The Reversible Desorption of H$_2$O$_2$ from the Inclusion Channel Complex 4Na$_2$SO$_4$·NaCl·2H$_2$O$_2$

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H$_2$O$_2$ can be reversibly desorbed from 4Na$_2$SO$_4$·NaCl·2H$_2$O$_2$ leaving a modified but intact host lattice of 4Na$_2$SO$_4$·NaCl.

Within the large variety of known inclusion compounds, sorption and desorption properties vary. Upon desorption of the guest, some retain their structure (e.g. zeolites[1]) whilst others modify their structure into a more compact but non-porous form.[2] These differences are often reflected in the sorptive abilities of the guest-free compound. Zeolites are able to successively sorb and desorb a wide variety of guests[1] whereas tetracyano-complexes lose their sorptive abilities once completely desorbed of guests.[3] In other cases, the non-porous structure is sometimes able to reconstruct into the porous form during guest sorption, depending on the particular host and guest.[4]

Persalts are important components of powder laundry detergents. Of interest is the inclusion compound 4Na$_2$SO$_4$·NaCl·2H$_2$O$_2$ (SSCP) developed for use with neutral detergents.[5] It is one of the few purely inorganic inclusion compounds not composed of Si–O or Al–O units, or transition metals. We are unaware of any other inorganic inclusion compounds containing H$_2$O$_2$ as the guest species. We report

here that when H$_2$O$_2$ is thermally desorbed, the host lattice is modified but that separation into NaCl and Na$_2$SO$_4$ phases does not occur. Upon exposure to H$_2$O$_2$-rich vapour, the inclusion compound is both chemically and structurally regenerated whereas water vapour causes phase separation of the NaCl and Na$_2$SO$_4$ components of the desorbed lattice.

The crystal structure of 4Na$_2$SO$_4$·NaCl·2H$_2$O$_2$ was determined by Adams et al.[6] and consists of channels defined by four sulfate oxygens in the ab plane. These channels run parallel to the c axis and contain disordered H$_2$O$_2$ molecules. Each H$_2$O$_2$ is involved in two hydrogen bonds which are believed to greatly influence the stability and properties of SSCP. There is an unusually high eightfold coordination of one of the nine sodium ions. The hydrogen peroxide O–O bond length is 1.47(1) Å[7] which is in good agreement with those generally found in perhydrates.[8] We are, however, unaware of any detailed studies into the guest desorption and subsequent resorption characteristics of SSCP.

A solution of 0.42 g NaCl in 8 g 30% H$_2$O$_2$ was added dropwise to a solution of 4.09 g of Na$_2$SO$_4$ in 20 g 30% H$_2$O$_2$. The resulting solution was left to crystallise in air to yield well formed crystals. These were ground and then heated to fully desorb the H$_2$O$_2$ (grinding did not affect the structure or H$_2$O$_2$ content). The resultant powder was then placed in contact with the vapour above a 60% solution of H$_2$O$_2$ and the whole covered with a large crystallising dish for 6 days. In the same way, the effect of water vapour was examined. The extent of guest desorption and resorption was followed by powder X-ray diffraction (PXRD), infrared spectroscopy (IR), thermal gravimetric analysis (TGA) and titrimetric available oxygen content (AVOX).[9]
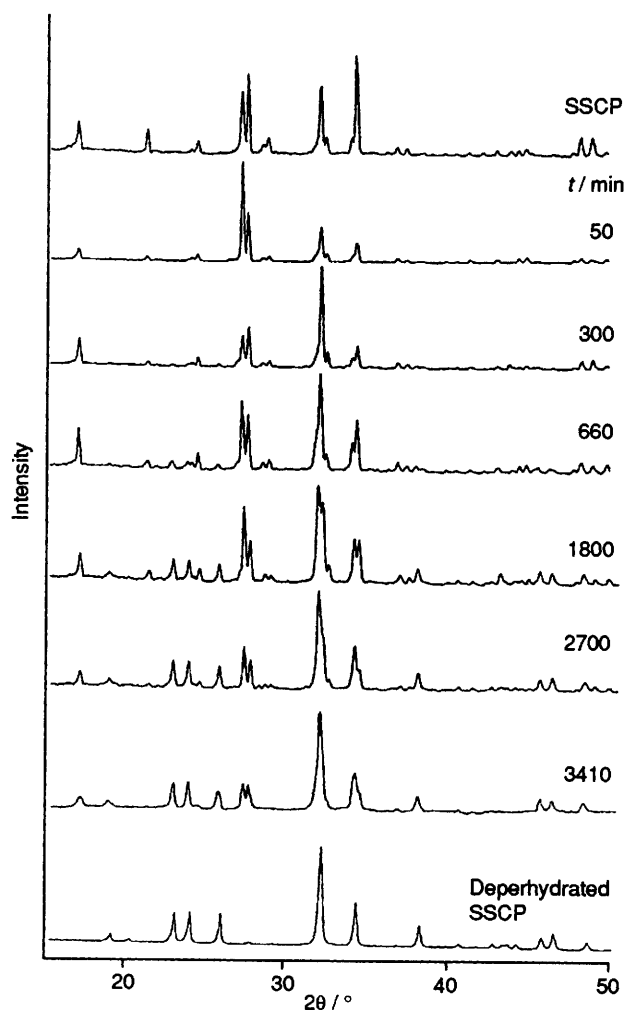

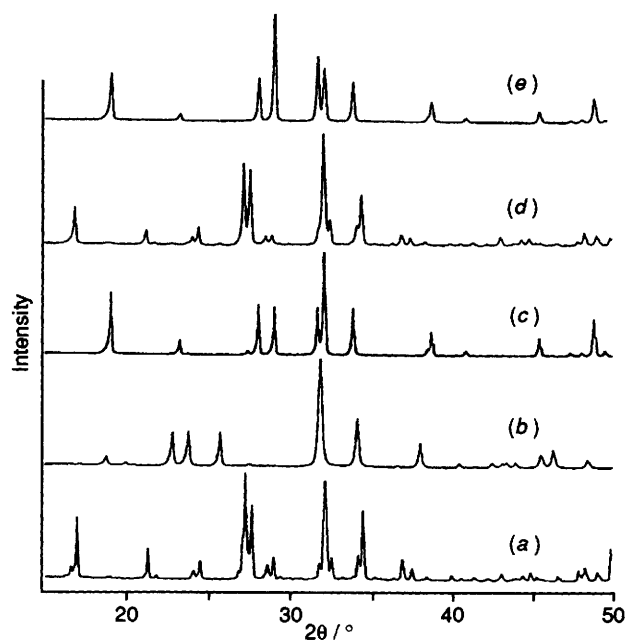Fig. 1 PXRD patterns showing partial desorption of H$_2$O$_2$ from SSCP at 126 °C

Fig. 2 PXRD patterns showing regeneration of SSCP: (a) SSCP, (b) the fully desorbed product; the products obtained after exposing the latter to (c) H$_2$O vapour and (d) H$_2$O$_2$-rich vapour; and (e) 4:1 mixture of Na$_2$SO$_4$ and NaCl
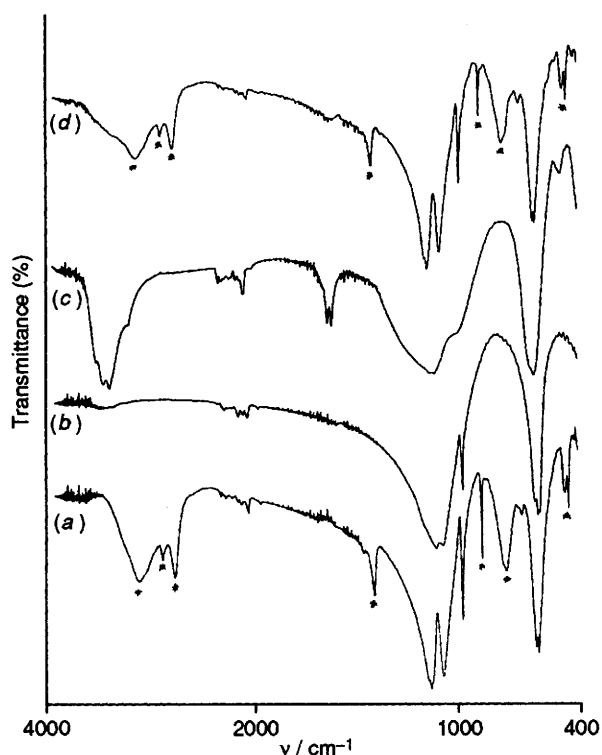
Fig. 3 IR spectra showing regeneration of SSCP: (a) SSCP, (b) the fully desorbed product, and the products obtained after exposing the latter to (c) H_2O vapour and (d) H_2O_2-rich vapour

Table 1 TGA weight loss and AVOX for SSCP, deperhydrated SSCP and regenerated SSCP

	AVOX (%)	TGA weight loss (%)
SSCP	100	9.8
Deperhydrated SSCP	0	0
Reperhydrated SSCP	96	7.3

TGA (heating rate 10 °C min⁻¹ in dry nitrogen) of SSCP gives a single weight loss of 9.8% complete by 220 °C, corresponding to desorption of $2H_2O_2$. Fig. 1 shows how successive partial desorption of H_2O_2 at 126 °C may be followed by PXRD. There is a gradual decrease in intensity of the peaks corresponding to the perhydrate and an increase in

intensity of peaks due to the deperhydrated product. This product is not a simple mixture of Na_2SO_4 and NaCl (Fig.2) and yet it clearly differs in structure to the included compound. The local structure of the desorbed host is also shown to differ from the starting material as shown by the sulfate infrared bands 1300–1000 cm⁻¹ in Fig. 3. The desorbed host lattice is stable under vacuum with no change occurring over several months.

The desorbed product readily reperhydrates. The degree of this resorption of H_2O_2 can be seen quantitatively from the AVOX and TGA weight loss values (Table 1). This is further confirmed by the presence of H_2O_2 infrared bands (asterisked) in Fig. 3. That the local structure is regenerated is confirmed by the similarity between the sulfate bands in the IR. Since the PXRD patterns are also very similar (Fig. 2), regeneration of the long range structure has also occurred.

Inclusion of water by the desorbed product does not occur. Rather, the powder is seen to moisten within several hours. Fig. 2 shows the PXRD of the desorbed product after exposure to water vapour and may be interpreted as a simple mixture of NaCl and Na_2SO_4.

The results discussed above show that H_2O_2 can be desorbed from $4Na_2SO_4 \cdot NaCl \cdot 2H_2O_2$ leaving a stable host lattice which has a modified structure. The perhydrate can be regenerated by exposing the desorbed powder to H_2O_2-rich vapour. Since in terms of the powder patterns and the AVOX values, the regeneration of the perhydrate is complete, it is interesting that phase separation of the desorbed product, by water vapour also present above the H_2O_2 solution, is not as favourable as the resorption of the H_2O_2.

References

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