

THERMAL ANALYSIS OF A HYDRATED SILICA–SODIUM THIOSULFATE–SULFUR SYSTEM

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Abstract

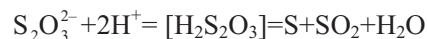
A system formed by concerted action of orthosilicic acid gelation and decomposition of sodium thiosulfate to afford highly dispersed elemental sulfur was studied by simultaneous methods, DTA, TG and DTG. A typical curve has been found to be an outcome of thermal processes associated with desorption of physically adsorbed water, condensation of surface silanol groups and thermal degradation of sodium thiosulfate. A large loss in mass over the lower temperature range was assigned to the loss of physically adsorbed water and condensation of silanol groups of the gel as indicated by accompanying strong endothermic effects. Subsequent strong exothermic effects were attributed to combustion of elemental sulfur embedded in the gel. Experiments were also conducted to control the extent of decomposition of the thiosulfate and generation of elemental sulfur by varying pH of the silicic acid solution. These have shown that acidification of the silicic acid – sodium thiosulfate system with sulfuric acid fostered decomposition of the thiosulfate and raised the quantity of elemental sulfur.

Keywords: DTA, DTG, orthosilicic acid, silica gel, sodium thiosulfate, sulfur, TG

Introduction

The synthesis of inorganic materials using sol-gel techniques has become a hot topic in current chemical researches. Sol-gel chemistry is also an area of material science providing commercial products ranging from optical devices and ceramic fibers to xerogels with encapsulated organics, proteins, enzymes [1], flavours, vitamins, agrochemicals [2] and even bacteria [3].

The purpose of this contribution was to prepare and investigate a system consisting of hydrated silica, sodium thiosulfate and elemental sulfur arising from partial decomposition of the thiosulfate by thermal methods. The specificity of the synthetic approach [4] consisted in utilizing orthosilicic acid for partial degradation of the dissolved thiosulfate [4]:



Highly dispersed elemental sulfur resulting from this reaction was immediately encapsulated by condensing orthosilicic acid thus preventing coagulation of the former. The silica gel with embedded sulfur was then dried to give a xerogel.

The advantage of the adopted procedure is that it eliminates the use of relatively expensive tetraalkyl orthosilicates commonly utilized as a source of silica and ethanol used as a co-solvent.

Another purpose of this contribution was to demonstrate that simultaneous thermal methods (DTA, TG and DTG) are useful for analyzing a complex system consisting of hydrated silica, sodium thiosulfate and elemental sulfur.

Experimental

Preparation of orthosilicic acid

Orthosilicic acid was obtained by ion-exchange from a water glass solution by a procedure reported by Yoshida [5]. Thus, a water glass R-145, manufactured by ZCh 'Rudniki', Rudniki, Poland (sp. gravity 1.45 g cm^{-3} ; $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 2.5), was diluted (1:5) with distilled water and passed through a glass column (500×40 mm) packed with a cation-exchange resin (Amberlite IR 120 in the H^+ form). The concentration of orthosilicic acid in the eluate was approx. 1 per cent based on SiO_2 .

Preparation of the hydrated silica–sodium thiosulfate–sulfur systems

The systems were prepared by two procedures, by reacting sodium thiosulfate with freshly prepared orthosilicic acid solution and by conducting this reaction in the presence of sulfuric acid.

In the first instance, to 100 mL of a 1% orthosilicic acid solution, increasing volumes of a thiosulfate solution were added as indicated in Table 1. After a few hours gelation took place. The gel was dried at 343 K to a constant mass to give a xerogel.

In the second series of experiments, to 50 mL volumes of orthosilicic acid solution, increasing volumes of the sodium thiosulfate solution were added and acidified with sulfuric acid as indicated in Table 2. After gelation, the gels were handled as described.

Determination of the contents of undecomposed sodium thiosulfate

The contents of undecomposed sodium thiosulfate in the xerogels were determined by classical iodometric titration against a starch indicator. Thus, a weighed sample (ca 300 mg) of the finely powdered xerogel was placed in a conical flask containing 30 mL of water and after vigorous agitation titrated with a standardized iodine solution using starch as indicator. The results are shown in Tables 1 and 2.

Thermal analysis

DTA, TG and DTG traces were recorded on an OD-103 derivatograph (MOM, Hungary) in the range of 293–1173 K at a heating rate of 5 K min⁻¹ in air atmosphere, α -Al₂O₃ being used as a reference. A 200 mg sample was placed in a platinum crucible of 9.5 mm in diameter.

Results and discussion

The results of analyses of the xerogels prepared without addition of sulfuric acid are summarized in Table 1. They show that sodium thiosulfate is partially decomposed by orthosilicic acid to produce finely dispersed elemental sulfur.

Table 1 Results of the analysis of xerogels obtained from 100 mL of 1% orthosilicic acid solution and increasing quantities of sodium thiosulfate

No.	Quantity of Na ₂ S ₂ O ₃ added/g	Quantity of the xerogel obtained/g	Quantity of Na ₂ S ₂ O ₃ decomposed/g	Decomposed Na ₂ S ₂ O ₃ /%	S in xerogel/%
1	0.3342	6.4149	0.0829	24.80	0.26
2	0.6358	7.4247	0.1041	16.37	0.28
3	0.9641	7.4958	0.1472	15.27	0.40
4	1.2711	8.2259	0.1987	15.63	0.48
5	1.5832	8.4806	0.2103	13.28	0.50
6	1.9038	10.0148	0.2951	15.50	0.59
7	2.5504	10.0701	0.3886	15.24	0.78
8	3.1959	10.6250	0.4659	14.58	0.90

By raising the quantity of the thiosulfate added to a fixed volume of orthosilicic acid solution, xerogels of elevated contents of both the thiosulfate and elemental sulfur are obtained. It has been noted that the higher the thiosulfate concentration in the orthosilicic acid solution, the larger quantity of the unreacted thiosulfate in the xerogel. Thus, the content of elemental sulfur in the xerogel is not linearly related to the quantity of the thiosulfate added.

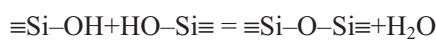
To verify this conclusion, thermal analysis of the products was carried out. The results are presented in Table 3 and in Figs 1–4.

The interpretation of the curves of the hydrated silica–sodium thiosulfate–sulfur systems (Table 2) was advanced by those of the silica xerogel (Fig. 1) and sodium thiosulfate alone (Fig. 2).

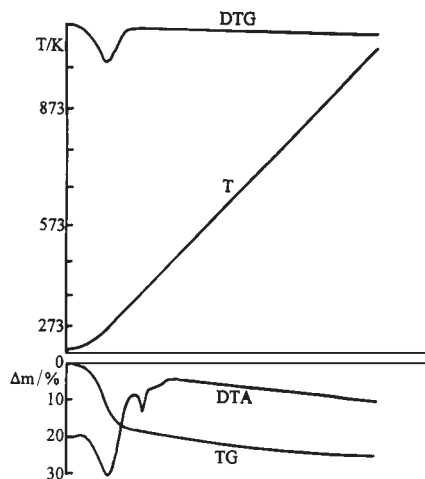
Table 2 Results of analysis of xerogels obtained from 1% orthosilicic acid solution and variable quantities of sodium thiosulfate and sulfuric acid

No.	Initial composition of solution			Decomposed thiosulfate/ mass%	Elemental S in xerogel/ mass%
	Silicic acid/mL	Na ₂ S ₂ O ₃ /mol	H ₂ SO ₄ /mol		
1	50	0.01	–	8.57	0.56
2	50	0.01	0.001	17.74	1.14
3	50	0.01	0.005	61.80	4.53
4	50	0.01	0.01	100	6.71
5	50	0.05	0.003	9.72	1.27
6	50	0.05	0.004	10.51	1.42
7	50	0.05	0.005	17.68	2.30
8	50	0.05	0.01	33.47	4.43
9	100	0.01	0.005	61.08	2.49
10	100	0.01	0.01	100	4.32

The mass loss of silica xerogel begins at 313 and is virtually completed at 453 K (TG and DTG traces in Fig. 1). It is accompanied by a massive endothermic effect (DTA in Fig. 1) due to the evaporation of physically adsorbed water and subsequent condensation of silanol groups of the xerogel:



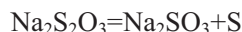
Another endothermic effect in the DTA curve at ca 473 K can be assigned to the condensation of more firmly bound silanol groups, as indicated by a further mass loss in the TG trace.

**Fig. 1** DTA, DTG and TG curves of thermal decomposition of hydrated silica

As recently reported by de Farias and Airoidi [6], there are three characteristic steps in a plot of the density of silanol groups on silica gels vs. temperature. The first one is characterized by a linear slope extending from 473 to 673 K, followed by another quasi-linear section from 673 to 1173 K. In the third step, the density of silanol groups decreases monotonously to zero.

The thermal decomposition pattern of sodium thiosulfate pentahydrate is more complex (Fig. 2). Over the range 313–473 K there is a large mass loss accompanied by two distinctly separated endothermic effects in the DTA trace. The effects can be assigned to the loss of water molecules. The overall mass loss corresponds to 4.11 moles of water per mol of the thiosulfate. This loss is in accordance with actual hydration degree of the salt which had been dried at 343 K before use to remove physically adsorbed water.

Another feature of the thermoanalytical curves is a strong exothermic effect over the range 573–723 K with a relatively small mass loss. This effect can be attributed to thermal degradation of the anhydrous salt:



followed by oxidation of the released sulfur with air oxygen to SO_2 . Desorption of the latter manifests itself by inflections on the left-hand side slope of the peak. The ac-

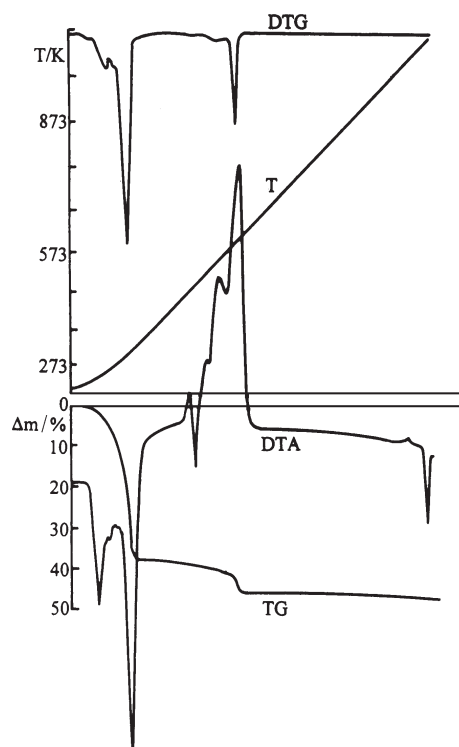


Fig. 2 DTA, DTG and TG curves of thermal decomposition of sodium thiosulfate hydrate

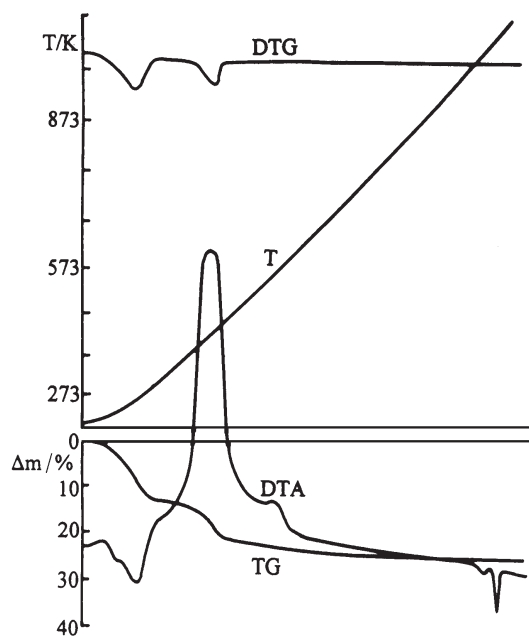


Fig. 3 Characteristic DTA, DTG and TG curves of thermal decomposition of a xerogel with embedded sulfur obtained from No. 8 (Table 2)

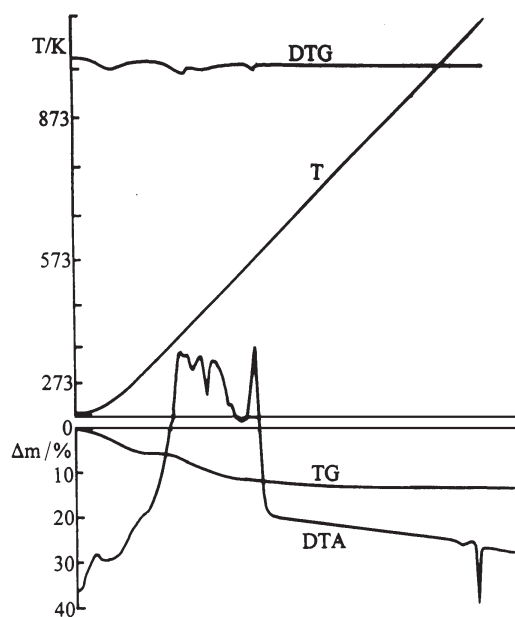
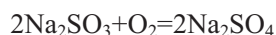


Fig. 4 Characteristic DTA, DTG and TG curves of thermal decomposition of a xerogel with embedded sulfur obtained from No. 5 (Table 2)

companying mass loss is relatively small (TG trace) as the sulfate(IV) is prone to oxidation with air oxygen:



to afford a stable sulfate(VI). A proof in favour of this suggestion is provided by an endothermic peak (DTA) at ca 1173 K assignable to the melting of sodium sulfate(VI) (*m.p.* 1158 K).

Table 3 Results of thermal analysis of the silica xerogel, sodium thiosulfate and the xerogels of composition specified in Table 2

No.	Sample analyzed	$\Delta T/\text{K}$	Mass loss/%	Loss of water/mmol	Loss of SO_2/mmol
1	Silica xerogel	313–453	17	1.89	–
2	$\text{Na}_2\text{S}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	313–473 553–723	37 7	4.11 –	– 0.22
3	No. 1 in Table 2	313–413 453–673	14 4	1.55 –	– 0.125
4	No. 2 in Table 2	313–433 473–533	13 4	1.44 –	– 0.125
5	No. 3 in Table 2	313–453 453–673	11 6	1.22 –	– 0.19
6	No. 4 in Table 2	313–453 453–623	12 7	1.33 –	– 0.228
7	No. 5 in Table 2	313–433 453–753	5 7	0.56 –	– 0.25
8	No. 6 in Table 2	313–433 453–753	5 7	0.56 –	– 0.22
9	No. 7 in Table 2	313–433 433–723	17 7	1.89 –	– 0.22
10	No. 8 in Table 2	313–433 433–673	13 10	1.44 –	– 0.31
11	No. 9 in Table 2	313–453 453–693	12 5	1.33 –	– 0.16
12	No. 10 in Table 2	313–453 453–593	13 5	1.44 –	– 0.16

Some of the representative curves of the silica xerogels containing sodium thiosulfate and elemental sulfur are presented in Figs 3 and 4. They are the outcome of thermal processes of degradation of each of the components of the system. Thus, there is a mass loss over the range 313–373 K corresponding to the dehydration and subsequent condensation of silanol groups of silica and strong exothermic effects due to combustion of elemental sulfur. In all the curves there is also an endothermic peak at ca 1173 K indicating the melting of sodium sulfate(VI).

Thermal analysis of the systems obtained by acidification of sols with sulfuric acid (Fig. 3) exhibit larger bands with more obtuse peaks over the range 433–723 K. On the other hand, somewhat untypical are exothermic peaks in the curves of systems obtained from 0.05 mole of thiosulfate and the least quantity of sulfuric acid added (Fig. 4).

Conclusions

It has been demonstrated that appropriate concerting of the gelation of orthosilicic acid with gradual decomposition of sodium thiosulfate gives preparations of highly dispersed (5–15 μm) elemental sulfur.

The contents of elemental sulfur in the preparation can be controlled by acidification of the orthosilicic acid–sodium thiosulfate system with sulfuric acid.

Thermal analysis of the preparations enabled to identify processes of evaporation of physically adsorbed water and condensation of silanol groups occurring on the surface of silica gel as highlighted by strong exothermic effects in the DTA curve. Successive strong exothermic effects can be assigned to the combustion of elemental sulfur released by degradation of the thiosulfate. A characteristic feature of the curves of all sulfur-bearing preparations is a large displacement (by ca 470 K) of the exothermic peak due to combustion of sulfur towards lower temperatures as compared with analogous peak of neat thiosulfate. This can be explained in terms of either high degree of dispersion of elemental sulfur or to catalytic effect of SiO_2 on its combustion.

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