Influence of Added Graphite on ZnO Sorbents for Gas Desulfurization

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The sorbents based on ZnO have good retaining properties for H2S from residual gases. The aim of this article is the improvement of sorbent properties through the structural, morphological and textural changes produced on zinc titanate sorbents for desulfurisation at hot temperatures adding graphite. The sorbents containing ZnO-TiO2+graphite were obtained through mechanical half-wet mixing of zinc oxide, titane dioxide and graphite method, drying the intermediate product and finally calcination at 700°C. The samples were characterized from compositional, structural and morphological point of view. The introduction of graphite during sorbent preparation favored only the formation of zinc titanate type Zn2TiO4 which is most stable and most reactive H2S adsorbent in relation to other forms of zinc titanate: ZnTiO3, Zn2Ti3O8.

Keywords: zinc titanate sorbents, Hot-Gas Desulfurization (HGD), graphite

The desulfurisation at high temperatures (HTGD) is one of the main process for retention of H2S from hot gasses.

In literature were studied many simple or mixed metallic oxide sorbents (Zn, Fe, Cu, Ce, Mn, Co, Ni, Sn etc) considering the retention and the regeneration capacity as well [1, 2]. A large number of metal oxide sorbents, single or mixed type (Zn, Fe, Cu, Ce, Mn, Co, etc.) have been analyzed from regeneration point of view.

From economic reasons the aim was to obtain sorbents from cheap raw materials.

These sorbents are based on ZnO [3,4]. For improvement of the sorbent stability the researchers have added TiO2, Fe2O3, Al2O3, SiO2, Cr2O3, ZrO2, La2O3, MnO2 in the sorbent mass, in order to prevent ZnO reduction at metallic Zn [5-16].

The studies made on sorbents of ZnO-TiO2 type show that TiO2 does not participate to the desulfurisation reaction, but his presence prevents ZnO reduction at volatile metallic Zn in reduction atmosphere [12, 13].

Experimental part

Previous researches [17] showed that sorbent with molar ratio ZnO:TiO2=2:1 has a good performance regarding the H2S retention capacity.

The sorbent regeneration is accomplished in air atmosphere using oxygen. This study put in evidence the structure and texture changes in ZnO-TiO2 sorbents due to graphite introduction in different quantities in order to increase the retention capacity of H2S.

Table 1

<table>
<thead>
<tr>
<th>No Crt</th>
<th>Cod of sample</th>
<th>Composition</th>
<th>Molar Ratio</th>
<th>Graphite content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZT</td>
<td>ZnO:TiO2</td>
<td>2:1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>ZTG 1</td>
<td>ZnO:TiO2</td>
<td>2:1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>ZTG 2</td>
<td>ZnO:TiO2</td>
<td>2:1</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>ZTG 3</td>
<td>ZnO:TiO2</td>
<td>2:1</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig. 1 XRD Spectrum of ZT sample

The desulfurisation sorbents of ZnO-TiO2 + graphite type (with molar ratio 2:1 and different graphite quantities) were obtained in accordance with the methodology presented in articles [17, 18], using zinc oxide (wurzitz crystallising form), titane dioxide (anatase crystallising form) and graphite (carbon 99% and humidity 1%).

The raw materials (zinc oxide and titane oxide, in a defined molar ratio) were grounding and mixing in a dry conditions for 40 min, then in half-wet mixing (obtaining a consistent paste with aqueose solution of 12% (NH4)2CO3) for 60 min. Then graphite was added and mixing was continued for a period of 40 min.

The paste obtained (a complex mixture of hydrated oxides, hydroxides and basic carbonates) was drying for 4 h at 105°C. The obtained product has been precalcinated in inert atmosphere at 380°C for 4 h, and the intermediate product obtained has been calcinate for 4 h 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 samples of ZnO have been characterised by: ray diffraction (XRD), electronic microscopy (SEM and EDAX) and textural analysis (BET).

In table 1 the studied samples are presented.

Results and discussions

Structural and compositional characterization

Structural characterization has been obtained from XRD spectrum of samples ZTG 1, ZTG 2 and ZTG 3, presented in figures 2, 3 and 4. The sample spectra were compared with ZT sorbent spectrum without graphite.(fig. 1).
In all three cases XRD spectrum put in evidence that, during calcination at 700 °C it forms zinc titanate type \( \text{Zn}_2\text{TiO}_4 \). The increasing of graphite content in sorbent composition does not lead to formation of other types of titanate.

From XRD spectrum of the ZTG 1 sample (fig. 2), with molar ratio \( \text{ZnO}:\text{TiO}_2=2:1 \) and graphite 1%, it is noted that the major crystalline phase which is formed is \( \text{Zn}_2\text{TiO}_4 \), with a mass concentration of about 78%.

In the case of XRD spectrum of ZTG 2 sample (fig. 3), with a graphite content 2.5%, the major phase is zinc titanate, \( \text{Zn}_2\text{TiO}_4 \), too, but its mass concentration is 90%, decreasing the percentage of nonreacted \( \text{ZnO} \) and \( \text{TiO}_2 \).

The spectrum of ZTG 3 sample having the percentage of 5% graphite (fig. 4) put in evidence the presence of the same phases, zinc titanate (\( \text{Zn}_2\text{TiO}_4 \)), \( \text{ZnO} \) and \( \text{TiO}_2 \), the major phase of zinc titanate being about 95%.

From this analysis it can be concluded that the addition of graphite in the sorbent composition of \( \text{ZnO}-\text{TiO}_2 \) type promote the formation \( \text{Zn}_2\text{TiO}_4 \), the most stable and reactive form from all types of titanates.

**Morphological sorbent characterization- SEM analysis**

The morphological data of sorbents, obtained through SEM analysis (at 100000 amplitude) are presented in figures 5, 6 and 7.

The presence of graphite induces an important change in morphological aspect of surface of sorbent granules. From the SEM images enlarged about 100,000 times one observed a regular shape of the crystallites; as superposed plates with well defined edges, the dimensions are relative small ranging from 72 to 200 nm (fig. 5).

The increase of graphite content determines the increasing grouping trend of crystallites explained by formation in increasing proportion of zinc titanate. The crystallites dimensions in the ZTG 2 case are higher, ranging between 175-250 nm, and ZTG 3 sample between 70-150 nm.

The EDAX spectra, associated with SEI images of ZTG 1, ZTG 2, ZTG 3, can provide a number of details regarding the distribution of main elements (Zn, Ti).

The results obtained for ZTG 1 sample (with the lower content of graphite) presented in figures 8a,b put in evidence the presence of two basic elements Zn and Ti corresponding to initial molar ratio \( \text{ZnO}:\text{TiO}_2 \) of 2:1.
For the sample with medium graphite content (ZTG 2), analysis EDAX was performed (figs. 9a, b) showing an increase of basic peak as a result of titanate formation in higher percentage than in sample ZTG 1.

The same observations could be made for the sample with maximum graphite, ZTG 3.

**Textural characterisation of the sorbents**

Textural characterization of the samples of ZnO-TiO₂ types with variable graphite contain was performed by experimental determination of the adsorption / desorption isotherms of nitrogen at liquefaction temperature with the Micromeritics ASAP 2020 device. Isotherms of adsorption / desorption obtained on ZT, ZTG 1, ZTG 2, ZTG 3 samples are shown in figures 10a, b, c, d

The adsorption/desorption behaves in a similar way as shown on the BET isotherms from figures 10b-d. At small pressures the absorption and desorption isotherms for all samples with the graphite addition are similar.

For p/p° = 0.75 the adsorption isotherms are different from the desorption isotherms being Langmuir isotherms type III. Retention of H₂S can be made in a multimolecular layer starting from a relative pressure p/p°=0.75. Up to this pressure the retention can be performed in a monomolecular layer. The pores may be classified as mesopores ones.

The addition of graphite in sorbent composition produces modifications of the specific surface and the average size of pores as presented in figures 11 and 12.

Although the sorbent specific surface decreases with introduction of graphite in the sorbent (fig. 11), this favours the formation of Zn₂TiO₄, the stable and reactive form of titanate. The introduction of graphite into the sorbent changes also the pore size (fig. 12). The value of average dimensions of the pores size grows with increasing of graphite content, but it is under the value of average dimensions of the pore size for sorbent without graphite addition.

The developing of Zn₂TiO₄ determines the increase of the sorbent retention capacity.
Conclusions

The addition of graphite into ZnO-TiO$_2$ sorbent favours the formation only of zinc titanate type Zn$_2$TiO$_4$, preventing the appearance of other forms of zinc titanate (ZnTiO$_3$, Zn$_2$Ti$_3$O$_8$). This fact could determine the increase of H$_2$S retention capacity from waste gases. Also the increase of graphite content favours the acceleration of crystallites group formation containing Zn$_2$TiO$_4$ in a higher proportion ensuring higher adsorption capacity.

References

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