Influence of the Oxalic Acid Addition Upon Properties of Desulfurization Sorbents Based on Zinc Oxide

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The paper aims morphological, structural and textural changes induced to zinc titanate sorbents by introducing oxalic acid during the preparation process. The $ZnO–TiO_2–Al_2O_3$ sorbents were obtained through semi wet mixing of oxides; then oxalic acid was added, followed by drying, precalcination and calcination steps. The presence of oxalic acid into sorbent composition favors the formation by calcinations at 700°C of zinc titanate stable forms, type Zn_2TiO_4, $ZnTiO_3$ and $Zn_6Al_2O_9$. This sorbents could be used in high temperatures gas desulfurization processes due to their higher specific surface

Keywords: zinc titanate, desulfurization, HTGD process, oxalic acid

In literature were studied a number of metal oxides in order to retain H_2S from hot gases through the HTGD process (high temperature gas desulfurization)[1,2].The choice of metal oxides (Zn, Fe, Cu, Co, Ce, etc) [3,4] was made based on H_2S retention capacity and cost price.

ZnO has a high retention capacity of H_2S, but it is slightly reduced to Zn metal. For this reason we tried to obtain some mixed oxides able to keep their H_2S retention properties. So it have been proposed TiO_2, Al_2O_3, Cr_2O_3, La_2O_4, SiO_2; the active charcoal added, improves the morphological properties stopping also the $ZnSO_4$ formation[5-15]

Experimental part

The sorbents type $ZnO-TiO_2-Al_2O_3$ sintezis has been done using zinc oxide (würtzit crystallisation form), titane dioxide (anatase crystallisation form) and alumine hidrate (obtained through precipitation and drying) and oxalic acid. The raw materials (zinc oxide, titan oxide and aluminate, in molar rapport 2:1:0.5) have been grounding and mixing in semi-wet condition mixing obtaining a consistent paste with aqueous solution of 12% $(NH_4)_2CO_3$ [16, 17].

After mixing the three oxides, oxalic acid has been added, mixing being continued for another 30 min. The intermediate product (a complex mixture of hydrated oxides, hydroxides and basic carbonates) was dryed for 4 h at 110°C, precalcinated at 380°C and finally calcinated at 700°C. The final product has been grounded and sifted in order to obtain sorbent samples with 0.5-0.63 mm granulation.

The desulfurization sorbents type $ZnO-TiO_2-Al_2O_3$ are presented in table 1.

The coding of sorbents samples was done as follows: Z – Zinc Oxide, T – Titanium Oxide de, A - Alumina, Ox – oxalic acid.

The compositional-structural, morphological and textural changes of the sorbents induced by oxalic acid addition (samples ZTA-Ox1, ZTA-Ox 2 and ZTA-Ox 3) were highlighted through ray diffraction (XRD), electronic microscopy (SEM and EDAX) and textural analysis (BET).

Results and discussions

Structural and compositional characterization

XRD analysis of the sorbents type $ZnO-Al_2O_3-TiO_2$-containing oxalic acid in variable percentages are shown in figures 2, 3 and 4 and compared with the sorbent without oxalic acid (fig.1).Structural changes are assigned to interactions between metal oxides from sorbent under the influence of high temperatures, with formation of mixed oxides type zinc titanate, zinc aluminate; no presence of aluminum titanate. In all samples the major crystalline phase is Zn_2TiO_4, with a mass content about 60-80%, corresponding to a molar ratio $ZnO:TiO_2:Al_2O_3$ 2:1:0.5.

Analyzing the diffraction spectrums of the three samples with oxalic acid addition in comparison with the basic sorbent one observe that two types of zinc titanate Zn_2TiO_4 and $ZnTiO_3$ are formed, the majority being the Zn_2TiO_4 phase.

The increasing of the amount of oxalic acid in sorbent mass favors the formation of the $ZnTiO_3$, present in the spectrum in the range of 40-80 2q, together with Zn_2TiO_4 stable form. Also it is noted that in all three samples containing oxalic acid remains a low percentage of unconverted zinc oxide and titanium oxide; the zinc aluminate exists in a similar proportion with the basic ZTA sample. Presence of these two types of titanates could have implications on the sorbent reactivity

Table 1
THE DESULFURIZATION SORBENTS TYPE $ZnO-TiO_2-Al_2O_3$

No. Sample	Sample Code	Composition	Molar Ratio	Addition of oxalic acid % mass
1	ZTA	$ZnO:TiO_2:Al_2O_3$	2:1:0.5	0
2	ZTA-Ox1			1
3	ZTA -Ox2			5
4	ZTA -Ox3			10

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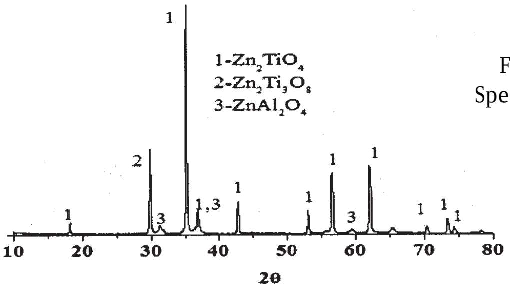

Fig.1. XRD Spectrum of ZTA sample

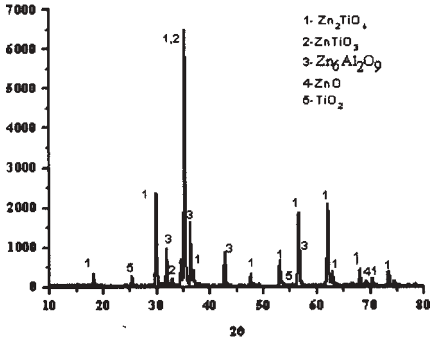

Fig.2. XRD Spectrum of ZTA-Ox 1 sample

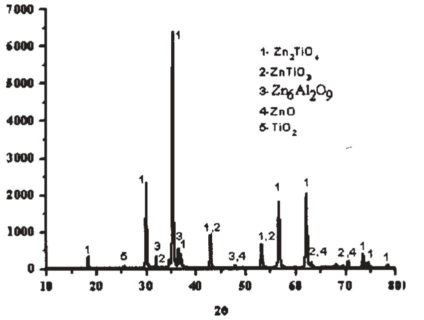

Fig. 3. XRD Spectrum of ZTA-Ox 2 sample

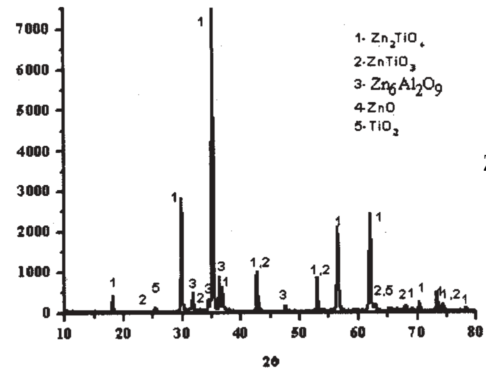

Fig. 4. XRD Spectrum of ZTA-Ox 3 sample

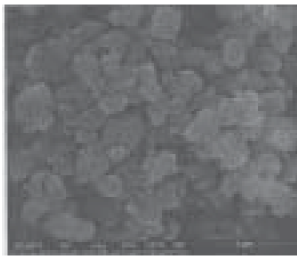
Fig. 5 The SEM analysis of the ZTA –Ox1 sample

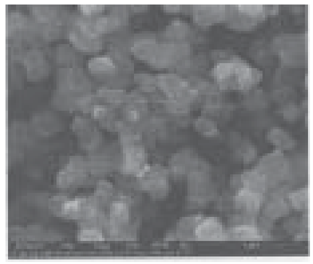
Fig 6 The SEM analysis of the ZTA –Ox2 sample

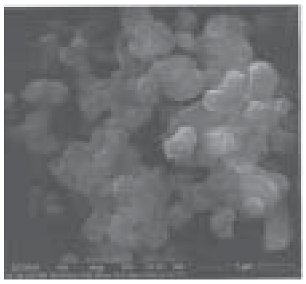
Fig. 7 The SEM analysis of the ZTA –Ox3 sample

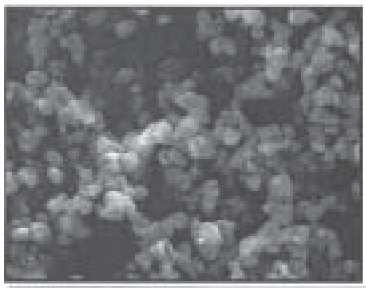
Fig 8a SEI image of ZTA –Ox 1sample

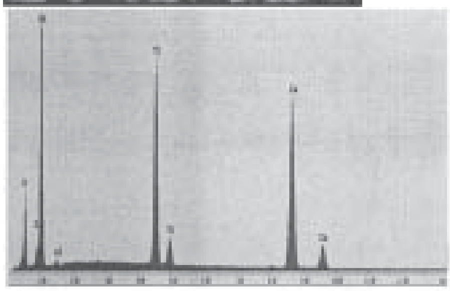
Fig 8b EDAX analysis of ZTA –Ox 1 sample

Morphological characterization

Morphological data obtained by SEM analysis (amplification of 100,000 times) of the sorbents based on ZnO-TiO_2-Al_2O_3 with variable content of oxalic acid are shown in figures 5-7. The presence of oxalic acid induces morphological changes of sorbent surfaces. In case of ZTA-Ox1 sample (fig..5.), with low oxalic acid content, the appearance of sorbent particle surface is uniform, the crystalline formations having quite clear contours (defined polyhedral edges).

The increase of oxalic acid content determines the crystallites reorganization by increasing the grouping tendency of them; the forms are no longer distinguish suggesting the crystallites agglomeration. Increasing the amount of oxalic acid in sorbent, crystallite sizes decrease, the values ranging from 275nm to 70-150 nm corresponding to samples ZTA-Ox 2 and ZTA-Ox 3.

The EDAX spectrums associated to SEI images, corresponding to the three sorbents (ZTA -Ox1, ZTA-Ox 2 ZTA-Ox 3) may provide some details regarding the distribution of the main elements (Zn, Ti and Al) into the sorbent mass figures (8b- 10b). As reflected by the three samples, the basic elements are evenly spread in the mass of sorbent, certifying that the semi-wet method of mixing ensures a good homogenization and interaction between metal oxides.

Textural characterization of the sorbents

The determination of specific surface and average size of the pores was performed using Micromeritics ASAP 2020 device with nitrogen. The changes induced by the presence of oxalic acid in the sorbent mass concerning the specific surface and the average pores size are shown in figures 11-12.

From the examination of the data presented in figures 11 and 12 it is noted that the introduction of oxalic acid in sorbent composition leads to an increase surface area as a result of the decrease the average pore diameter.

According to IUPAC nomenclature of pores classification, the pores in all samples are macro pore type. An amount of 2.5% of oxalic acid in the mass of sorbent, induces the increase of specific surface area and average pore size. Addition of 5% oxalic acid does not bring substantial improvements to sorbent texture compared with ZTA-Ox 2 sample, the specific surface area and average pore diameter recording a slight decrease compared to the sample

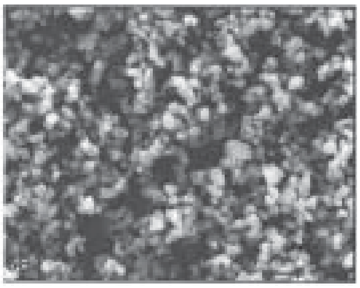

Fig 9a SEI image of ZTA –Ox 2sample

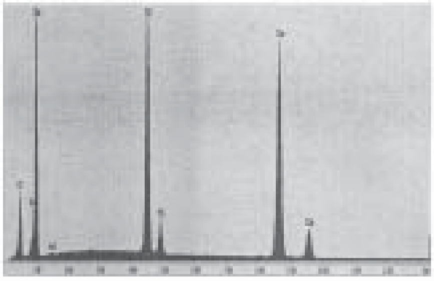

Fig 9b. EDAX analysis of ZTA –Ox 2 sample

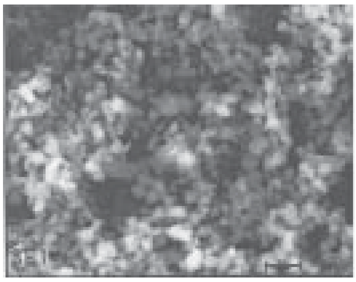

Fig 10a SEI image of ZTA –Ox 3sample

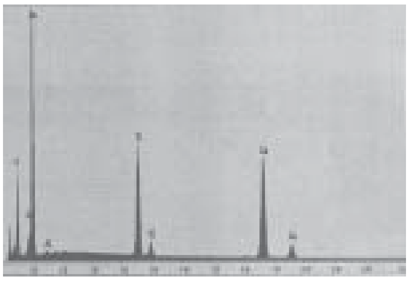

Fig 10b. EDAX analysis of ZTA –Ox 3 sample

ZTA-Ox 2. In comparison with the ZTA sample, the specific surface is much higher and the average pore diameter is smaller. The increase of the specific surface area brings the possibility to retain a larger amount of H_2S in the form of ZnS. So the addition of oxalic acid can improve the retention capacity of the sorbent based on zinc oxide, titanium and aluminum.

Conclusions

The introducing of oxalic acid in the composition of the desulfurization sorbents type $ZnO\text{-}TiO_2\text{-}Al_2O_3$, made in order to improve their performance, determines the compositional, structural, morphological and textural changes, ensuring better interaction between sorbent and hydrogen sulphide in the desulphurization process. XRD spectrums of sorbents type $ZnO\text{-}TiO_2\text{-}Al_2O_3$ with variable content of oxalic acid revealed that the major crystalline phase is Zn_2TiO_4, containing a mass of about 70-80%. In all samples were identified the zinc titanate type $ZnTiO_3$, whose mass content is about 20% by weight.

The type $Zn_2Ti_3O_8$ is less stable than the other ones. That's why it is very important to obtain Zn_2TiO_4.

In all three samples the presence of zinc titanate type $Zn_2Ti_3O_8$, has not been evidentiated because it is the most instable zinc titanate form. The explanation may consist in the relatively high initial molar ratio of ZnO and TiO_2 (2:1), which favors the formation of a higher proportion of zinc titanate type Zn_2TiO_4 (the molar ratio Zn: Ti is similar).The

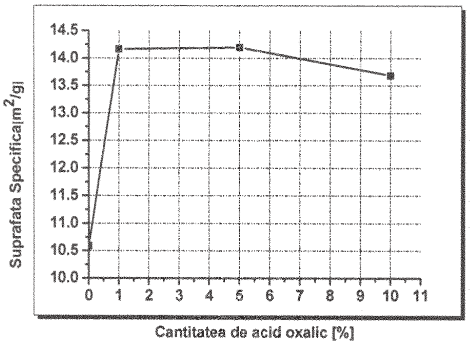

Fig.11. The influence of the oxalic acid addition on the sorbent specific surface

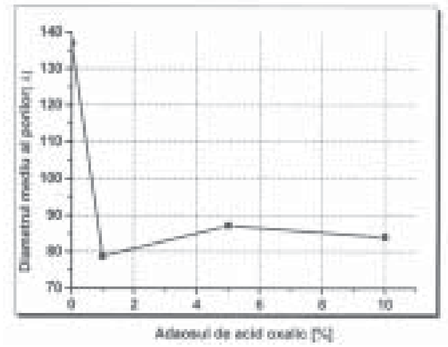

Fig 12. The influence of the oxalic acid addition on the average size of pores

adding of oxalic acid favors the formation of zinc titanate type $ZnTiO_3$, which is more thermodynamically stable than $Zn_2Ti_3O_8$. The presence of oxalic acid brings changes in the morphological structure of the sorbent grains, causing the reorganization of the crystallites, suggesting major textural changes in the sorbent granules, respectively a significant increase of the specific surface area.

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