accessible from observations on non-transparent composite materials, such as zeolite–ceramics. We also included in the present paper the study of template removal from thin unconsolidated layers of silicalite-1 crystals of various size with a flow of fluid agent in parallel to the surface of the crystal layer, which simulates some features of the template removal from zeolitic membranes.

2. Experimental

2.1. Zeolites used

All measurements were performed on large 90°-intergrown silicalite-1 crystals synthesized in our laboratory using Kornatowski's protocol [11]. The crystals were grown in teflon-lined stainless steel autoclaves at a temperature of 457 K and autogenous pressure, by reacting silica sol (Czech industrial product Tosil produced by Tonaso Neštemice), tetrapropylammonium bromide—TPABr (Fluka-purum) and sodium bicarbonate (Solway France Qualité 0-13) without stirring the batch. A typical molar composition of a synthesis batch was 90 SiO_2:12 Na_2O:2000 H_2O:5 TPABr. The synthesis time was 190 h.

A micrograph from light microscopy in polarized light shows a typical external and internal

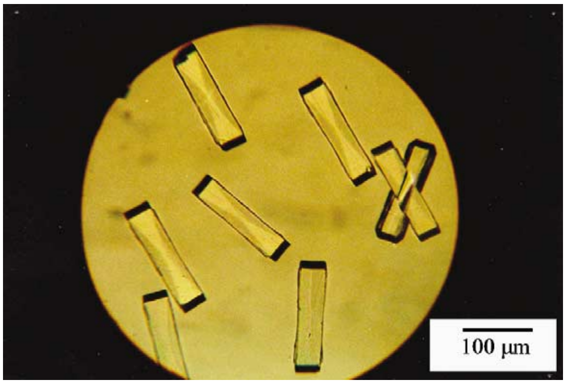

Fig. 1. Light microscopy micrograph in polarized light of silicalite-1-90°-intergrowth.

Table 1
Silicalite-1 crystal size

Sample	$L_a \cong L_b$ (μm)	L_c (μm)
1	23	130
2	41	190
3	53	230

morphology of silicalite-1-90°-intergrowths from our synthesis (cf. Fig. 1).

Table 1 summarizes the dimensions of three samples of silicalite-1 crystals used in this study.

Fig. 2 shows the three sections of different crystallographic order of the crystals obtained by our synthesis procedure.

The fact that only the sinusoidal channels have their pore mouth openings in the crystal surface (planes: BCFG, AEHD, ABFE and DCGH) is the consequence of the above crystallographic arrangement. At the same time the axes of the straight channels are oriented in parallel to the crystal basal and lateral planes, and they have their pore mouth openings at the domain interfaces (cf. shadowed triangles FIB, GIC, EIA, HID and open triangles F′I′B′, G′I′C′, E′I′A′, H′I′D′). A schematic representation of the channel system in our 90°-intergrowth silicalite-1 crystals is shown in Fig. 3.

This drawing refers to a channel arrangement in a plane cut of the crystal perpendicular to the axis *c* It can be seen that only sinusoidal channels communicate with the crystal surface. Thus the template degradation products can escape from the crystal either via sinusoidal channels or via domain boundaries FIB (F′I′B′), GIC (G′I′C′), EIA (E′I′A′), HID (H′I′D′) and the corresponding line sinks at crystal edges.

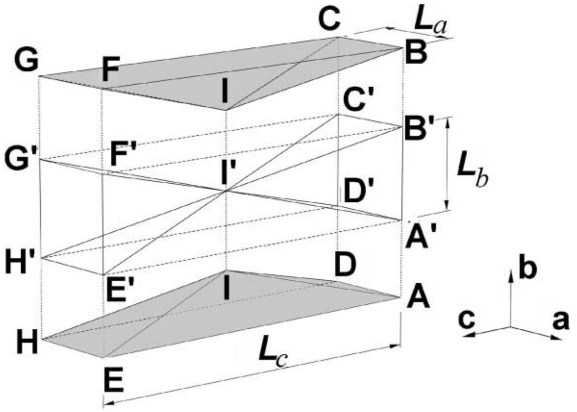

Fig. 2. Model of silicalite-1-90°-intergrowth in a coordinated system of crystallographic axes according to Weidenthaler et al. [12].

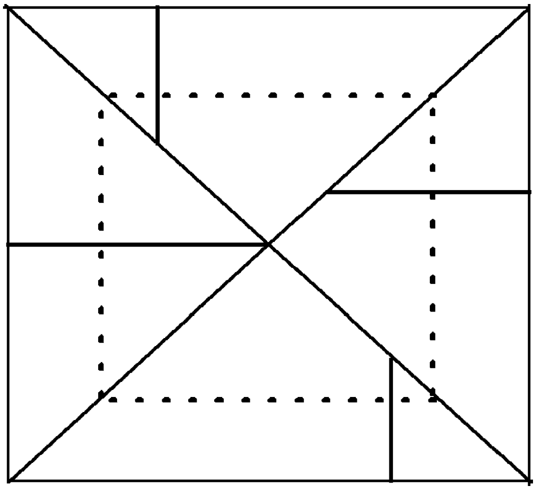

Fig. 3. The silicalite-1-90°-intergrowth channel arrangement in a plane cut of the crystal perpendicular to the axis *c*. (···) straight channel, (—) sinusoidal channel.

2.2. Template removal

The process of template removal consisted of the following sequence of operations: (i) first calcination, (ii) washing of the crystals with aqueous NH_4NO_3 solution and drying in air at laboratory temperature, (iii) second calcination. The washing operation was introduced to remove occluded species stemming from the synthesis mixture. During both calcinations the following standard temperature program was used: heating rate $r_1 = 10$ °C/h up to the first plateau at $T_1 = 120$ °C for 12 h, heating up to the second plateau (temperature T_{max}) at the rate $r_2 = 30$ °C/h for 12 h, spontaneous cooling. The temperature T_{max} was the only varying process parameter, and its value was chosen in the interval of 150–530 °C.

The template removal was carried out in the following regimes (cf. Fig. 4).

In the parallel N_2 flow and parallel air flow regimes the silicalite-1 crystals were spread on a quartz boat with nitrogen/air flowing in parallel to the layer. In the N_2 cross-flow and air cross-flow regimes the silicalite-1 crystals were placed on a glass sintered disc fused into a glass tube and nitrogen/air passed through the crystal bed. The conditions of the template removal experiments are summarized in Table 2.

Elemental analysis. The composition of the template residues remaining in the silicalite-1 channels, after partial template removal, was estimated on the basis of the elemental analysis performed on a 2400 Perkin–Elmer CHNS/O analyzer. The degree α_I of species removal is defined as $\alpha_I = [m_I^0 - m_I]/m_I^0$ where m_I^0 and m_I are the masses of the element I (C or N) contained in the mass m_Z^0 of the starting zeolite sample, and that contained in the actual mass m_Z of the sample, respectively. The quantity α_I is related to a free space which arises from removing the amount of species I.

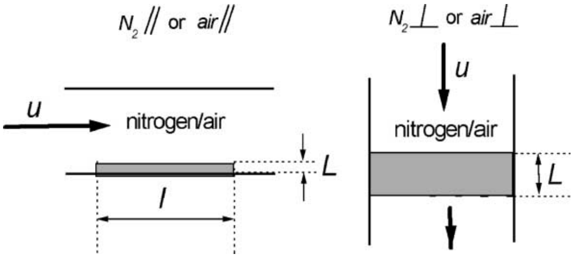

Fig. 4. Experimental arrangements of the template removal process: nitrogen or air flows parallel to the silicalite-1 crystal layer (denoted N_2 ∥ or air ∥) and nitrogen or air flow crossing the silicalite-1 crystal layer (denoted N_2 ⊥ or air ⊥).

Table 2
Specific parameters of the experimental arrangement

Specific parameter	Experimental arrangement			
	N_2 ∥	Air ∥	N_2 ⊥	Air ⊥
Mass of silicalite-1, m_Z^0 (mg)	400	400	400	400
Length of the layer, l (cm)	9	9	–	–
Depth of the layer, L (cm)	0.02	0.02	0.3	0.3
Number of the crystal monolayers, N	2	5	30	65
Gas linear velocity, u (cm/s)	0.2	0.2	1.9	1.9

Nitrogen adsorption isotherms. The samples were outgassed for 4 h at a temperature of 240 °C. Nitrogen adsorption isotherms were plotted for all the samples at 77 K using a Coulter SA 3100 analyzer. The analyzer used was based on a volumetric method. Prior to any sorption run with nitrogen, the dead space volume was measured by filling it with He after reducing the pressure to 10^{-4} Pa. The channel accessibility Y for the N_2 molecule can be defined as $Y = a_{N_2}/(a_{N_2})_{max}$, where a_{N_2} is the adsorbed amount of N_2 at 77 K, and $p/p_s = 0.99$ and $(a_{N_2})_{max}$ is the corresponding adsorbed amount of N_2 on template-free silicalite-1 at 77 K. $(a_{N_2})_{max}$ was taken equal to 32.82 molecules per unit cell here—there may be many reasons in a non-ideal crystal preventing the number of sorbed molecules from being an integer.

Light microscopy. This technique has been used to establish the outer morphology and size of the crystals and to estimate the formation of crystal cracks that were due to template removal procedures. Optical observations were performed using transmission light microscopy with a microscope Peraval Interphako, Carl Zeiss Jena, coupled with a digital camera (Coolpix 950).

Iodine indicator technique. Light microscopy was also used in combination with the iodine indicator technique [9,10] to evaluate the channel accessibility for the iodine molecular probe. The coloring of the silicalite-1 crystals by iodine molecules took place from the gas phase at 298 K under air. The crystals were spread to form a monolayer on the bottom of the cavity slide. Several crystals of iodine were then added, and the cavity was closed by a coverglass. The iodine crystals can be seen on the micrographs as almost black particles. The crystal coloring intensity was taken as a qualitative measure of the adsorbed amount of iodine. It has been found that for silicalite-1-90°-intergrowths with $L_a \cong L_b = 40$ μm, the limiting coloring intensity with iodine vapor is homogeneous dark violet, and it is assumed to correspond to the limiting adsorbed amount of iodine in silicalite-1.

3. Results

3.1. Channel system accessibility from nitrogen adsorption measurements

The adsorption isotherms of nitrogen were plotted for samples at different stages of template removal. In all cases, the amount of adsorbed nitrogen increases monotonously with increasing T_{max}. When a certain fraction of the micropore volume became free of organics, a step on the isotherms started to develop. The lower plateau on the nitrogen isotherm corresponds to 24 molecules per unit cell and the upper one to 31–33 molecules per unit cell for template-free samples. This result is in accordance with literature data [5–8].

Fig. 5 shows that the channel accessibility Y depends on T_{max}, on the presence of oxygen in the atmosphere and on the hydrodynamic regime used during the template removal process. Our experimental results show that (i) the height of the upper step in the sorption isotherm of N_2 increases as the content of residual organic species decreases (α increases), (ii) the lower the content of residual organic species in the channel system, the sharper is the step in the isotherms, (iii) the position of the step is displaced to lower values of the relative nitrogen pressure, as the residual content of organic species decreases.

3.2. Light microscopy observations

3.2.1. Colored patterns in crystals due to partial template removal

Sample treated in a parallel gas flow. Dark patterns, visualizing the domain boundaries in silicalite-1-90°-intergrowths, were found in the crystals treated at low temperature (T_{max} = 300–315 °C). These samples were calcined using parallel gas flow (N_2 or air), see Fig. 6a and b.

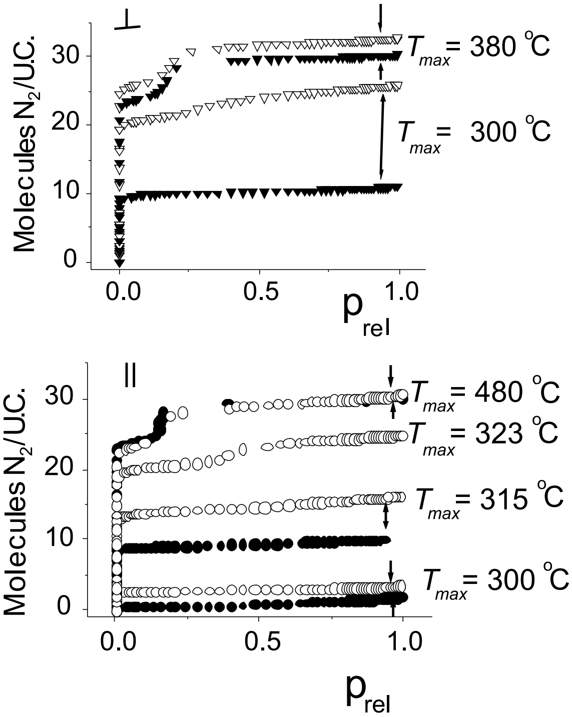

Fig. 5. Adsorption isotherms of nitrogen on partially template removed silicalite-1 and on template-free silicalite-1 in different regimes of template removal: cross-flow (top: ▼ in N_2, ▽ in air), and parallel flow (bottom: ● in N_2, ○ in air).

On uniformly colored crystals, the patterns could not be identified any more when the treatment temperature exceeded 315 °C, i.e., when α_C exceeded 0.52.

Note that the loss of color does not indicate a total loss of carbon, as shown, for instance, by the elemental analysis of the colorless sample 1 (12% remaining C after parallel air flow treatment at 330 °C maximum temperature).

Samples treated in a cross-flow. Experiments under similar conditions on samples treated in the cross-flow mode did not show colored patterns. It should be noticed that this experimental arrangement led to a relatively high degree of template removal even at the lowest temperature (T_{max} = 300 °C). The value of α_C at 300 °C was 0.60 for nitrogen in the cross-flow mode and 0.80 for air in the cross-flow mode.

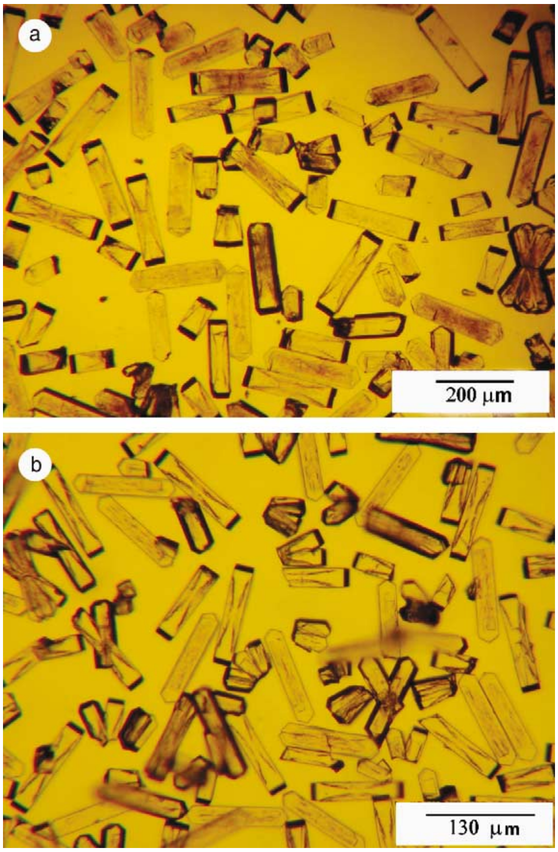

Fig. 6. Silicalite-1 crystals after partial template removal at $T_{max} = 300$ °C: (a) parallel nitrogen flow, (b) parallel air flow.

3.2.2. Iodine saturation kinetics in template-free MFI crystals

The sorption of iodine from the vapor phase after template removal at a T_{max} higher than 480 °C always led to a uniform coloring with the limiting intensity in the dark violet (saturation). Such samples treated at high temperature are examined here from the point of view of their iodine saturation kinetics.

When using the parallel air flow mode, the saturation time was 10 min (sample with $L_c = 130$ µm) to 20 min ($L_c = 230$ µm). However, when using nitrogen, this saturation lasted up to 3 h (sample with $L_c = 130$ µm) or even 160 h ($L_c = 230$ µm), cf. Fig. 7a and b.

On the other hand the adsorption saturation with nitrogen at 77 K is accomplished in about 3–5 h.

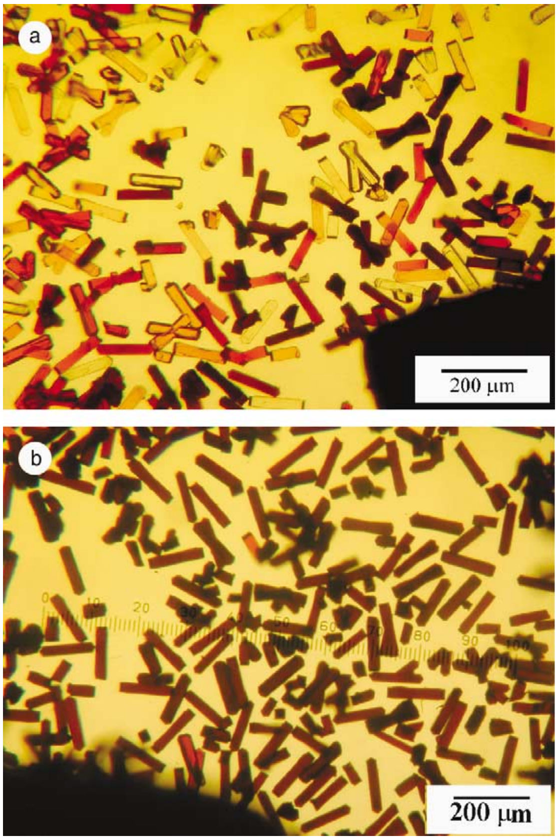

Fig. 7. Kinetics of crystal coloring calcined in the $N_2 \parallel$ regime at $T_{max} = 550$ °C: (a) after 5 min, (b) after 3 h in contact with I_2 molecules from the gas phase.

3.2.3. Iodine-accessible space after template removal at low temperature

Fig. 8 shows lowly iodine-saturated crystals, both calcined in air at $T_{max} = 300$°C in the parallel and cross-flow regimes.

It can be seen that, for lower temperature treatments, only intercrystalline boundaries are accessible to iodine, when the sample was treated with a parallel gas flow. For cross-flow treated samples, the whole crystal is homogeneously accessible to iodine.

3.2.4. Crack formation

No cracks were observed using light microscopy after template degradation performed in an air flow (parallel and cross-flow regimes). Fig. 9 shows an example.

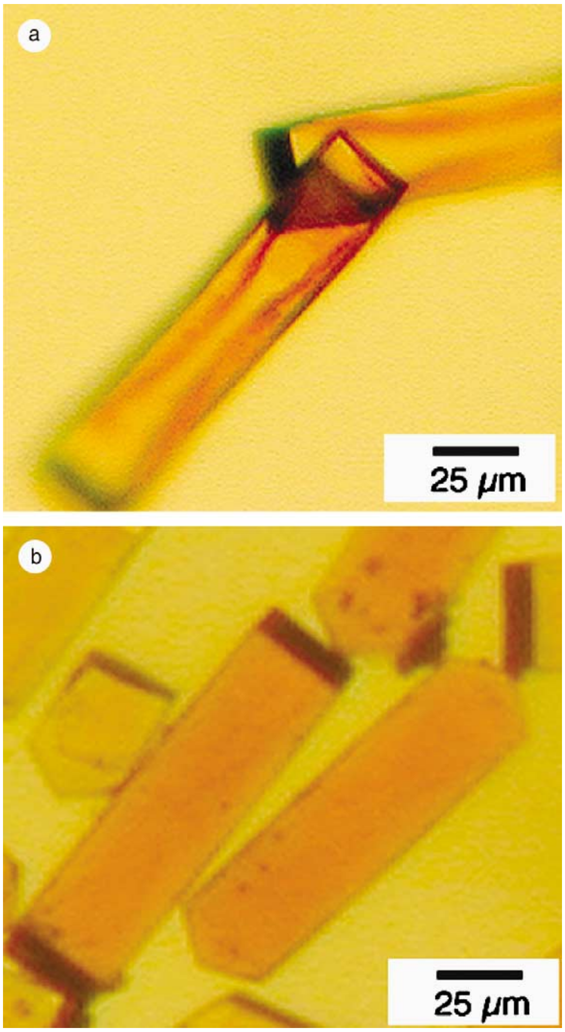

Fig. 8. Silicalite-1 crystals ($L_c = 130$ μm) calcined in air in the parallel (a) and cross-flow (b) regimes at $T_{max} = 300$ °C after 8 min in contact with I_2 molecules from the gas phase.

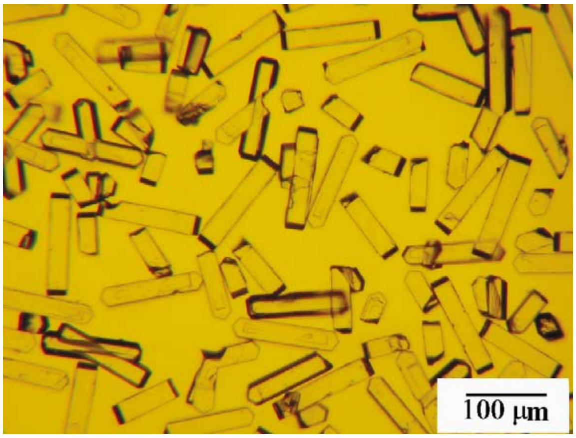

Fig. 9. Template-free crystals (sample 1) calcined in air $\parallel$ at $T_{max} = 530$ °C. Note that no cracks are visible.

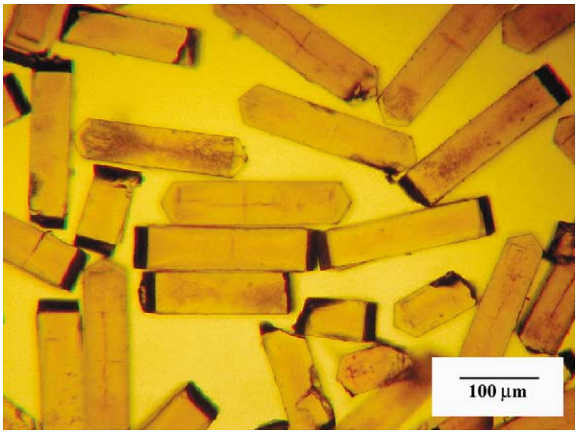

Fig. 10. Silicalite-1 crystals (sample 3) calcined in nitrogen in the cross-flow regime at $T_{max} = 380$ °C. Note that longitudinal and a transversal cracks exist in most crystals.

A different situation arose with larger crystals (samples 2 and 3). No matter which atmosphere was used, cracks always appeared after calcination and washing with NH_4NO_3 solution.

In medium-size crystals ($L_c = 190$ μm, sample 2) cracks appeared in template-free crystals after treatment at 550 °C and washing, whereas in larger crystals ($L_c = 230$ μm, sample 3), cracks were already formed after the first calcination at 315 °C. Fig. 10 shows crystals treated in N_2 in the cross-flow regime at $T_{max} = 380$ °C. It can be seen that almost each crystal has at the same time a longitudinal and a transversal crack.

4. Discussion

4.1. Channel system accessibility from nitrogen adsorption measurements

The isotherms obtained here show two plateaus. The first one is difficult to define due to its short length. In order to explain the behavior in nitrogen adsorption, one can discuss the position of the inflexion step between the first and the second plateau and the position of that first plateau.

p_{rel_1} is defined as the pressure characteristic of the first short plateau. It can be estimated as the first minimum of the $\mathrm{d}Y/\mathrm{d}p_{\mathrm{rel}}$ vs. p_{rel} plot (Fig. 11). $(p_{\mathrm{rel}})_{\mathrm{inf}}$ is defined as the position of the second step inflexion, that is the maximum abscissas of the same plot.

Y_1 and Y indicate the amount of nitrogen adsorbed on the first and second adsorption isotherm plateaus, respectively. Y and Y_1 are defined as $Y_1 = a_{\mathrm{N}_2}(p_{\mathrm{rel}_1})/(a_{\mathrm{N}_2})_{\mathrm{max}}$. Table 3 quantifies the relation between the position of the upper step inflexion in the isotherm and the accessible space in the silicalite-1 crystals, characterized by both Y and Y_1.

The spreading of the step on the adsorption isotherms (Fig. 5, Table 3) may be due to the presence of organic residues, and would then indicate the heterogeneous centers in the channel system of silicalite-1. In this respect, the organic residues seem to have a similar effect on the surface heterogeneity as the presence of aluminum tetrahedra in MFI type zeolites with their corresponding cations (cf. Ref. [13]). Moreover, the organic residues in the channel cross-sections may hinder the rearrangement of the adsorbed N_2 layer. Therefore, a higher driving force would be needed to reach the degree of adsorption necessary to fill the space corresponding to the upper plateau of the adsorption isotherm. This seems to be a proper explanation of the step shift to higher relative pressure values.

Table 3
Relation between the upper step position in the isotherm, characterized by $(p_{\mathrm{rel}})_{\mathrm{inf}}$, and the accessible space in the silicalite-1 crystals in the first plateau (Y_1) and in the second plateau (Y)

Regime	T_{max} (°C)	Y_1	Y	$(p_{\mathrm{rel}})_{\mathrm{inf}}$
N_2 ∥	300	–	0.07	–
	315	–	0.32	–
	330[a]	0.58	0.67	0.56
	380	0.69	0.87	0.22
	430	0.70	0.91	0.17
	480	0.71	0.94	–[b]
Air ∥	300	–	0.11	–
	308	–	0.27	–
	315	–	0.49	–
	323[a]	0.63	0.76	0.39
	330	0.67	0.80	0.35
	380	0.71	0.88	0.18
	530	0.75	0.94	0.17
N_2 ⊥	300	–	0.34	–
	315	–	0.58	–
	330[a]	0.58	0.77	0.68
	380	0.67	0.93	0.20
	430	0.72	0.92	–[b]
	480	0.71	0.94	–[b]
Air ⊥	300[a]	0.65	0.79	0.28
	315	0.66	0.82	0.24
	330	0.71	0.89	0.20
	380	0.79	0.18	

[a] Stands for T^{*}_{max}, that is the lowest temperature with a step in the isotherm.

[b] Not a valuable inflexion point, due to the lack of experimental points.

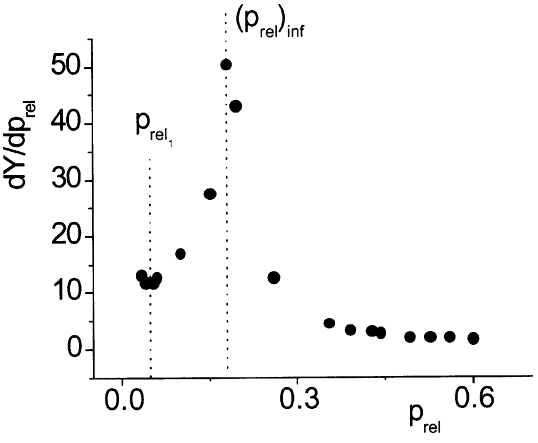

Fig. 11. Derivative of the Y vs. p_{rel} plot with respect of p_{rel} (air ∥ regime at 380 °C).

In conclusion to the analysis of the nitrogen adsorption isotherms of silicalite-1 samples with different content of residual organic species, one can state that all the above results are consistent with the explanation that the step in the isotherm is due to a rearrangement of the adsorbed layer [6].

4.2. Empirical relationship between template removal and nitrogen accessibility

Figs. 12 and 13 show the dependence of the space accessibility Y of silicalite-1 on the degree of species removal α_N or α_C (cf. *Elemental analysis* in

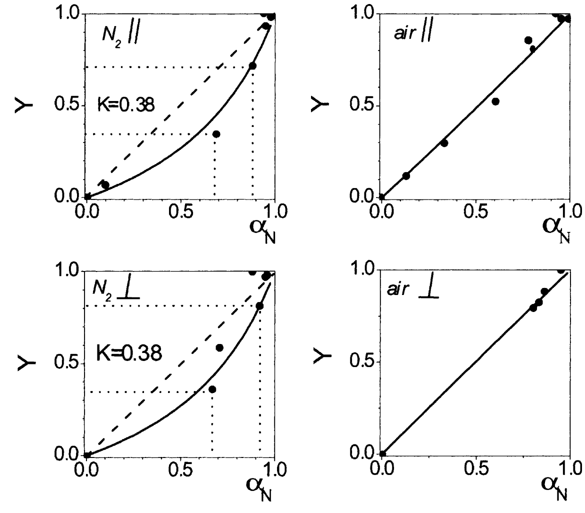

Fig. 12. Plot of the N_2 gas channel accessibility Y on the degree of removal of N-containing species α_N in the different calcination regimes.

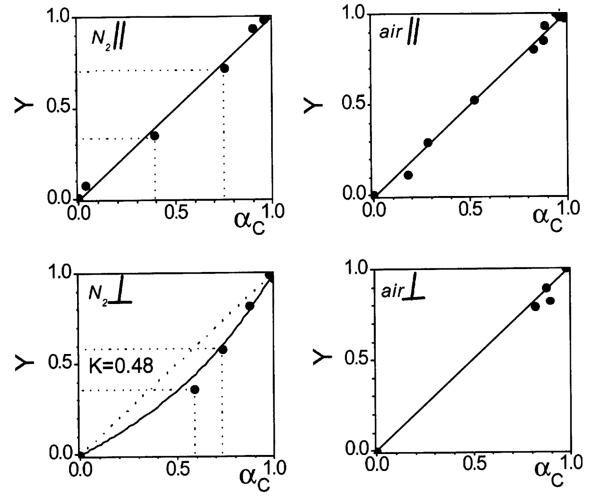

Fig. 13. Plot of the N_2 gas channel accessibility Y on the degree of removal of C-containing species α_C in the different calcination regimes.

Section 2.2). It was found that this dependence could be generally fitted by the empirical relation:

$$Y = \frac{K\alpha_I}{1 + (K - 1)\alpha_I} \tag{1}$$

provided that the deviations from linearity are moderate.

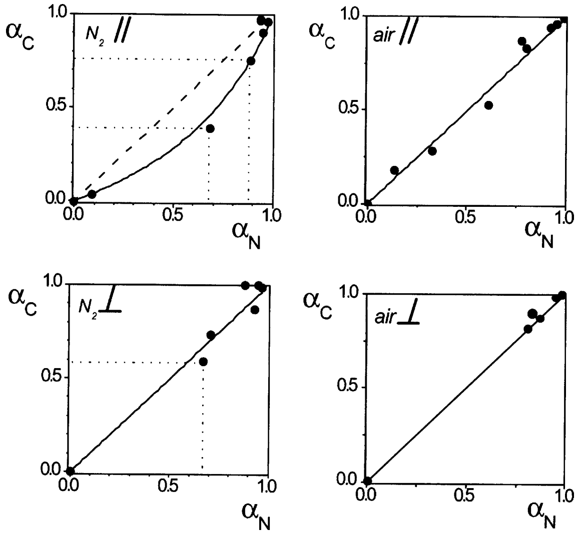

Fig. 14. Development of the degree of removal of C-containing (α_C) and N-containing (α_N) species from silicalite-1 samples treated in different regimes. For each calcination regime, each point represents a different calcination temperature T_{max} and, therefore, different degrees of template removal.

The parameter K quantifies the channel accessibility lagging behind the degree of species removal. Thus, when using air as calcination gas, $K \cong 1$, $Y = \alpha_N$ and $Y = \alpha_C$. This means that the whole volume from where the template was removed was fully accessible for nitrogen molecules. In contrast, when using nitrogen as calcination gas, the dependencies show in most cases a perceptible deviation from linearity ($K < 1$, see Figs. 12 and 13). This means that the accessible space is no more proportional to the removal of N-containing species. Particularly, when the template removal was performed in a parallel N_2 flow, an enrichment of organic residues by carbon occurred. This is clearly seen from the plot of α_C vs. α_N in Fig. 14.

Plots of α_C vs. α_N can be fitted by a similar equation as Y vs. α. The degrees of removal of N-containing and C-containing species are proportional ($\alpha_C = \alpha_N$), except in the case of zeolite samples treated with a *parallel N_2 flow* (see Fig. 14).

4.3. Mechanism of template decomposition

When nitrogen is used as calcination gas, the template decomposition in the low-temperature region ($T_{max} = 300$–330 °C) seems to occur together the formation of species with a higher content of carbon. These compounds remain in the channel system and reduce the accessible space for N_2 sorption. Carbon deposition is most likely due to a slow kinetic step in the removal of template degradation products from the crystals and their neighborhood. One can also think of side (condensation) reactions of the intermediates which take place in the channel system when the overall desorption time of the intermediates from the crystals is too long. The desorption of the degradation products starts when the mobility of the molecules reaches the percolation threshold. The conceivable rate determining steps for a slow desorption kinetics of the intermediates and products of the pyrolytic process, after attaining the percolation threshold, are as follows: (i) a slow intracrystalline diffusion of intermediates, (ii) a slow desorption rate of nitrogen-containing species (amines) from the crystals, (iii) a slow intercrystalline transport of the species across the crystal layer to the stream of carrier gas. Steps (ii) and (iii) are consistent with the findings from our previous study [14], that there is practically no gradient of the total nitrogen content (stemming from the template) in any crystal cut perpendicular to the *c*-axis. If steps (ii) and/or (iii) control the overall kinetics of template removal, the lowering of the concentration of the above degradation products in the crystal neighborhood and in the outer shell of the crystals due to oxidation may intensify the process.

The presence of oxygen in the calcination gas on the other hand, strongly reduces the deposition of species with an enhanced carbon content. When using air as a calcination gas, the strongest intensification of template removal due to the presence of O_2 occurs for $T_{max} = 300$–315 °C. For higher T_{max} the effect of the oxygen presence becomes insignificant. It is interesting that the maximum effect of the oxygen presence on the quantity Y occurs at a T_{max} that is below the autoignition temperature of propylene ($T_{ign} \approx 460$ °C) [15, Table 1–20.4]. Propylene is the most abundant pyrolytic product of TPAOH with a content of about 60–73 vol.% in the gas flow at the reactor outlet [16]. As a consequence, the decomposition of the template cannot be carried out by a burning process.

4.4. Template removal pathways

In the case of parallel gas flow calcination, the observation of the dark patterns in Fig. 6a and b can lead to the conclusion that, at least in the earlier stages of the calcination ($T_{max} \leqslant 315$ °C), the products of template degradation leave the crystals along the domain interfaces. These interfaces are illustrated as shadowed triangles FIB, GIC, EIA, HID and open triangles F′I′B′, G′I′C′, E′I′A′, H′I′D′ in Fig. 2. The application of the iodine indicator technique to the crystals with a low degree of template removal confirms this finding (cf. Fig. 8a). Low values of α allow the domain boundaries to become partially permeable for I_2 molecules (critical diameter of ≈0.40 nm). On the other hand, the bulk of the individual domains remains practically full of template, and therefore inaccessible to iodine, i.e. uncolored.

In the case of cross-flow regimes, even low-temperature calcinations did not lead to the observation of a similar pyramide shape in the crystals. A more intensive removal of template degradation products from the crystal surface can explain this (compare the values of nitrogen channel accessibility in Table 3). Therefore, in this case, the template removal process must have started at a lower temperature than in the parallel mode.

4.5. Differences between the kinetics of adsorption of nitrogen and iodine molecules

It is of interest that, regardless of the template removal regime used and the degree of template removal α achieved, the application of the iodine indicator technique always revealed some crystal inhomogeneity at the start of the experiment. One can assess the sample inhomogeneity when evaluating the coloring intensity of crystals located at equal distance from the surface of an iodine particle (cf. Fig. 7a). For the theory of the coloring procedure see Ref. [10]. Nevertheless, the coloring always became homogeneous after a certain period, as noticed earlier (see Section 3.2).

It has already been stated that organic residues are always present in a small extent when using the parallel N_2 flow regime. It follows from elemental analysis that the content of residual carbon in crystals calcined at 480 °C is about 2.5 wt.% based on the carbon content in the parent silicalite-1. These carbon deposits had no large influence on the adsorption kinetics of N_2 molecules (critical diameter 0.30 nm). Nevertheless, the carbon residues are most likely the reason for the enormous differences in the coloring kinetics of the bigger I_2 molecule (critical diameter 0.40 nm). This can be interesting from the point of view of adsorption separation processes of gas mixtures.

4.6. Crack formation

Based on the crack formation observations, it is obvious that the tendency to crystal cracks increases as the crystal size increases. Particularly, a contact of the crystals with liquid phase NH_4NO_3 molecules revealed that stresses in crystals during adsorption could enhance this trend.

5. Conclusion

Nitrogen adsorption isotherms were carefully analyzed, and the development of the channel accessibility upon calcination was modelled and studied. The most plausible explanation for the upper step in the nitrogen adsorption isotherm appears to be a rearrangement of the adsorbed layer.

A strong positive effect of the oxygen presence in the low-temperature calcination gas has been established. Oxygen seems to favor the channel accessibility by removing some key template degradation products from the crystal surface.

Considering the structure of silicalite-1-90°-intergrowth crystals and the results of light microscopy and elemental analysis, the template removal mechanism has been assessed. At least in the earlier stages of the process, the residues seem to leave the crystals through the domain boundaries.

The above study stresses the importance of the calcination gas flow regime. This significant result has been obtained from two different observations (light microscopy and nitrogen adsorption). When using a cross-flow regime, the template removal efficiency is higher, particularly at lower temperatures. This effect is even more pronounced when air is used instead of nitrogen. This should be taken into account when considering the calcination of zeolite membranes.

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