Spontaneous crystallization of zincophosphate sodalite by means of dry substrate grinding

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Zincophosphate sodalites can be obtained by simple grinding of the substrate salts [$ZnCl_2$, $Zn(NO_3)_2$, Na_2HPO_4, Na_2CO_3] in a mortar, provided that at least one of the applied salts contains crystallization water.

The hydrothermal synthesis of zeolites or zeolite-like materials usually comprises forming an initial gel and its subsequent crystallization often at enhanced temperature and sometimes for extended times. Stucky and coworkers[1,2] demonstrated the unusual possibility to obtain faujasite (FAU) or sodalite (SOD) (zincophosphate, zincoarsenate, zincoantimonate) structures by means of spontaneous crystallization upon mixing aqueous solutions of the substrates at low temperatures. The above zeolite-like materials have been extensively studied by several research groups.[3] Such spontaneous crystallization can be useful for encapsulation of certain compounds inside the inner cages upon their formation. Our earlier attempts to prepare ultramarine analogs by introduction and further transformation of sodium polysulfides inside zincophosphate sodalite prepared according to the Stucky recipe[1] have not been successful[4] because of the low stability of the crystalline structure. The crystallization of zincophosphate with sodium polysulfide present in the initial mixture did not lead to formation of the sodalite structure. Another attempt to introduce polysulfides into the zincophosphate upon crystallization comprised simple grinding of the substrates without any water. Although mixtures containing polysulfides did not form a sodalite, it was interesting that a blank sample containing no sulfides formed the sodalite structure merely by grinding of the substrates.

The following study presents series of syntheses of zincophosphate sodalite by means of spontaneous, *dry* crystallization. The following principal substrates have been applied: $ZnCl_2$, $Zn(NO_3)_2 \cdot 6H_2O$, Na_2HPO_4, $Na_3PO_4 \cdot 12H_2O$, NaOH, Na_2CO_3, $Na_2CO_3 \cdot 12H_2O$ (all supplied by POCh, Poland). In some cases additional compounds (such as KBr, NaCl, CdS, elemental S) were admitted to the initial mixtures. The Zn/P ratio was always 0.85 and Na/Zn was 3.5, *i.e.* similar to that applied by Stucky and coworkers for synthesis of the SOD structure.[1,2] NaOH applied in preliminary experiments was replaced by sodium carbonate because of easier grinding of the latter. The procedure comprised grinding of the substrate mixture (usually *ca.* 2 g) in a ceramic mortar for *ca.* 10 min, then washing of the products with water and drying at 60 °C. The sequence of admittance of the substrates to the mixture varied. The obtained samples were characterized by means of XRD, IR, DTA, DTG and SEM.

The grinding of the mixture [*e.g.* $Zn(NO_3)_2 \cdot 6H_2O$, Na_2HPO_4, Na_2CO_3] led to release of water from the hydrated salts which made the sample wet. The evolution of CO_2 on grinding was noticeable due to Na_2CO_3 decomposition in the presence of Zn salts. Table 1 indicates the composition and sequence of adding the substrates as well as the structure and pH of the first drops of the filtrate on washing. Fig. 1 indicates high crystallinity SOD structures of the samples obtained from mixtures of Na_2HPO_4, Zn salts and Na_2CO_3 provided that one of components contains crystallization water. The as-made samples (before washing) usually contain a noticeable amount of NaCl or $NaNO_3$ (indicated in Fig. 1 for the sample ZnP-1*), which can then be washed out. It is remarkable that the sequence of substrate admittance affects the crystallinity and purity of the products. The sample obtained by merging all the substrates together (ZnP-0) contains more hopeite impurities than the samples ZnP-2 and ZnP-1, where either acidic (Zn) or alkaline (Na_2CO_3) components are admitted last. The SOD structure does not appear if Na_3PO_4 is used as the P source. The sequence of admittance as well as the P source influence the pH of the resulted products. It is likely that the pH of the mixture is an important factor for obtaining the SOD structure. The best results were achieved at pH ~ 7. The value of pH was as high as 11–12 for the samples prepared from Na_3PO_4 (with a similar molar ratio). The SOD structure was not formed on grinding when anhydrous salts were used (*e.g.* sample ZnP-4*), however, this sample attained the SOD structure upon washing with water

Table 1 Results of *dry* crystallization of zincophosphates

Sample	Substrates (order of admission)	pH	Structure
ZnP-SOD[1]	$H_3PO_4 + NaOH + Zn(NO_3)_2 + H_2O$	7.5	SOD + H
ZnP-0	$Na_2HPO_4 + Na_2CO_3 + Zn(NO_3)_2 \cdot 6H_2O$; all substrates mixed together	6.8	SOD + H
ZnP-1*	$Na_2HPO_4 + Na_2CO_3 + Zn(NO_3)_2 \cdot 6H_2O$		SOD + $NaNO_3$
ZnP-1	$Na_2HPO_4 + Na_2CO_3 + Zn(NO_3)_2 \cdot 6H_2O$	6.8	SOD
ZnP-2	$Na_2HPO_4 + Zn(NO_3)_2 \cdot 6H_2O + Na_2CO_3$	6.8	SOD
ZnP-3	$Na_2CO_3 + Zn(NO_3)_2 \cdot 6H_2O + Na_2HPO_4$	6.5	SOD + H
ZnP-4*	$Na_2HPO_4 + Na_2CO_3 + ZnCl_2$		NaCl
ZnP-4	$Na_2HPO_4 + Na_2CO_3 + ZnCl_2$	6.5	SOD
ZnP-5*	$Na_2HPO_4 + Na_2CO_3 \cdot 10H_2O + ZnCl_2$	8.2	NaCl + SOD
ZnP-6*	$Na_3PO_4 \cdot 12H_2O + Zn(NO_3)_2 \cdot 6H_2O$	12	$NaNO_3$
ZnP-7*	$Na_3PO_4 \cdot 12H_2O + ZnCl_2$	11	NaCl

* The as made samples (not washed); H-hopeite; the pH was measured for the first drops of the filtrate on washing.

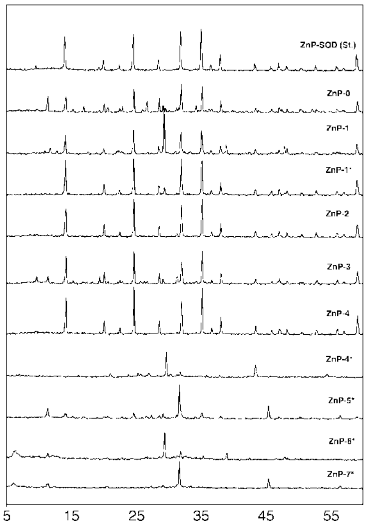

Fig. 1 XRD patterns of indicated samples. ZnP-SOD (St) indicates the sample prepared according to the Stucky recipe.[1] Samples indicated by asterisks were not washed before the diffraction measurements.

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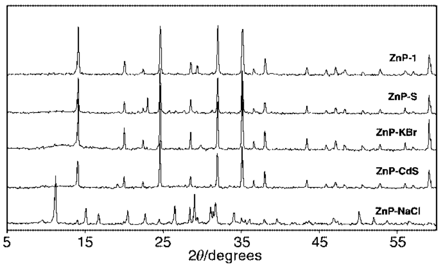

Fig. 2 XRD patterns of the indicated samples.

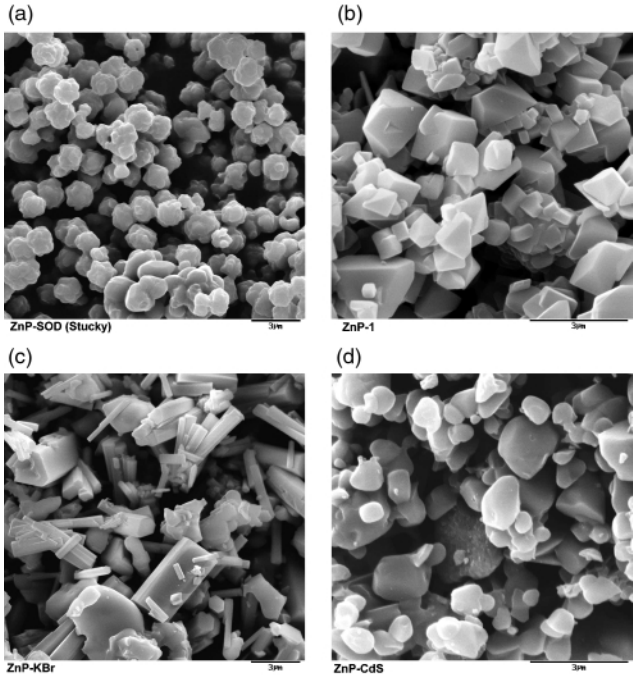

Fig. 3 SEM pictures of (a) sodium zincophospate sodalite prepared according to Stucky;[1] (b) sample ZnP-1; (c) sample ZnP-KBr; (d) sample ZnP-CdS.

(ZnP-4). The sodalite structure has also been attained when some additional compounds were admitted (KBr, S, CdS, see Table 2), whereas other salts (*e.g.* NaCl, Na_2S_n) impeded formation of the SOD structure (Fig. 2). No bromide was detected in the sample prepared with KBr, although its presence affected the morphology of the product (Fig. 3). The size of crystallites obtained using this *dry* method (*ca.* 2 μm) was similar to those prepared from solution as well as aluminosilicate sodalite (Fig. 3). CdS is most likely encapsulated inside the sodalite cages and only at high CdS loading (CdS/Zn > 0.2) do the SEM images indicate the presence of sulfide particles on the surface of sodalite crystallites.

The thermal properties of the samples obtained by grinding [examined by thermal (DTA) and gravimetric (TG, DTG) analyses (Fig. 4)] indicate the most significant effects attributed to removal of water. The dehydration temperatures differed for the samples prepared from different substrates or in the presence of additional components (*e.g.* KBr). It is interesting that regardless of the differences in dehydration temperatures, the amount of water removed is always the same (*ca.* 10%), which corresponds to empirical formula of the products: $NaZnPO_4 \cdot H_2O$. For sample ZnP–CdS the weight loss on heating to 200 °C is only *ca.* 5%. This lower content of water results from encapsulation of CdS. The XRD data of the samples calcined at 200 °C indicate decomposition of the structure after removal of water which is not regenerated upon contact with atmospheric moisture.

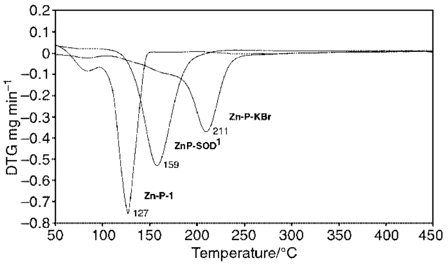

Fig. 4 Typical DTG curves (in air) for the indicated samples.

Table 2 Syntheses with additional compounds (main procedure as for ZnP-1)

Sample	Additional reagents	Remarks
ZnP-S	S dissolved in CS_2 (Zn/S = 1,33)	SOD, yellow
ZnP-KBr	KBr ground with mixture (Zn/KBr = 0,35)	SOD, no Br^-
ZnP-CdS	CdS powder ground with mixture (Zn/CdS = 0,04)	SOD, yellow
ZnP-NaCl	NaCl (Zn/NaCl = 0,7)	Poor crystallinity

Another series of experiments with anhydrous substrate salts ground with a small admixture of various polar reagents such as ethanol, phenol, amines, acetone, nitrobenzene, acetonitrile, DMSO, DMF or liquid ammonia sometimes resulted in crystalline structures analogous to zeolites.[5]

The present preliminary results indicate a great affinity of zinc salts and phosphates to form a sodalite crystalline structure. Spontaneous crystallization of the sodalite structure can take place even upon grinding of substrate salts. The *dry* crystallization, however, requires some water, which is supplied from crystallization water present in at least one of the components of the substrate mixture. The sequence of adding the mixture components as well as the pH of the mixture affects the results of the syntheses. It seems that some additional compounds (*e.g.* S, CdS) can be encapsulated into the sodalite cages on *dry* crystallization. The admittance of a small amount of polar reagents (other than water) to an anhydrous substrate mixture can sometimes result in structures similar to zeolites.

Notes and references

1 W. T. A. Harrison, T. E. Gier, K. L. Moran, J. M. Nicol, H. Eckert and G. D. Stucky, *Chem. Mater.*, 1991, **3**, 27.
2 T. E. Gier and G. D. Stucky, *Nature*, 1991, **349**, 508.
3 W. T. A. Harrison, T. E. Gier, J. M. Nicol and G. D. Stucky, *J. Solid State Chem.*, 1995, **114**, 249; M. J. Castagnola and P. K. Dutta, *Microporous Macroporous Mater.*, 1998, **20**, 149; X. Bu, T. E. Gier, P. Feng and G. D. Stucky, *Microporous Macroporous Mater.*, 1998, **20**, 371; H. Y. Ng and W. T. A. Harrison, *Microporous Macroporous Mater.*, 1998, **23**, 197; R. W. Broach, R. L. Bedard and S. G. Song, *Chem. Mater.*, 1999, **11**, 2076.
4 S. Kowalak, M. Stróżyk, M. Pawłowska, M. Miluśka and J. Kania, *Stud. Surf. Sci. Catal.*, 1997, **105**, 237.
5 S. Kowalak and A. Jankowska, study in progress.