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

ANNETTE MADELENE DANCILA1*, EUGENIU VASILE2
1 Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Ghe. Polizu Str., 011061, Bucharest, Romania
2 Institute of Research and Development "METAV" SA, 31 C.A.Rosetti Str., 020011, Bucharest, Romania

The paper aims morphological, structural and textural changes induced to zinc titanate sorbents by introducing oxalic acid during the preparation process. The ZnO–TiO2–Al2O3 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 Zn2TiO4, ZnTiO3 and ZnAl2O4. 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 H2S 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 H2S retention capacity and cost price.

ZnO has a high retention capacity of H2S, but it is slightly reduced to Zn metal. For this reason we tried to obtain some mixed oxides able to keep their H2S retention properties. So it have been proposed TiO2, Al2O3, Cr2O3, La2O4, SiO2; the active charcoal added, improves the morphological properties stopping also the ZnSO4 formation[5-15]

Experimental part

The sorbents type ZnO-TiO2-Al2O3 sintezis has been done using zinc oxide (wurtzit 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% (NH4)2CO3 [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 dryerd 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-TiO2-Al2O3 are presented in table 1.

The coding of sorbents samples was done as follows:

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Code</th>
<th>Composition</th>
<th>Molar Ratio</th>
<th>Addition of oxalic acid % mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZTA</td>
<td>ZnO:TiO2:Al2O3</td>
<td>2:1:0.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>ZTA-Ox1</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>ZTA-Ox2</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>ZTA-Ox3</td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

Results and discussions

Structural and compositional characterization

XRD analysis of the sorbents type ZnO-Al2O3-TiO2 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 Zn2TiO4, with a mass content about 60-80%, corresponding to a molar ratio Zn2TiO4:Al2O3:2:1:0.5.

Analyzing the diffraction spectrums of the three samples with oxalic acid addition in comparison with the basic sorbent one observe that two types of titanates ZnTiO3 and ZnTiO4 are formed, the majority being the Zn2TiO4 phase.

The increasing of the amount of oxalic acid in sorbent mass favors the formation of the ZnTiO4 present in the spectrum in the range of 40-80 2q, together with Zn2TiO4 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-TiO2-Al2O3

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* email: dancila.madelene@yahoo.com; Tel.: 0725922192

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Morphological characterization

Morphological data obtained by SEM analysis (amplification of 100,000 times) of the sorbents based on ZnO-TiO2-Al2O3 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.
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 H₂S 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-TiO₂-Al₂O₃, 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-TiO₂-Al₂O₃, with variable content of oxalic acid revealed that the major crystalline phase is Zn₂TiO₄, containing a mass of about 70-80%. In all samples were identified the zinc titanate type ZnTiO₃, whose mass content is about 20% by weight.

The type Zn₂TiO₄ is less stable than the other ones. That's why it is very important to obtain Zn₂TiO₄.

In all three samples the presence of zinc titanate type Zn₂TiO₄ has not been evidenced because it is the most instable zinc titanate form. The explanation may consist in the relatively high molar ratio of ZnO and TiO₂ (2:1), which favors the formation of a higher proportion of zinc titanate type Zn₂TiO₄ (the molar ratio Zn: Ti is similar).

adding of oxalic acid favors the formation of zinc titanate type Zn₂TiO₄, which is more thermodynamically stable than Zn₂₃Ti₃O₈. 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.

References
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