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Mechanochemical Synthesis of Sodium Thiosulphate Pentahydrate

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Abstract

Mechanochemical synthesis of sodium thiosulphate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) was carried out for the first time in a planetary ball mill by mechanical activation of a suspension of sodium sulphate (Na_2SO_3) and sulphur (S). The degree of $Na_2SO_3 + S = Na_2S_2O_3$ reaction in suspension solution at soft and short mechanical activation conditions is almost 95 %, as established by methods of iodometric titration, X-ray phase and thermal analysis.

Key words: sulphur, sodium sulphite, solution, suspension, mechanical activation, synthesis, sodium thiosulphate pentahydrate

INTRODUCTION

Monodisperse spherical sulphur nanoparticles (nano-sulphur [1]) were synthesized for the first time from acidified solutions of $Na_2S_2O_3$ [2–4]. The range of the resulting sizes, phases and application areas of nano-sulphur [4–10] is wide. The latter are based on a number of sulphur's unique properties [11], such as antibacterial, antiviral, and antineoplastic in medicine and biotechnology; pesticide and fungicide in agriculture; hydrophobic in construction; catalytic and analytical in physical chemistry; electrochemical in energetics.

The relevance of obtaining nano-sulphur from thiosulphates increases in the light of the need for solving environmental problems [12–15] and the issues of technogenic sulphur disposal [15–18] in the areas of oil and gas fields and their processing. These problems are also inherent to oil and gas complex of the Republic of Kazakhstan [19, 20].

Numerous patents on preparation of ammonium and alkaline metal thiosulphates, also including sodium thiosulphate pentahydrate, by the reaction of elemental sulphur and solutions of appropriate sulphites using various additives and process temperature variations are known [21–27].

However, mechanochemistry methods that assume the use of various mechanochemical reactors (MR) for mechanoactivation (MA) of various solid-phase chemical processes, including the use of gases and liquids are attracted in none of the known techniques. As a rule, various grinding devices are considered as MR; particularly, planetary mills find broad applications [4, 28, 29].

The present paper suggests for the first time a new mechanochemical method for preparation of sodium thiosulphate pentahydrate.

EXPERIMENTAL

Activator-2SL double-drum planetary mill (Machine-building plant Activator LTD, Novosibirsk) was used to carry out MA. The main characteristics of the mill are adjustable rotation frequencies of the spider within the interval ω = 100–1500 min^{-1} corresponding to the opposite rotation of the reels is 1.5ω = 150–1500 min^{-1}; engine power is 2.2 kW.

The following fittings were selected as MR for mechanosynthesis of $Na_2S_2O_3 \cdot 5H_2O$ (balancing drums was carried out by the corresponding ball load; ball diameter in all cases was 1 cm):

(*1*) A steel drum with a capacity of 250 mL and a combined ball load of silicon nitride (30 pcs) and tungsten carbide (20 pcs);

(*2*) A drum of silicon nitride with a capacity of 80 ml and a ball load of tungsten carbide in a quantity of 30 pcs (the Mohs hardness of fittings is 9).

This selection minimised fitting corrosion in a solution.

An aqueous solution of chemically pure ("ch. ch.") sodium sulphite (GOST 195–77) with a concentration of 16.8 g per 100 mL of solution (the solubility of Na_2SO_3 at 20 °C is 20.8 g/100 mL) was prepared in a suspension of sulphur for $S(s) + Na_2SO_3(sol) \rightarrow Na_2S_3O_3(sol)$ reaction. The solution (150 mL) was introduced into reactor (*1*) with equimolar amounts of S: 6.41 g into drum (*1*) and 1.28 g – into (*2*), $Na_2S_2O_3$ is stable only in alkaline solutions, therefore 25 % ammonia solution was additionally introduced into the reactors: 15 mL into drum (*1*) and 5 mL into (*2*).

Mechanical activation of suspensions was carried out for 35 min at $\omega = 350$ min^{-1}. The resulting suspensions were filtered off and the filtrates were subjected to a standard crystallization procedure. The dried out solid phases were placed into hermetic vials.

The resulting samples were studied by XPA and thermal analysis (thermogravimetry, TG and differential scanning calorimetry, DSC), and also by iodometric titration (a commonly used method for quantitative determination of the thiosulfate ion in solutions [30]).

The XPA data were obtained using Bruker AXS D8 Advance diffractometer using copper irradiation with a monochromator. Sample shooting mode: voltage is 40 kV with power current of 40 mA, scanning step is $2\theta = 0.02°$; information time at the point with this step is 1 s. The processing of the XPA data was carried out using EVA.exe and PCPDFWIN programs with PDF-2 database.

Thermal analysis (TG and DSC) of samples was carried out in the nitrogen atmosphere using Netzsch 449F3A-0372M instrument to 1000 °C at 10 °C/min heating rate.

RESULTS AND DISCUSSION

Figures 1 and 2 demonstrate the XPA data of solid phases obtained from filtrates. The data are correlated with the reference sample, *i.e.* sodium thiosulphate pentahydrate [31]. As one can see, almost the sole phase of samples is a compound corresponding to $Na_2S_2O_3 \cdot 5H_2O$. Product line broadening (see Fig. 2, *a*) is driven by the formation of nanocrystals during sample preparation for XPA by grinding in a pre-heated agate mortar (crystallization from thinnest layers of a saturated solution of $Na_2S_2O_3 \cdot 5H_2O$ [32] and the loss of crystallization water (Fig. 3, *b*). This is to a much lesser degree typical for sample lines in Fig. 1, *a*, since the probe was prepared from predried crystals obtained from reactor (*1*) filtrate.

Thermal analysis findings prove these data (Fig. 3): curves (*1*, *2*) in Fig. 3, a belong to sodium

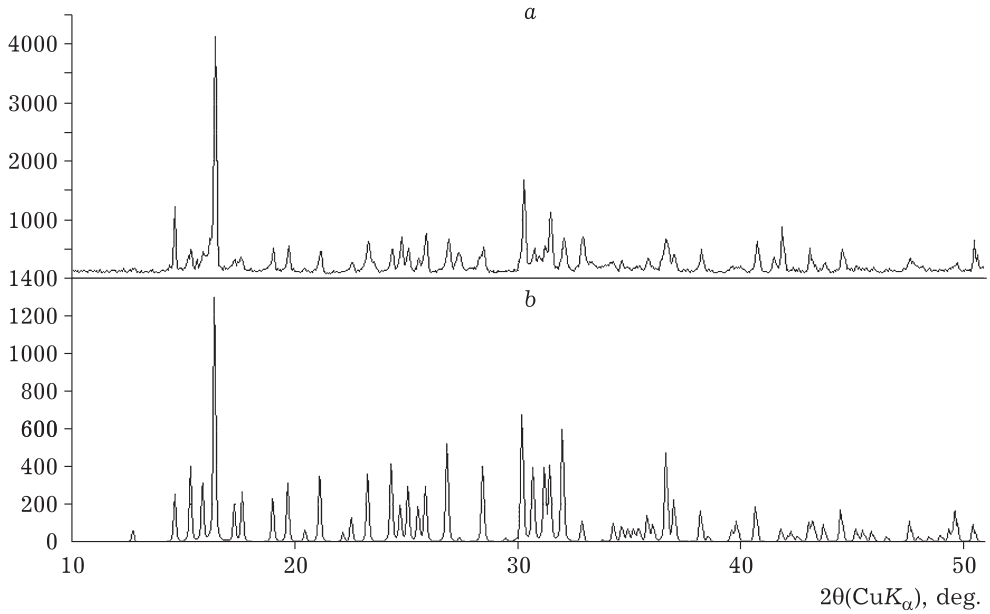

Fig. 1. XPA results of the crystallization product of the filtrate from drum 1 (*a*) in correlation with the standard $Na_2S_2O_3 \cdot 5H_2O$ (PDF 31-1325) (*b*).

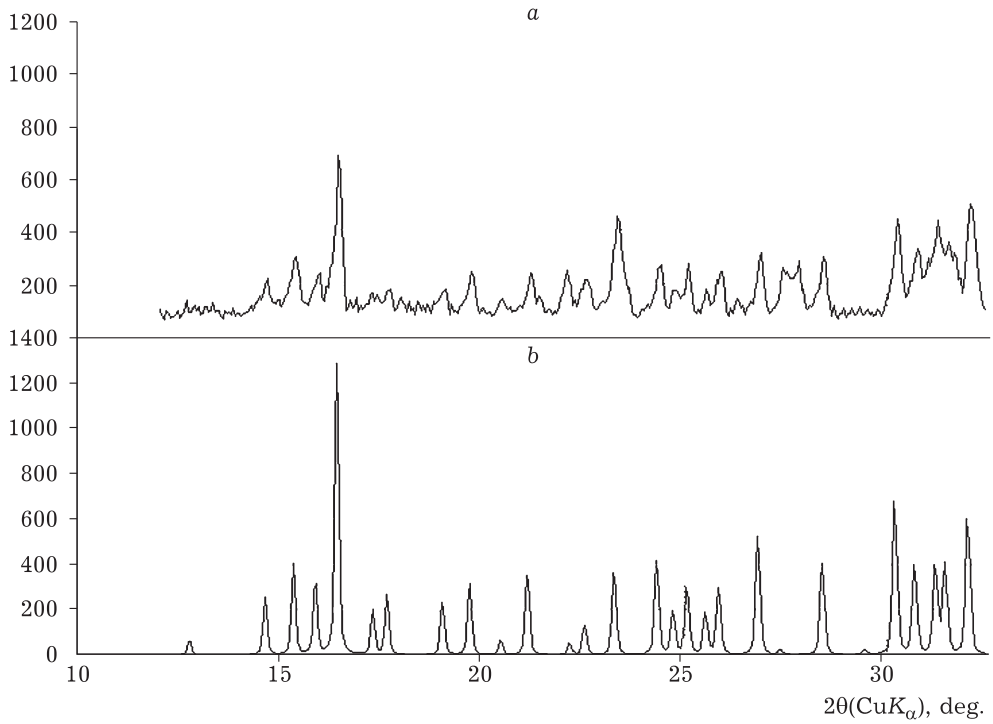

Fig. 2. XPA result of the crystallization product of the filtrate from drum 2 (*a*) in correlation with the the standard $Na_2S_2O_3 \cdot 5H_2O$ (PDF 31-1325) (*b*).

thiosulfate pentahydrate from a standard titrimetric substance and the resulting sample from reactor (*1*); the curves in Fig. 3, *b* – a sample of sodium thiosulfate from reactor (*2*). Judging by TG/DSC curves, it is the matter of one compound sodium thiosulphate ($Na_2S_2O_3$) with a different degree of the loss of crystallization water relative to the reference sample $Na_2S_2O_3 \cdot 5H_2O$ [33, 34] during their preparation to carry out measurements. For a sample from reactor (*1*), this value is (34.11–29.43) / 34.11 = 13.72 %, which corresponds to a sample of $Na_2S_2O \cdot 4.314H_2O$, and for a sample from reactor (*2*) – (34.11–8.56)/34.11 = 74.90 % or the composition of $Na_2S_2O_3 \cdot 1.255H_2O$.

One can also see, that at a temperature above 450 °C, the second stage of the mass loss related to decomposition of $Na_2S_2O_3$ also takes place.

According to gravimetric data, the yield of $Na_2S_2O_3 \cdot 5H_2O$ from the reactors exceeds 90 %: for the reactor (*1*), it is 96.6 %, and for the reactor (*2*) – 93.8 %.

The content of $Na_2S_2O_3$ in solutions of the resulting samples of crystalline phases determined by iodometric titration was no less than 98 %.

Note that the presented method of synthesis of sodium thiosulphate pentahydrate is close to that for anhydrous sodium thiosulphate [35] but more implementable in practice in the technological aspect.

CONCLUSION

A method for preparation of sodium thiosulphate pentahydrate including the interaction of elemental sulphur with a solution of sodium sulphite in the presence of ammonia, suspension generation, and crystallization of the target product is presented. The process is carried out by mechanical activation of sulphur in a planetary ball mill "Activator -2SL" at rotation frequencies of the spider of no less than 350 min^{-1} and duration of no less than 35 min.

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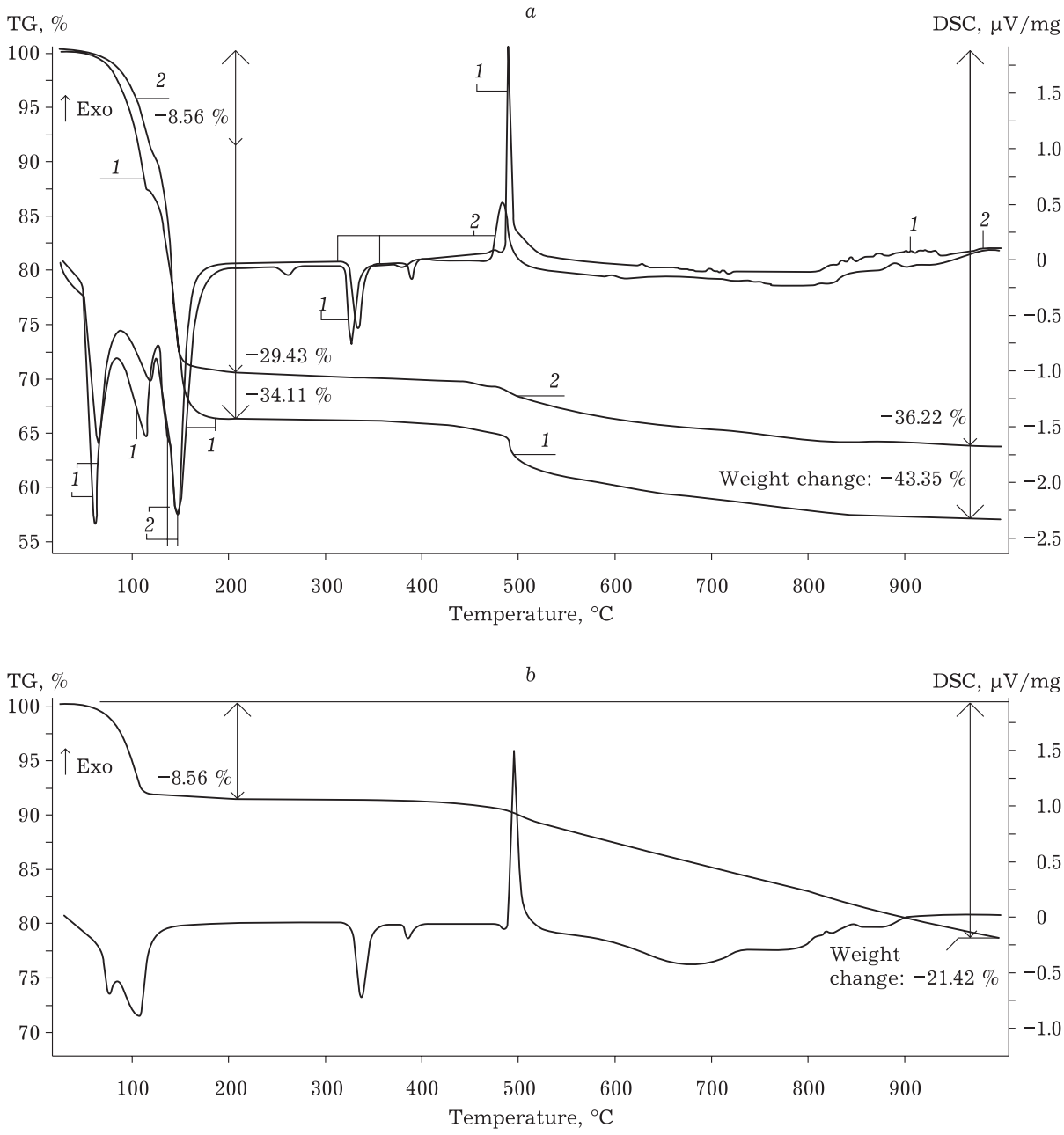

Fig. 3. TG/DSC curves of the samples of the solid phases: *a* – for reference pentahydrate $Na_2S_2O_3 \cdot 5H_2O$ (*1*) and a sample from the filtrate of drum (*1*) corresponding to the composition of $Na_2S_2O_3 \cdot 4.3H_2O$ (*2*); *b* – a sample from the filtrate of drum (*2*) (corresponding to the composition of $Na_2S_2O_3 \cdot 1.3H_2O$).

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