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Preparation of various color ultramarine from zeolite A under environment-friendly conditions

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Abstract

The ultramarine analogs of various colors have been prepared by calcination (mostly at 800 °C) of the mixtures of zeolite A and sodium polysulfides or elemental sulfur and sodium carbonate. The color and structure of the products depend very much on alkalinity of the mixture. Low alkalinity leads to green products with retained LTA structure. Blue products with SOD structure are attained at high alkalinity. Alkalinity affects also the weight loss on heating (i.e. emission of volatile compounds) as well as the amount of salts removed on washing.

Keywords: Ultramarine; Zeolite A; Various colors; Pollution control; Influence of alkalinity

1. Introduction

The natural ultramarine (lazurite, lapis lazuli) has been known since the ancient times. It was valued as semiprecious gem applied for jewelry and decoration [1]. In the middle ages the natural ultramarine was applied for manufacturing of the luxury and very expensive pigment used only for artistic painting. The ultramarine blue was prized for its intense deep color and for the great stability and resistance to fading. The synthesis of artificial ultramarine has been invented in the 1820s by J.B. Guimet in France and independently by C.G. Gmelin in Germany. The synthesis consisted in calcination of the mixture of kaolin, sulfur, sodium carbonate and reductive agents (charcoal, tar, etc.) at high temperature (800–900 °C) for a long time. The first industrial production of ultramarine has commenced in 1834 in Germany. As many as almost a 100 factories were in operation in Europe by the end of 19th century. Although the ultramarine blue is still used as valuable inorganic pigment, most of old factories have been closed now because of air pollution resulting from the emission of a large amount of volatile sulfur compounds (mostly SO_2) in waste gases. The existing factories have to neutralize the polluting gases to fulfil the requirements of environment protection law regulation.

Both natural and synthetic ultramarine exhibit the SOD structure and the sulfides (mostly NaS_3 and NaS_2) encapsulated in the β-cages play a role of chromophores. The ultramarine analogs can be obtained from zeolites by encapsulation of sulfur radicals inside the cages [2,3]. The use of zeolites is promising, particularly now, when their price has become relatively low because of a large scale of their production (mainly zeolite A). The important advantage of zeolites is a much lower emission of SO_2 compared to conventional synthesis with kaolin. They also allow to modify the synthesis in order to obtain various coloration, various properties and the structure of the products [3]. Usually the sulfur radical precursors, such as sodium polysulfides or elemental sulfur, are mixed with zeolite and calcined at high temperature (500–800 °C). It is very likely that the reactions of the sulfur compounds inside cavities are affected by zeolite catalytic sites. The catalytic activity of zeolites for reactions of sulfur compounds (e.g. the Claus reaction) is very well known [4]. The original zeolite structure (LTA) is usually transformed to SOD, but colored products with unchanged structure can be obtained too [5]. The ultramarine analogs with various colors can attain a commercial meaning as a possible substitute to the inorganic pigments based on heavy metal compounds which are, in contrast to ultramarine, toxic, and consequently are going to be withdrawn from the market.

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The aim of the present study is to prepare ultramarine analogs with various colors from zeolite A and sulfur sources, such as elemental sulfur and alkalis as well as sodium polysulfides. A special attention will be paid to the transformation of sulfur compounds during heating and subsequent weight changes of the mixtures.

2. Experimental

Zeolite A (from Atofina, Poland) was employed as the main substrate. Zeolite contained 11 wt.% of adsorbed water. Powder samples of 2.5 g were mixed with either elemental sulfur and sodium carbonate or with sodium polysulfides. The total sulfur content was always 40% of zeolite weight. The Na_2/S ratios in sulfur precursors varied in the range 0–1. The respective sodium polysulfides were obtained by merging of sodium sulfide ($Na_2S{\cdot}9H_2O$, P.O.Ch.) with adequate amount of sulfur. The mixtures were maintained in ceramic crucibles, covered with lids and then inserted into a hot furnace (500–800 °C). The thermal treatment took 2 h. Then the samples were cooled down, washed with distilled water and dried at 100 °C. A similar procedure was applied to the mixture with kaolin, sulfur and sodium carbonate. In one experiment the reducing agent (tar pitch) was added to the mixture to mimic the conventional industrial procedure.

The products were characterized by means of XRD (Tur M-62), UV-Vis spectroscopy (Cary 100, Varian, diffuse reflectance), IR spectroscopy (Bruker, Vector 22), thermal analyses such as TG, DTG, DTA (Setaram, type Sentys 12) conducted either in air or helium with 10 °C/min temperature rate and ESR (Radiopan, Poland), measured in liquid nitrogen.

3. Results and discussion

The synthesis experiments were conducted without any reductive agent and the crucible containing the initial mixtures were covered with lids. The lids restricted a circulation of the gases to some extent, but they could not completely prevent the contact of some oxygen with the other reagents. Thus, we shall have to consider some contribution of sulfur or sulfide oxidation as reaction affecting the course of the synthesis. Nevertheless, we believe that the disproportionation of sulfur with the aid of alkalis, as well as the scission of polysulfide chain, play an important role in the generation of sulfur radicals responsible for the color of the resulting products:

$$3S^0 \rightarrow S^{4+} + 2S^{2-}$$

In the case of disproportionation, the resulting sulfide react with the remaining sulfur to form a polysulfide. SO_2, and subsequently the sodium sulfite, reacts with elemental sulfur too and forms thiosulfate [6]. The polysulfides can produce the radicals by a cleavage of the S–S bonds:

$$S_n{}^{2-} \rightarrow {}^{\bullet}S_a{}^{-} + {}^{\bullet}S_b{}^{-}, \quad a + b = n$$

Radicals can be also formed by mild oxidation of polysulfides:

$$3S_2{}^{2-} + O_2 \rightarrow 2{}^{\bullet}S_3{}^{-} + {}^{\bullet}2O^{2-}$$

Table 1
The weight changes on calcination of the mixtures at 800 °C

(A) Mixtures of zeolite NaA, elemental sulfur and sodium carbonate						
Na_2/S	0	0.2	0.4	0.6	0.8	1
Structure, color	LTA, green	LTA, green	NEP[a], turquoise	SOD, turquoise	SOD, dark blue	SOD, blue
Weight loss on calcination (%)	30.3	20.5	17.7	14.3	12.9	18.2
Weight loss on washing (%)	4.4	6.8	36.2	46.1	54.8	60.2
Total weight loss (%)	33.4	25.9	47.5	53.8	60.6	67.4
(B) Mixtures of zeolite NaA and polysulfides						
Na_2S_n	Na_2S_8	Na_2S_6	Na_2S_4	Na_2S_3	Na_2S_2	Na_2S
(Na_2/S)	0.12	0.17	0.25	0.33	0.5	1
Structure, color	LTA, green	LTA, green	NEP[a], green	NEP[a], green	SOD, dark blue	SOD, blue
Weight loss on calcination (%)	33.5	34.7	35.1	35.3	36.8	46.7
Weight loss on washing (%)	10.4		26.0		35.0	59.8
Total weight loss (%)	40.4		58.5		58.9	78.6
(C) Mixtures of kaolin, sulfur and sodium carbonate						
Na_2/S	1	1.35[b]				
Structure, color	SOD, blue	SOD, blue				
Weight loss on calcination (%)	54.5	29				

[a] Pseudonepheline.
[b] Usage of tar pitch as a reducer (10 wt.%).

The radicals $^{\bullet}S_3^-$ and $^{\bullet}S_2^-$ are the most stable and their mutual proportions in the product are decisive for the resulting coloration. We have found that the alkalinity of the initial mixture of zeolite A with the sulfur sources affects very much the coloration of the products [5].

All mixtures used for syntheses contained the same zeolite content (2.5 g) and the same total sulfur content (1.0 g). The growing alkalinity in the series, with elemental sulfur, was attained by adding an increasing amount of Na_2CO_3. It was expected that the carbonate decomposition would substantially contribute to the weight loss due to the emission of CO_2. Another series was synthesized with polysulfides presenting various sulfur chain lengths. They were prepared by merging $Na_2S \cdot 9H_2O$ with different amounts of sulfur. The removal of the crystallization water during mixture heating contributes markedly in the total weight loss.

As indicated in Table 1A, heating of the mixture of zeolite A with sulfur (without any alkalis) at 800 °C results in a green product with unchanged LTA structure. The small amount of alkalis admitted ($Na_2/S = 0.2$) leads to the similar product. The further increase in alkalinity ($Na_2/S > 0.4$) brings about the structure transformation towards sodalite and pseudonepheline [7]. The color of the samples changes into blue at high sodium content. The UV-Vis spectra of the samples [5] always indicate two absorption peaks in the visible range. One at ~600 nm reflects the blue color and results from $^{\bullet}S_3^-$ radicals, whereas another one at ~400 nm corresponds to yellow coloration and is due to radicals $^{\bullet}S_2^-$. The contribution of each component plays a decisive role in the observed coloration of the samples. The presence of the mentioned radicals was confirmed by the ESR spectra [5].

The weight loss on calcination depends very much on the mixture alkalinity (Fig. 1A). The sample without any sodium carbonate loses as much as 30% of the initial weight. Since no CO_2 was released from the mixture on calcination, the main reason of the weight loss is the oxidation of sulfur. The resulting SO_2 cannot be retained in the zeolite phase, because of a lack of additional sodium cations. The sodium

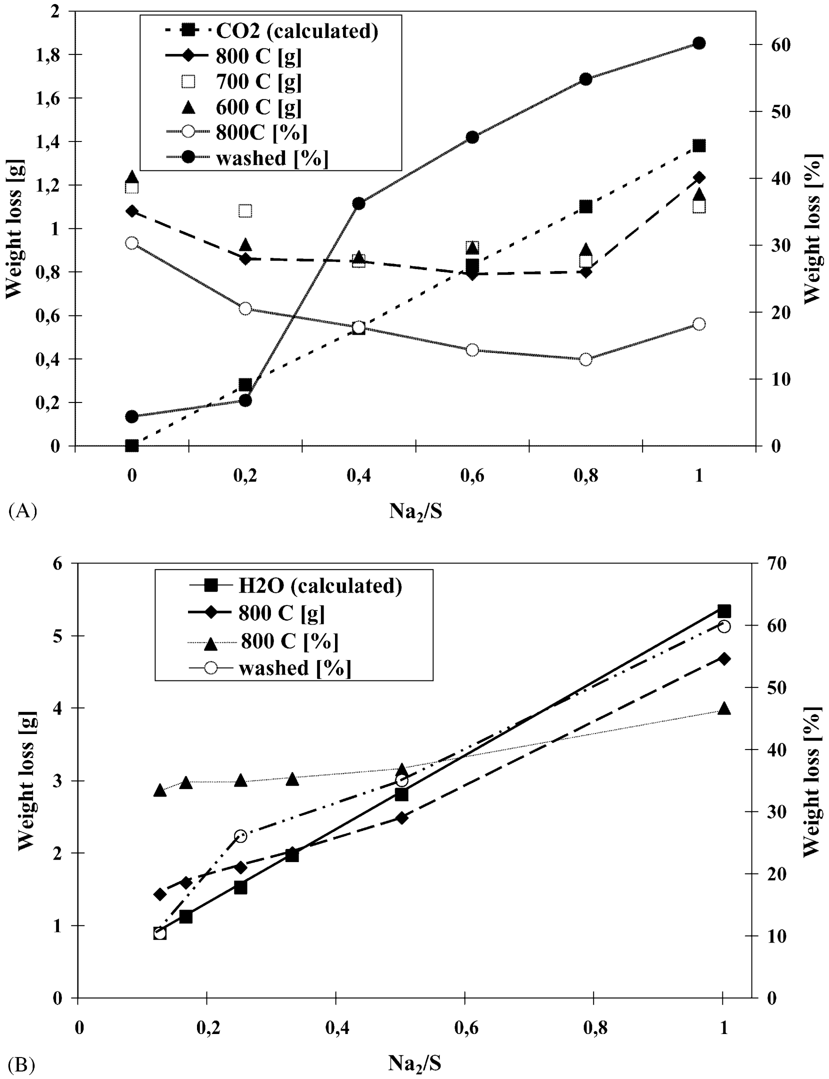

Fig. 1. Correlations between the sample alkalinity and weight loss. Samples obtained from zeolites A mixed with (A) S and Na_2CO_3; (B) Na_2S_n.

carbonate introduced causes a considerable lowering of the weight loss on heating (20.5% for mixture with $Na_2S = 0.2$ and 12.9% for $Na_2S = 0.8$). The amounts of the gases released from the samples with Na_2/S in the range 0.2–0.8 are almost the same (0.8–0.85 g). The presence of alkalis (i.e. Na_2CO_3 and subsequently Na_2O after its decarboxylation), evokes the sulfur disproportionation and the resulting SO_2 and S^{2-} are combined with sodium cations to form sodium sulfite and sulfide, respectively. Both products react with the remaining sulfur to form polysulfides and thiosulfate. The latter compounds are not volatile and can undergo further transformations within the zeolite phase. Some increase in weight loss is seen for the sample with the highest alkalinity ($Na_2S = 1.0$). It is interesting to notice, that the weight losses on heating do not depend much on temperature. The values recorded at various calcination temperatures do not differ markedly from each other, despite the differences in the product colors and structures [5]. The calculated correlation between the Na_2/S ratio (which corresponds to the amount of Na_2CO_3 added to the constant amount of sulfur) and the content of CO_2 released from mixtures differs considerably from the weight changes recorded during syntheses. Only the values for mixtures with $Na_2/S = 0.6$ are consistent with the calculated value of CO_2 removal. The mixtures with Na_2/S ratios below 0.6 result in much larger weight lost, and above 0.6, in slightly lower values of weight losses, than the values calculated for released CO_2. The values lower than calculated for CO_2 result probably from more pronounced contribution of oxidation towards SO_3 at high alkalinity. It means the products gain some weight due to a capture of oxygen from air.

The correlation between the alkalinity and the coloration of the products, for the series prepared with various polysulfides, is similar to that for the series with elemental sulfur. The weight loss increases with growing alkalinity (Table 1B). The correlation is almost linear (Fig. 1B) and it is very alike the calculated content of crystallization water in the added $Na_2S{\cdot}9H_2O$. A good agreement of both correlations suggests that a *cracking* of polysulfide chain is an important reaction upon heating and it prevails over the oxidation. Some discrepancies between values of calculated water loss, and the measured weight loss (the measured values of weight are slightly higher for mixtures with low alkalinity and somewhat lower for the alkalinity above $Na_2/S = 0.4$) result from partial oxidation of polysulfides. The resulting SO_2 cannot be bound completely to the mixtures with deficit of sodium, whereas the mixtures with high sodium loading adsorb most of sulfur oxides. They gain some weight by the reaction with the oxygen of air.

The sulfur analysis of the washed samples shows some decrease in sulfur content when the alkalinity is rising. For instance, it is 10.7% for the sodium carbonate-free mixture, 9.3% for mixture with $Na_2/S^{\bullet} = 0.2$, and 4.9 for $Na_2/S^{\bullet} = 1.0$. In the series prepared with polysulfides, the sulfur content is slightly lower: 6.5% for the mixture with Na_2S_8, 6.8% for Na_2S_6 and 5.4% for Na_2S.

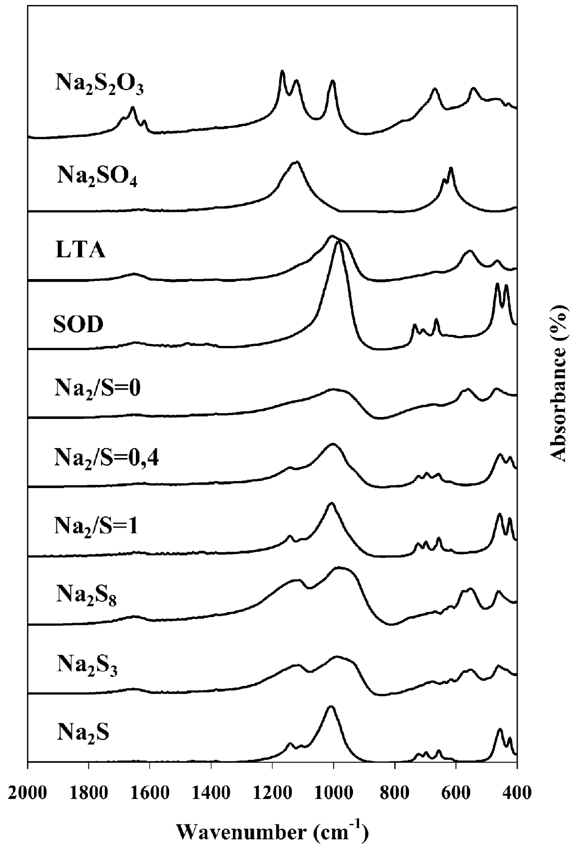

Fig. 2. IR spectra (KBr) of the indicated samples after calcination.

The series of syntheses with kaolin did not lead to products with such a variety of colors, as observed for zeolites. Most of samples were gray or beige. Only the samples prepared from mixtures with the highest alkalinity showed a blue coloration. The weight loss was considerably higher than that for analogous mixture with zeolites (Table 1C).

The IR spectra (Fig. 2) of the products show the presence of thiosulfate and sulfate in the products after calcination. The detailed interpretation of the spectra is not easy because the bands of aluminosilicate (mostly the asymmetric stretch at ~1000 cm^{-1}) overlaps with the bands of sulfate compounds. The bands of sulfate salts disappear after washing the samples. The presence of both salts is quite more distinct in spectra of the salts recovered from the filtrates after washing. The spectra illustrate the structural changes of the zeolite and the structure sensitive bands in the range 800–400 cm^{-1} allow to distinguish between LTA and SOD structures.

The washing of the products removes the sodium salts. The weight loss on washing is quite remarkable and depends almost linearly on alkalinity of the initial mixtures (Fig. 1, Table 1). In the case of the products with the highest sodium loading, the weight of the samples remaining after washing is even lower than the weight of the parent zeolite A. It indicates that the re-crystallization of LTA towards SOD involves

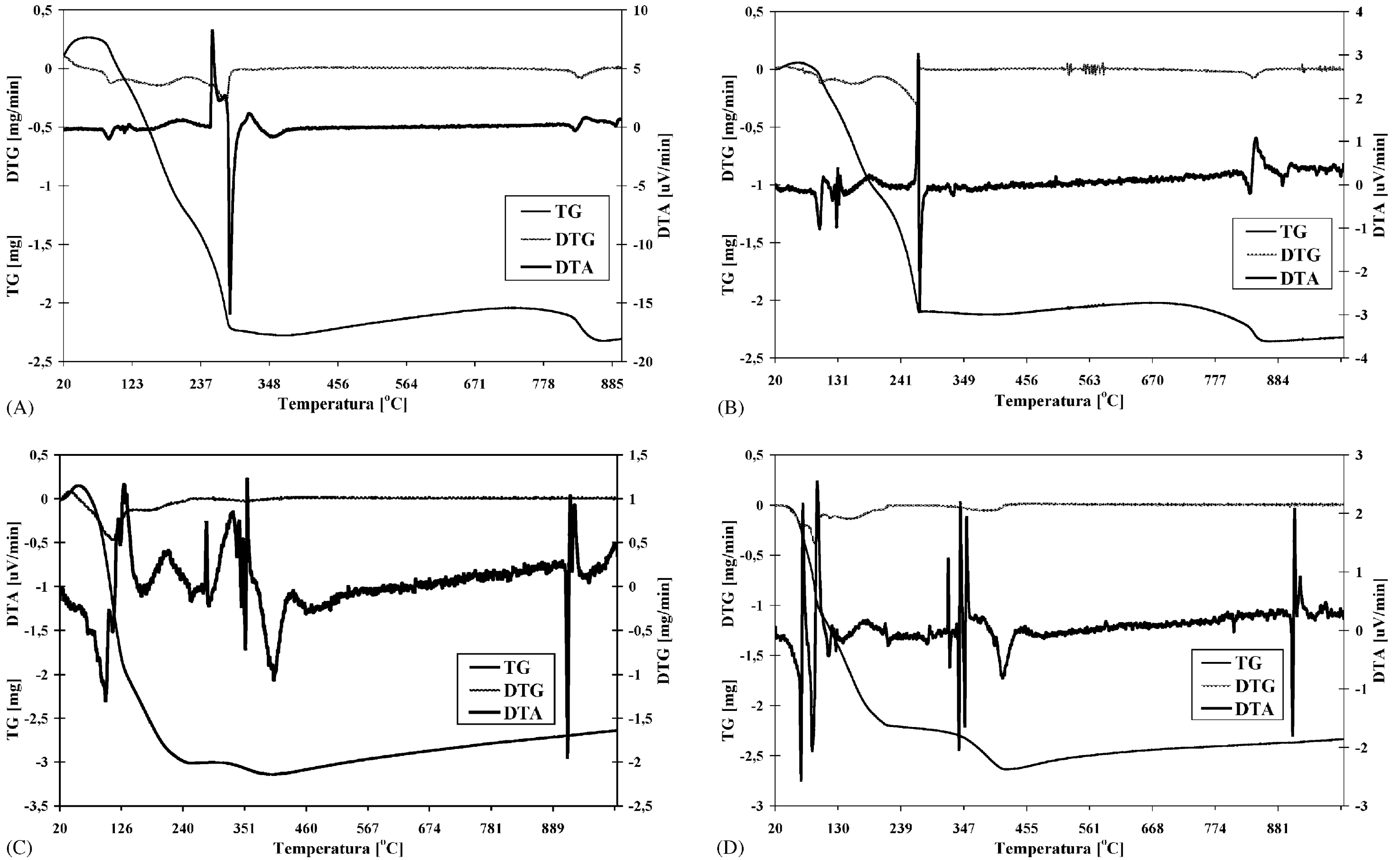

Fig. 3. TG, DTG, DTA curves for the mixtures of zeolite with sulfur and Na_2CO_3 ($Na_2/S = 0.2$) in air (A) and helium (B). The mixture with Na_2S_2 heated in air (C) and in helium (D).

a removal of some silicate and aluminate from the original aluminosilicate phase and this fraction can be washed out.

The thermal and thermogravimetric analyses (TG, DTG, DTA) have been conducted (Fig. 3) either in air (A, C) or in helium (B, D). The mixture with sulfur and sodium carbonate ($Na_2/S = 0.2$) shows the main weight loss at temperatures below 300 °C (∼20%), regardless of the heating atmosphere. It comprises the release of the zeolite water (∼10%) with maximum at temperatures ∼100 and 160 °C (zeolitic water). A further decrease in the sample weight at ∼250 °C can result from the development of volatile sulfur compounds such as (mostly) SO_2 and H_2S. They can result from disproportionation of sulfur. The contribution of oxidation is probably not very significant, because the exothermic effects noticed at ∼250 °C both in air, and in helium are similar and they are not accompanied by very remarkable increase in weight loss (Fig. 3A and B). As it was discussed before, the content of alkalis was not sufficient to bound all the acidic volatile products in this range of temperature. Some weight loss is also seen above 800 °C and it reflects the decomposition of remnant of sodium carbonate.

The samples with polysulfide Na_2S_2 (Fig. 3C and D) show also similar course of the weight loss regardless of the atmosphere. About 25% of the initial weight is lost below 300 °C and it reflects the release of water. Some exothermic effects are seen on heating in air, but these effects, most likely due to oxidation, do not affect the weight changes. Some thermal effects are noticeable at ∼870 °C, they can reflect some structure transformations, since they do contribute in weight changes.

4. Conclusions

The presented results indicate a possibility to prepare the ultramarine analogs of various colors by means of calcination of zeolites A with sodium polysulfides or elemental sulfur and alkalis (Na_2CO_3). The alkalinity of the initial mixtures is a decisive factor that affects the color and structure of the products. Low alkalinity ($Na_2/S = 0$–0.2) leads to green products with unchanged LTA structure. The mixtures with medium sodium content ($Na_2/S = 0.2$–0.6) lead to green or turquoise samples with SOD or pseudonepheline structures. The high alkalinity always causes a structure transformation to SOD and blue coloration of the products. The analogous syntheses with kaolin do not result in various coloration of the products. Only at high alkalinity the blue color is attained.

The values of weight loss on calcination of the mixtures with polysulfides are commensurable with the amounts of water (from $Na_2S{\cdot}9H_2O$), which suggests that the *cracking* of the polysulfide chain plays an important role in generation of sulfur radicals, since it does not cause any weight changes. The weight changes on heating the samples prepared with elemental sulfur and sodium carbonate do not reflect the evolution of CO_2 resulted from decomposed carbonate. The lack, or low content of Na_2CO_3 brings about a very substantial weight loss on calcination. The oxidation of sulfur is a prevailing process and the resulting SO_2 cannot be bound because of sodium deficit. The increase in alkali content results in a lower evolution of gaseous products, because they form sodium sulfides and sulfites and subsequently thiosulfates and sulfates as well as polysulfides. The major process in this series is disproportionation of sulfur. The resulting polysulfides are crucial for a radical generation.

The sodium salts (mostly sulfates and thiosulfates), formed on calcination, can be removed on washing. Their content increases with growing alkalinity of the samples.

The presented results indicate, that using zeolites as starting material for the synthesis of ultramarine analogs, allows to modify the synthesis in a broad range and to obtain products of various properties. The process with kaolin was much less successful and resulted in markedly larger amount of waste gases. The green pigment of potential commercial interest can be obtained from a mixture of zeolite A and long polysulfides. Such a synthesis does not result in a considerable amount of undesired wastes. A great advantage of zeolites applied as substrates over conventional kaolin results from well ordered intracrystalline porous structure of zeolites that provides a room for the sulfur compound transformations. The catalytic action of zeolites (mostly the basic active sites) must be also taken into an account.

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